Preface

This manual contains more or less complete solutions for every problem in the book. Should you find errors in any of the solutions, please bring them to my attention.

Over the years, I have tried to enrich my lectures by including historical information on the significant developments in thermodynamics, and biographical sketches of the people involved. The multivolume *Dictionary of Scientific Biography*, edited by Charles C. Gillispie and published by C. Scribners, New York, has been especially useful for obtaining biographical and, to some extent, historical information. [For example, the entry on Anders Celsius points out that he chose the zero of his temperature scale to be the boiling point of water, and 100 to be the freezing point. Also, the intense rivalry between the English and German scientific communities for credit for developing thermodynamics is discussed in the biographies of J.R. Mayer, J. P. Joule, R. Clausius (who introduced the word entropy) and others.] Other sources of biographical information include various encyclopedias, Asimov's Biographical Encyclopedia of Science and Technology by I. Asimov, published by Doubleday & Co., (N.Y., 1972), and, to a lesser extent, Nobel Prize Winners in Physics 1901-1951, by N.H. deV. Heathcote, published by H. Schuman, N.Y.

Historical information is usually best gotten from reading the original literature. Many of the important papers have been reproduced, with some commentary, in a series of books entitled "Benchmark Papers on Energy" distributed by Halsted Press, a division of John Wiley and Sons, N.Y. Of particular interest are:

Volume 1, *Energy: Historical Development of the Concept*, by R. Bruce Lindsay.

Volume 2, *Applications of Energy, 19th Century*, by R. Bruce Lindsay.

Volume 5, *The Second Law of Thermodynamics*, by J. Kestin and

Volume 6, *Irreversible Processes*, also by J. Kestin.

The first volume was published in 1975, the remainder in 1976.

Other useful sources of historical information are "The Early Development of the Concepts of Temperature and Heat: The Rise and Decline of the Caloric Theory" by D. Roller in Volume 1 of *Harvard Case Histories in Experimental Science* edited by J.B. Conant and published by Harvard University Press in 1957; articles in *Physics Today*, such as "A Sketch for a History of Early Thermodynamics" by E. Mendoza (February, 1961, p.32), "Carnot's Contribution to Thermodynamics" by M.J. Klein (August, 1974, p. 23); articles in Scientific American; and various books on the history of science. Of special interest is the book *The Second Law* by P.W. Atkins published by Scientific American Books, W.H. Freeman and Company (New York, 1984) which contains a very extensive discussion of the entropy, the second law of thermodynamics, chaos and symmetry.

I also use several simple classroom demonstrations in my thermodynamics courses. For example, we have used a simple constant-volume ideal gas thermometer, and an instrumented vapor compression refrigeration cycle (heat pump or air conditioner) that can brought into the classroom. To demonstrate the pressure dependence of the melting point of ice, I do a simple regelation experiment using a cylinder of ice (produced by freezing water in a test tube), and a 0.005 inch diameter wire, both ends of which are tied to the same 500 gram weight. (The wire, when placed across the supported cylinder of ice, will cut through it in about 5 minutes, though by refreezing or regelation, the ice cylinder remains intact.—This experiment also provides an opportunity to discuss the movement of glaciers.) Scientific toys, such as "Love Meters" and drinking "Happy Birds", available at novelty shops, have been used to illustrate how one can make practical use of the temperature dependence of the vapor pressure. I also use some professionally prepared teaching aids, such as the three-dimensional phase diagrams for carbon dioxide and water, that are available from laboratory equipment distributors.

Despite these diversions, the courses I teach are quite problem oriented. My objective has been to provide a clear exposition of the principles of thermodynamics, and then to reinforce these fundamentals by requiring the student to consider a great diversity of the applications. My approach to teaching thermodynamics is, perhaps, similar to the view of John Tyndall expressed in the quotation

"It is thus that I should like to teach you all things; showing you the way to profitable exertion, but leaving the exertion to you—more anxious to bring out your manliness in the presence of difficulty than to make your way smooth by toning the difficulties down."

Which appeared in The Forms of Water, published by D. Appleton (New York, 1872).

Finally, I usually conclude a course in thermodynamics with the following quotation by Albert Einstein:

"A theory is more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended its area of applicability. Therefore, the deep impression classical thermodynamics made upon me. It is the only physical theory of universal content which, within the framework of the applicability of its basic concepts, I am convinced will never by overthrown."

1.1 (a) Thermostatic bath imposes its temperature T on the system.

(b) Container imposes constraint of constant volume. Thermal isolation implies that heat flow must be zero, while mechanical isolation (and constant volume) implies there is no work flow. Consequently there is no mechanism for adding or removing energy from the system. Thus, system volume and energy are constant.

(c) Thermally isolated $\Rightarrow$ adiabatic

Frictionless piston $\Rightarrow$ pressure of system equals ambient pressure (or ambient pressure + wg/A if piston-cylinder in vertical position. Here w = weight of piston, A = its area and g is the force of gravity.)

(d) Thermostatic bath $\Rightarrow$ constant temperature T.

Frictionless piston $\Rightarrow$ constant pressure (see part c above).

(e) Since pressure difference induces a mass flow, pressure equilibrates rapidly. Temperature equilibration, which is a result of heat conduction, occurs much more slowly. Therefore, if valve between tanks is opened for only a short time and then shut, the pressure in the two tanks will be the same, but *not* the temperatures.

1.2 (a) Water is inappropriate as a thermometric fluid between 0°C and 10°C, since the volume is not a unique function of temperature in this range, i.e., two temperatures will correspond to the same specific volume,

$$\hat{V}(T = 1°C) \sim V(T = 7°C); \quad \hat{V}(T = 2°C) \sim V(T = 6°C); \text{ etc.}$$
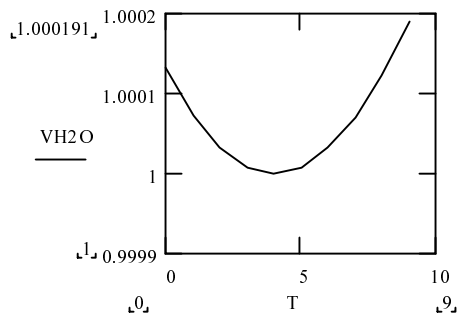
$$\left[T \text{ in } °C \text{ and } \hat{V} \text{ in cc / g}\right]$$

Consequently, while T uniquely determines, $\hat{V}$, $\hat{V}$ does not uniquely determine T.

(b) Assuming that a mercury thermometer is calibrated at 0°C and 100°C, and that the specific volume of mercury varies linearly between these two temperatures yields

$$\hat{V}(T) = \hat{V}(0^{\circ}\text{C}) + \frac{\hat{V}(T=100^{\circ}\text{C}) - \hat{V}(T=0^{\circ}\text{C})}{100^{\circ}\text{C} - 0^{\circ}\text{C}}(T_{\text{s}} - 0^{\circ}\text{C})$$

$$= 0.0735560 + 0.000013421\, T_{\text{s}} \qquad\qquad (*)$$

where T is the actual temperature, and T_{s} is the temperature read on the thermometer scale. At 10°C, $\hat{V}_{\text{exp}}(T = 10^{\circ}\text{C}) = 0.0736893$ cc/g. However, the scale temperature for this specific volume is, from eqn. (*) above

$$T_{\text{s}} = \frac{\hat{V}_{\text{exp}}(T) - 0.0735560}{1.3421 \times 10^{-5}} = \frac{0.0736893 - 0.0735560}{1.3421 \times 10^{-5}} = 9.932^{\circ}\text{C}$$

Thus, $T - T_{\text{s}}$ at 10°C $= -0.068^{\circ}$C. Repeating calculation at other temperatures yields figure below.
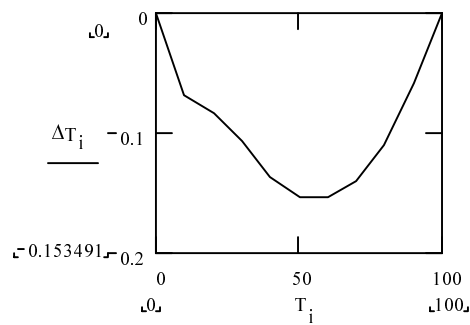
The temperature error plotted here results from the nonlinear dependence of the volume of mercury on temperature. In a real thermometer there will also be an error associated with the imperfect bore of the capillary tube.

(c)   When we use a fluid-filled thermometer to measure ΔT we really measure ΔL, where

$$\Delta L = \frac{\Delta V}{A} = \frac{M(\partial \hat{V}/\partial T)\Delta T}{A}$$

A small area A and a large mass of fluid M magnifies ΔL obtained for a given ΔT. Thus, we use a capillary tube (small A) and bulb (large M) to get an accurate thermometer, since $(\partial \hat{V}/\partial T)$ is so small.

2.1 (a) By an energy balance, the bicycle stops when final potential energy equals initial kinetic energy. Therefore

$$\frac{1}{2}mv_i^2 = mgh_f \text{ or } h_f = \frac{v_i^2}{2g} = \frac{\left(20\,\dfrac{km}{hr} \times 1000\,\dfrac{m}{km} \times \dfrac{1\,hr}{3600\,sec}\right)^2}{2 \times 9.807\,\dfrac{m}{sec^2}}$$

or h=1.57 m.

(b) The energy balance now is

$$\frac{1}{2}mv_f^2 = \frac{1}{2}mv_i^2 + mgh_i \text{ or } v_f^2 = v_i^2 + 2gh_i$$

$$v_f^2 = \left(20\,\frac{km}{hr}\right)^2 + 2 \times 9.807\,\frac{m}{sec^2} \times 70\,m \times \left(\frac{km}{1000\,m} \times \frac{3600\,sec}{hr}\right)^2$$

v_f = 134.88 km/hr. Anyone who has bicycled realizes that this number is much too high, which demonstrates the importance of air and wind resistance.

2.2 The velocity change due to the 55 m fall is

$$\left(\Delta v^2\right) = 2 \times 9.807\,\frac{m}{sec^2} \times 55\,m \times \left(\frac{km}{1000\,m} \times \frac{3600\,sec}{hr}\right)^2$$

v_f = 118.24 km/hr. Now this velocity component is in the vertical direction. The initial velocity of 8 km/hr was obviously in the horizontal direction. So the final velocity is

$$v = \sqrt{v_x^2 + v_y^2} = 118.51\,\frac{km}{hr}$$

2.3 (a) System: contents of the piston and cylinder
(closed isobaric = constant pressure)
M.B.: $M_2 - M_1 = \Delta M = 0 \Rightarrow M_2 = M_1 = M$

E.B.: $M_2\hat{U}_2 - M_1\hat{U}_1 = \Delta M(\hat{H})^0 + Q + \cancel{W_s}^{\,0} - \int P\,dV$

$M(\hat{U}_2 - \hat{U}_1) = Q - \int P\,dV = Q - P\int dV = Q - P(V_2 - V_1)$

$M(\hat{U}_2 - \hat{U}_1) = Q - PM(\hat{V}_2 - \hat{V}_1)$

$Q = M(\hat{U}_2 - \hat{U}_1) + M(P\hat{V}_2 - P\hat{V}_1) = M\left[(\hat{U}_2 + P\hat{V}_2) - (\hat{U}_1 + P\hat{V}_1)\right]$

$\qquad = M(\hat{H}_2 - \hat{H}_1)$

$P = 1.013 \text{ bar} \approx 0.1 \text{ MPa}$

	$\hat{V}$	$\hat{U}$	$\hat{H}$
$T = 100$	1.6958	2506.7	2676.2
$T = 150$	1.9364	2582.8	2776.4

Linear interpolation

$T = 125°\text{C}$	1.8161	2544.8	2726.3	Initial state

Final state $P = 0.1 \text{ MPa}$, $\hat{V}_2 = 3.6322 \text{ m}^3/\text{kg}$

$T = 500°\text{C}$	3.565		3488.1
$T = 600°\text{C}$	4.028		3704.7

Linear interpolation

$$\frac{3.6322 - 3.565}{4.028 - 3.565} = \frac{T_2 - 500}{600 - 500} \qquad T_2 = 514.5°\text{C}$$

$$\frac{514.5 - 500}{600 - 500} = \frac{\hat{H}_2 - 3488.1}{3704.7 - 3488.1} \qquad \hat{H}_2 = 3519.5$$

$$Q = 1 \text{ kg}(3519.5 - 2726.3)\text{kJ/kg} = 793.2 \text{ kJ}$$

$$W = -\int PdV = -1 \text{ bar} \times (V_2 - V_1) = -1 \text{ bar} \times (3.6322 - 1.8161) \text{ m}^3/\text{kg}$$

$$= -1 \text{ bar} \times 100{,}000 \; \frac{\text{Pa}}{\text{bar}} \times \frac{1 \text{ kg}}{\text{m} \cdot \text{s}^2 \cdot \text{Pa}} \times \frac{1 \text{ J}}{\text{m}^2 \cdot \text{s}^2 \cdot \text{kg}} \times 1.8161 \text{ m}^3/\text{kg}$$

$$= -181.6 \text{ kJ/kg}$$

(b) System is closed and constant volume

M.B.: $M_2 = M_1 = M$

E.B.: $M_2 \hat{U}_2 - M_1 \hat{U}_1 = \Delta M (\hat{H})^{\;0} + Q + W_s^{\;0} - \int PdV^{\;0}$

$$Q = M(\hat{U}_2 - \hat{U}_1)$$

Here final state is $P = 2 \times 1.013 \text{ bar} \sim 0.2 \text{ MPa}$; $\hat{V}_2 = \hat{V}_1 = 1.8161 \text{ m}^3/\text{kg}$
(since piston-cylinder volume is fixed)

$P = 0.2 \text{ MPa}$; $\hat{V}_2 = 1.8161$

$T(°\text{C})$	$\hat{V}$	$\hat{U}$
500	1.7814	3130.8
600	2.013	3301.4

$$\frac{1.8161 - 1.7814}{2.013 - 1.7814} = \frac{T - 500}{600 - 500} = \frac{0.0347}{0.2316} = 0.1498 \sim 0.15$$

$$T = 515°\text{C}$$

$$\frac{\hat{U}_2 - 3130.8}{3301.4 - 3130.8} = 0.1498 \qquad \hat{U}_2 = 3156.4 \text{ kJ/kg}$$

$$Q = 1 \text{ kg} \times (3156.4 - 2544.8) \text{ kJ/kg} = 611.6 \text{ kJ}$$

(c) Steam as an ideal gas—constant pressure

$$N = \frac{PV}{RT} \Rightarrow \frac{P_1 V_1}{RT_1} = \frac{P_2 V_2}{RT_2} \text{ but } V_2 = 2V_1 \; ; \; P_1 = P_2$$

$$\frac{P_1 \underline{V}_1}{T_1} = \frac{P_1 2 \underline{V}_1}{T_2} \Rightarrow T_2 = 2 \times T_1$$

$$T_1 = 273.15 + 125 = 398.15 \text{ K}$$

$$T_2 = 2 \times T_1 = 796.3 \text{ K} = 523.15°\text{C}$$

$$Q = N \Delta \underline{H} = \frac{1000 \text{ g/kg}}{18 \text{ g/mol}} \times 34.4 \text{ J/mol K} \times (796.3 - 398.15) \text{ K} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$= 760.9 \text{ kJ}$$

$$W = -\int P dV = -P \Delta V = -P\left(\frac{NRT_2}{P} - \frac{NRT_1}{P_1}\right) = -NR(T_2 - T_1)$$

$$= -\frac{1000}{18} \times 8.314 \times 398.15 = -183.9 \text{ kJ}$$

(d) Ideal gas - constant volume

$$\frac{P_1 \underline{V}_1}{RT_1} = \frac{P_2 \underline{V}_2}{RT_2} \text{ here } \underline{V}_1 = \underline{V}_2 \text{ ; } P_2 = 2P_1$$

So again $\dfrac{P \underline{V}_1}{T_1} = \dfrac{2P_1 \cdot \underline{V}_1}{T_2}$; $T_2 = 2T_1 = 796.3 \text{ K}$.

$$Q = N \Delta \underline{U} = \frac{1000 \text{ g/kg}}{18 \text{ g/mol}} \times (34.4 - 8.314) \times (796.3 - 398.15) \times \frac{1}{1000}$$

$$C_V = C_P - R \text{ ; } Q = 577.0 \text{ kJ}$$

2.4

$$M_w \hat{U}_{w,\ f} - M_w \hat{U}_{w,\ i} = W_s = M_{weight} \times g \times 1 \text{ m}$$

$$M_w = M_{weight} = 1 \text{ kg}$$

$$1 \text{ kg} \times C_P (T_f - T_i) = 1 \text{ kg} \times 9.807 \text{ m/s}^2 \times 1 \text{ m} \times \frac{1 \text{ J}}{\text{m}^2 \text{kg/s}^2} = 9.807 \text{ J}$$

$$1 \text{ kg} \times 4.184 \text{ J/g K} \times \frac{1000 \text{ g}}{\text{kg}} \times \Delta T = 9.807$$

$$\Delta T = \frac{9.807}{4.184 \times 1000} \text{ K} = 2.344 \times 10^{-3} \text{ K}$$

2.5   From Illustration 2.3-3 we have that $\underline{H}(T_1,\ P_1) = \underline{H}(T_2,\ P_2)$ for a Joule-Thomson expansion. On the Mollier diagram for steam, Fig. 2.4-1a, the upstream and downstream conditions are connected by a horizontal line. Thus, graphically, we find that $T \sim 383 \text{ K}$. (Alternatively, one could also use the Steam Tables of Appendix III.)
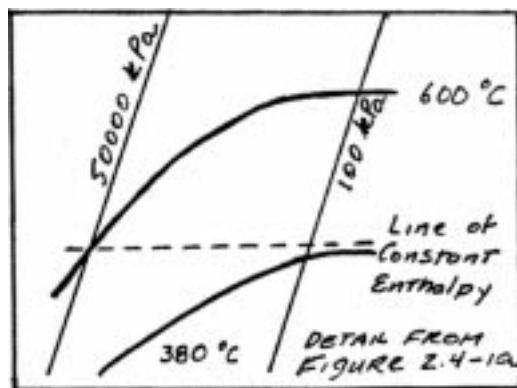
For the ideal gas, enthalpy is a function of temperature only. Thus, $\underline{H}(T_1,\ P_1) = \underline{H}(T_2,\ P_2)$ becomes $\underline{H}(T_1) = \underline{H}(T_2)$, which implies that $T_1 = T_2 = 600°\text{C}$.
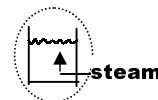
2.6 System: Contents of Drum (open system)

mass balance: $M\big|_{t_2} - M\big|_{t_1} = \Delta M$

energy balance:

$M\hat{U}\big|_{t_2} - M\hat{U}\big|_{t_1} = \Delta M\hat{H}_{\text{in}} + Q + W_{\text{s}} - \int PdV$

but $Q = 0$ by problem statement, $W_{\text{s}} = 0$

and $\int PdV = P\Delta V$ is negligible. (Note $\hat{V}(T = 25°\text{C}) = 1.003 \times 10^{-3}\ \text{m}^3/\text{kg}$, $\hat{V}(T = 80°\text{C}) = 1.029 \times 10^{-3}\ \text{m}^3/\text{kg}$). Also from the Steam Tables

$$\hat{H}_{\text{in}} = \hat{H}(T = 300°\text{C},\ P = 3.0\ \text{bar} = 300\ \text{kPa}) = 3069.3\ \text{kJ/kg}$$

and recognizing that the internal energy of a liquid does not depend on pressure gives

$$\hat{U}\big|_{t_1} = \hat{U}(T = 25°\text{C},\ 1.013\ \text{bar}) = \hat{U}(\text{sat.},\ T = 25°\text{C}) = 104.88\ \text{kJ/kg}$$

and

$$\hat{U}\big|_{t_2} = \hat{U}(T = 80°\text{C},\ 1.013\ \text{bar}) = \hat{U}(\text{sat.},\ T = 80°\text{C}) = 334.86\ \text{kJ/kg}$$

Now using mass balance and energy balances with $M\big|_{t_1} = 100\ \text{kg}$ yields

$$M|_{t_2} \times 334.86 \text{ kJ} - 100 \times 104.88 \text{ kJ} = \left[M|_{t_2} - 100 \right] \times 3069.3 \text{ kJ}$$

Thus

$$M|_{t_2} (3069.3 - 334.86) = 100 \times (3069.3 - 104.88)$$

$M|_{t_2} = 108.41 \text{ kg}$, and $\Delta M = M|_{t_2} - M|_{t_1} = 8.41 \text{ kg}$ of steam added.

2.7 (a) Consider a change from a given state 1 to a given state 2 in a closed system. Since initial and final states are fixed, U_1, U_2, V_1, V_2, P_1, P_2, etc. are all fixed. The energy balance for the closed system is

$$U_2 - U_1 = Q + W_s - \int P dV = Q + W$$

where $W = W_s - \int P dV$ = total work. Also, $Q = 0$ since the change of state is adiabatic. Thus, $U_2 - U_1 = W$.

Since U_1 and U_2 are fixed (that is, the end states are fixed regardless of the path), it follows that W is the same for all *adiabatic* paths. This is not in contradiction with Illustration 2.5-6, which established that the sum $Q + W$ is the same for all paths. If we consider only the subset of paths for which $Q = 0$, it follows, from that illustration that W must be path independent.

(b) Consider two different adiabatic paths between the given initial and final states, and let W^* and W^{**} be the work obtained along each of these paths, i.e.,

Path 1: $U_2 - U_1 = W^*$; Path 2: $U_2 - U_1 = W^{**}$

Now suppose a cycle is constructed in which path 1 is followed from the initial to the final state, and path 2, in reverse, from the final state (state 2) back to state 1. The energy balance for this cycle is

$$U_2 - U_1 = W^*$$
$$\underline{-(U_2 - U_1) = -W^{**}}$$
$$0 = W^* - W^{**}$$

Thus if the work along the two paths is different, i.e., $W^* \neq W^{**}$, we have created energy!

2.8 System = contents of tank at any time

mass balance: $M_2 - M_1 = \Delta M$

energy balance: $\left(M\hat{U} \right)_2 - \left(M\hat{U} \right)_1 = \Delta M \hat{H}_{in}$

(a) Tank is initially evacuated $\Rightarrow M_1 = 0$

Thus $M_2 = \Delta M$, and $\hat{U}_2 = \hat{H}_{in} = \hat{H}(5 \text{ bar}, 370°C) = 3209.6 \text{ kJ/kg}$ (by interpolation).   Then $\hat{U}_2 = \hat{U}(P = 5 \text{ bar}, T = ?) = 3209.6 \text{ kJ/kg}$.   By interpolation, using the Steam Tables (Appendix III) $T = 548°C$

$$\hat{V}(P = 5 \text{ bar}, T = 548°C) \cong 0.756 \text{ m}^3/\text{kg}$$

Therefore $M = V/\hat{V} = 1 \text{ m}^3/(0.756 \text{ m}^3/\text{kg}) = 1.3228 \text{ kg}$.

(b) Tank is initially filled with steam at 1 bar and 150°C $\Rightarrow \hat{V}_1 = \hat{V}(P = 1 \text{ bar}, T = 150°C) = 1.94 \text{ m}^3/\text{kg}$ and $\hat{U}_1 = 2583 \text{ kJ/kg}$, $M_1 = V/\hat{V} = 1/\hat{V} = 0.5155 \text{ kg}$. Thus, $M_2 = 0.5155 + \Delta M \text{ kg}$. Energy balance is $M_2\hat{U}_2 - 0.5155 \times 2583 = (M - 0.5155) \times 3209.6$. Solve by guessing value of T_2, using T_2 and $P_2 = 5 \text{ bar}$ to find $\hat{V}_2$ and $\hat{U}_2$ in the Steam Tables (Appendix III). See if energy balance and $M_2 = 1 \text{ m}^3/\hat{V}_2$ are satisfied. By trial and error: $T_2 \sim 425°C$ and $M_2 \cong 1.563 \text{ kg}$ of which 1.323 kg was present in tank intially. Thus, $\Delta M = M_2 - M_1 = 0.24 \text{ kg}$.

2.9 a) Use kinetic energy $= mv^2/2$ to find velocity.

$$1 \text{ kg} \times \frac{v^2}{2} \frac{\text{m}^2}{\text{sec}^2} = 1000 \text{ J} = 1000 \frac{\text{kg}}{\text{m}^2 \text{ sec}^2} \quad \text{so } v = 44.72 \text{ m/sec}$$

b) Heat supplied = specific heat capacity × temperature change, so

$$1000\text{g} \times \frac{1 \text{ mol}}{55.85\text{g}} \times 25.10 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times \Delta T = 1000 \text{ J} \text{ so } \Delta T = 2.225 \text{ K}.$$

2.10 System = resistor

Energy balance: $dU/dt = \dot{W}_s + \dot{Q}$

where $\dot{W}_s = E \cdot I$, and since we are interested only in steady state $dU/dt = 0$. Thus

$$-\dot{Q} = \dot{W}_s = 1 \text{ amp} \times 10 \text{ volts} = 0.2 \times (T - 25°C) \text{ J/s}$$

and 1 watt $= 1 \text{ volt} \times 1 \text{ amp} = 1 \text{ J/s}$.

$$\Rightarrow T = \frac{10 \text{ watt} \times 1 \text{ J/s} \cdot \text{watt}}{0.2 \text{ J/s} \cdot \text{K}} + 25°C = 75.0°C$$

2.11 System = gas contained in piston and cylinder (closed)

Energy balance: $U|_{t_2} - U|_{t_1} = Q + \cancel{W_s}^{\,0} - \int PdV$

(a) $V = \text{constant}$, $\int PdV = 0$, $Q = U|_{t_2} - U|_{t_1} = N\left(U|_{t_2} - U|_{t_1}\right) = NC_V(T_2 - T_1)$

From ideal gas law

$$N = \frac{PV}{RT} = \frac{114{,}367 \text{ Pa} \times 0.120 \text{ m}^3}{8.314 \text{ Pa} \cdot \text{m}^3/\text{mol} \cdot \text{K} \times 298 \text{ K}} = 5.539 \text{ mol} \text{ (see note following)}$$

Thus

$$T_2 = T_1 + \frac{Q}{NC_V} = 298 \text{ K} + \frac{10,500 \text{ J}}{5.539 \text{ mol} \times 30.1 \text{ J/mol} \cdot \text{K}}$$

$$= 298 + 63.0 = 361.0 \text{ K}$$

Since N and V are fixed, we have, from the ideal gas law, that

$$\frac{P_2}{P_1} = \frac{T_2}{T_1} \text{ or } P_2 = \frac{T_2}{T_1} P_1 = \frac{361.0}{298.0} \times 114.367 \text{ kPa} = 1.385 \times 10^5 \text{ Pa}$$

(b) $P = \text{constant} = 1.14367 \times 10^5 \text{ Pa}$;

$C_P = C_V + R = 30.1 + 8.314 = 38.414 \text{ J/mol} \cdot \text{K}$

Energy balance $U|_{t_2} - U|_{t_1} = Q - P\Delta V$, since $P = \text{constant}$

$\Rightarrow NC_V(T_2 - T_1) = Q - P(V_2 - V_1) = Q - N(RT_2 - RT_1)$

$\Rightarrow Q = NC_P(T_2 - T_1)$

$$T_2 = T_1 + \frac{Q}{NC_P} = 298 + \frac{10,500}{5.539 \times 38.414} = 347.35 \text{ K}$$

and

$$\Delta V = \frac{NR\Delta T}{P} = \frac{5.539 \text{ mol} \times 8.314 \text{ Pa} \cdot \text{m}^3/\text{mol} \cdot \text{K} \times 49.35 \text{ K}}{114,367 \text{ Pa}} = 0.01987 \text{ m}^3$$

$$V = 0.12 + 0.0199 = 0.1399 \text{ m}^3$$

Note: The initial pressure $P = P_{\text{atm}} + P_{\text{wt of piston}}$

$P_{\text{atm}} = 1.013 \text{ bar} = 1.013 \times 10^5 \text{ kPa}$

$$P_{\text{wt piston}} = \frac{200 \text{ kg}}{0.15 \text{ m}^2} \times \frac{1 \text{ Ns}^2}{\text{kg} \cdot \text{m}} \times 9.8 \text{ m/s}^2 = 13,067 \text{ N/m}^2 = 13,067 \text{ Pa}$$

$$= 13.067 \text{ kPa}$$

Thus, intial pressure $= 114.367 \text{ kPa}$.

2.12 System = contents of storage tank (open system)

Mass balance: $M_2 - M_1 = \Delta M$

Energy balance: $\left(M\hat{U}\right)_2 - \left(M\hat{U}\right)_1 = (\Delta M)\hat{H}_{\text{in}}$ since $Q = W = 0$ and steam entering is of constant properties.

Initially system contains 0.02 m^3 of liquid water and $(40 - 0.02) = 39.98 \text{ m}^3$ of steam.

Since vapor and liquid are in equilibrium at 50°C, from Steam Tables, $P = 12.349 \text{ Pa}$.   Also   from   Steam   Tables $\hat{V}^L = 0.001012 \text{ m}^3/\text{kg}$, $\hat{V}^V = 12.03 \text{ m}^3/\text{kg}$, $\hat{H}^V = 2592.1 \text{ kJ/kg}$, $\hat{H}^L = 209.33 \text{ kJ/kg}$, $\hat{U}^L = 209.32 \text{ kJ/kg}$, and $\hat{U}^V = 2443.5 \text{ kJ/kg}$.

$$M_1^L = \frac{0.02 \text{ m}^3}{0.001012 \text{ m}^3/\text{kg}} = 19.76 \text{ kg;}$$

$$M_1^V = \frac{39.98 \text{ m}^3}{12.03 \text{ m}^3/\text{kg}} = 3.32 \text{ kg;}$$

$$\left. \vphantom{\frac{1}{1}} \right\} M_1 = M_1^L + M_1^V = 23.08 \text{ kg.}$$

$$U_1 = 19.76 \times 209.32 + 3.32 \times 2443.5 = 12{,}248.6 \text{ kJ}$$

Also

$$\hat{H}_{in} = 0.90 \times 2676.1 + 0.10 \times 419.04 = 2450.4 \text{ kJ/kg}$$

Possibilities for final state: 1) vapor-liquid mixture, 2) all vapor, and 3) all liquid. First possibility is most likely, so we will assume V-L mixture. Since $P = 1.013 \text{ bar}$, T must be 100°C. Thus we can find properties of saturated vapor and saturated liquid in the Steam Tables: $\hat{V}^L = 0.001044 \text{ m}^3/\text{kg}$, $\hat{V}^V = 1.6729 \text{ m}^3/\text{kg}$, $\hat{U}^L = 418.94 \text{ kJ / kg}$, $\hat{H}^V = 2676.1 \text{ kJ/kg}$, and $\hat{U}^V = 2506.5 \text{ kJ / kg}$.

$\hat{V}_2 = x(1.6729) + (1 - x)0.001044 = 0.001044 + 1.6719x \text{ m}^3/\text{kg}$, where $x = $ quality

$\hat{U}_2 = x(2506.5) + (1 - x)418.94 = 418.94 + 2087.56x \text{ kJ/kg}$

Substituting into energy balance

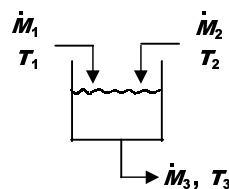$$M_2(418.94 + 2087.56x) - 12{,}248.6 = (M_2 - 23.08) \cdot 2450.4$$

where

$$M_2 = \frac{V}{\hat{V}_2} = \frac{40 \text{ m}^3}{0.001044 + 1.6719x}$$

Solving by trial and error yields $x = 0.5154$ (quality), $M_2 = 46.36 \text{ kg}$, and $\Delta M = 23.28 \text{ kg}$. Also the final state is a vapor-liquid mixture, as assumed.

2.13   System = tank and its contents (open system)
(a)   Steady state mass balance

$$\frac{dM}{dt} = 0 = \dot{M}_1 + \dot{M}_2 + \dot{M}_3$$

$$\Rightarrow \dot{M}_3 = -(\dot{M}_1 + \dot{M}_2) = -10 \text{ kg/min}$$

Steady state energy balance

$$\frac{dU}{dt} = 0 = \dot{M}_1 \hat{H}_1 + \dot{M}_2 \hat{H}_2 + \dot{M}_3 \hat{H}_3$$

$\hat{H}_3 = \hat{H}$ exit stream $= \hat{H}$ at temperature of tank contents

Also $T_3 = T =$ temperature of tank contents

Now $\hat{H} = \hat{H}_0 + C_P(T - T_0)$, assuming C_P is not a function of temperature

$$0 = 5\{\hat{H}_0 + C_P(T_1 - T_0)\} + 5\{\hat{H}_0 + C_P(T_2 - T_0)\} - 10\{\hat{H}_0 + C_P(T - T_0)\}$$

$$\Rightarrow T = \frac{5T_1 + 5T_2}{10} = \frac{1}{2}(T_1 + T_2) = 65°C$$

(b) mass balance: $\dfrac{dM}{dt} = 0 = \dot{M}_1 + \dot{M}_2 + \dot{M}_3$ (no useful information here)

energy balance: $\dfrac{dU}{dt} = \dot{M}_1\hat{H}_1 + \dot{M}_2\hat{H}_2 + \dot{M}_3\hat{H}_3$

but $\dfrac{dU}{dt} = \dfrac{d}{dt}\left(M\hat{U}\right) = M\dfrac{d\hat{U}}{dt} = MC_V\dfrac{dT}{dt} \sim MC_P\dfrac{dT}{dt}$ since $C_P \approx C_V$ for

liquids. Thus $MC_P\dfrac{dT_3}{dt} = 5C_P T_1 + 5C_P T_2 - 10C_P T_3$ and $M = 50$ kg .

$$10\frac{dT_3}{dt} + 2T_3 = (80 + 50) = 130 \Rightarrow T_3 = Ae^{-t/5} + C \ \ (t = \text{minutes})$$

At $t \to \infty$, $T_3 = C = 65°C$

At $t = 0$, $T_3 = A + C = 25°C \Rightarrow A = -40°C$

So finally $T_3 = 65°C - 40°Ce^{-t/5}$ ($t =$ minutes)

E.B: $M^F\hat{U}^F - M^i\hat{U}^i = \Delta M\hat{H}_{in}$

$$\left(M_L^F\hat{U}_L^F + M_V^F\hat{U}_V^F\right) - \left(M_L^i\hat{U}_L^i + M_V^i\hat{U}_V^i\right) = \left[M_L^F + M_V^F\right]\left[0.1\hat{H}_{L,\,in} + 0.9\hat{H}_{V,\,in}\right]$$

Also known is that $V = 60$ m$^3 = M_L^F\hat{V}_L^F + M_V^F\hat{V}_V^F$. $\Rightarrow$2 equations and 2 unknowns

$$\frac{V - M_V^F\hat{V}_V^F}{\hat{V}_L^F} = M_L^F$$

$$\left(\frac{V - M_V^F\hat{V}_V^F}{\hat{V}_L^F}\hat{U}_L^F + M_V^F\hat{U}_V^F\right) - \left(M_L^i\hat{U}_L^i + M_V^i\hat{U}_V^i\right)$$

$$= \left[\frac{V - M_V^F\hat{V}_V^F}{\hat{V}_L^F} + M_V^F\right]\left[0.1\hat{H}_{L,\,in} + 0.9\hat{H}_{V,\,in}\right]$$

2.14 Thermodynamic properties of steam from the Steam Tables
Initial conditions:
Specific volume of liquid and of vapor:

$$\hat{V}_L^i = 1.061 \times 10^{-3}\,\frac{\text{m}^3}{\text{kg}}; \quad \hat{V}_V^i = 0.8857\,\frac{\text{m}^3}{\text{kg}}$$

Specific internal energy of liquid and of vapor

$$\hat{U}_L^i = 313.9\,\frac{\text{kJ}}{\text{kg}}; \quad \hat{U}_V^i = 2475.9\,\frac{\text{kJ}}{\text{kg}}$$

M.B: $M^f - M^i = \Delta M_i$

$M^i = M^i_L + M^i_V$; $M^i_L = \dfrac{200 \text{ liters}}{\hat{V}^i_L} = 194.932 \text{ kg;}$

$M^i_V = \dfrac{60 \text{ m}^3 - 200 \text{ liters}}{\hat{V}^i_V} = 14.476 \text{ kg and so}\quad M^i = 209.408 \text{ kg}$

E.B.

$\quad M^f \hat{U}^f - M^i \hat{U}^i = \Delta M \hat{H}_{in}$

$\quad \left(M^f_L \hat{U}^f_L + M^f_V \hat{U}^f_V \right) - \left(M^i_L \hat{U}^i_L + M^i_V \hat{U}^i_V \right) = \left[M^f_L + M^f_V \right] \left[0.1 \hat{H}_{L,\,in} + 0.9 \hat{H}_{V,\,in} \right]$

Total internal energy of steam + water in the tank
194.932×313.0 + 14.476×2475.9 = 9.686×10⁴ kJ
Properties of steam entering, 90% quality
Specific volume = $\hat{V}_{in} = 0.1 \times 1.061 \times 10^{-3} + 0.9 \times 0.8857 = 0.797 \text{ m}^3/\text{kg}$

Specific enthalpy = $\hat{H}_{in} = 0.1 \times 504.70 + 0.9 \times 2706.7 = 2.486 \times 10^3 \text{ kJ/kg}$

Also have that $V = 60 \text{ m}^3 = M^f_L \hat{V}^f_L + M^f_V \hat{V}^f_V$.

This gives two equations, and two unknowns, M^f_L and M^f_V.

The solution (using MATHCAD) is $M^f_L = 215.306 \text{ kg}$ and $M^f_V = 67.485 \text{ kg.}$

Therefore, the fraction of the tank contents that is liquid by weight is 0.761.

2.15 System = contents of both chambers (closed, adiabatic system of constant volume.
Also $W_s = 0$).

Energy balance: $U(t_2) - U(t_1) = 0$ or $U(t_2) = U(t_1)$

(a) For the ideal gas u is a function of temperature only.   Thus,
$U(t_2) = U(t_1) \Rightarrow T(t_2) = T(t_1) = 500 \text{ K}$. From ideal gas law

$\qquad P_1 V_1 = N_1 R T_1 \qquad$ but $\quad N_1 = N_2$ since system is closed
$\qquad P_2 V_2 = N_2 R T_2 \qquad\qquad\quad T_1 = T_2$ see above
$\qquad\qquad\qquad\qquad\qquad$ and $\quad V_2 = 2V_1$ see problem statement.

$\Rightarrow P_2 = \dfrac{1}{2} P_1 = 5 \text{ bar} = 0.5 \text{ MPa} \Rightarrow T_2 = 500 \text{ K}, P_2 = 0.5 \text{ MPa}$

(b) For steam the analysis above leads to $U(t_2) = U(t_1)$ or, since the system is
closed $\hat{U}(t_2) = \hat{U}(t_1)$, $\hat{V}(t_2) = 2\hat{V}(t_1)$. From the Steam Tables, Appendix III,

$\qquad \hat{U}(t_1) = \hat{U}(T = 500 \text{ K}, \ P = 1 \text{ MPa}) = \hat{U}(T = 226.85°\text{C}, \ P = 1 \text{ MPa})$
$\qquad\qquad \cong 2669.4 \text{ kJ/kg}$
$\qquad \hat{V}(t_1) = \hat{V}(T = 226.85°\text{C}, \ P = 1 \text{ MPa}) \cong 0.2204 \text{ m}^3/\text{kg}$

Therefore $\hat{U}(t_2) = \hat{U}(t_1) = 2669.4 \text{ kg/kg}$ and
$\hat{V}(t_2) = 2\hat{V}(t_1) = 0.4408 \text{ m}^3/\text{kg}$.   By, essentially, trial and error, find that
$T \sim 216.3°\text{C}$, $P \sim 0.5 \text{ MPa}$.

(c) Here $U(t_2) = U(t_1)$, as before, except that $U(t_1) = U^I(t_1) + U^{II}(t_1)$, where superscript denotes chamber.

Also, $M(t) = M^I(t_1) + M^{II}(t_1)$ {mass balance} and

$$\hat{V}(t_2) = 2V_1 / M(t_2) = 2V_1 / \left[M^I(t_1) + M^{II}(t_1) \right]$$

For the ideal gas, using mass balance, we have

$$\frac{P_2(2V_1)}{T_2} = \frac{P_1^I V_1}{T_1^I} + \frac{P_1^{II} V_1}{T_1^{II}} \Rightarrow \frac{2P_2}{T_2} = \frac{P_1^I}{T_1^I} + \frac{P_1^{II}}{T_1^{II}} \tag{1}$$

Energy balance: $N_2 \underline{U}_2 = N_1^I \underline{U}_1^I + N_1^{II} \underline{U}_1^{II}$

Substitute $\underline{U} = \underline{U}_0 + N C_V (T - T_0)$, and cancel terms, use $N = PV/RT$ and get

$$2P_2 = P_1^I + P_1^{II} \tag{2}$$

Using Eqns. (1) and (2) get $P_2 = 7.5 \times 10^5$ Pa $= 0.75$ MPa and $T_2 = 529.4$ K $(256.25°C)$.

(d) For steam, solution is similar to (b). Use Steam Table to get M_1^I and M_1^{II} in terms of V.

Chamber 1: $\hat{U}_1^I = 2669.4$ kJ/kg; $\hat{V}_1^I = 0.2204$ m^3/kg;

$M^I = V_1 / \hat{V}_1^I = 4.537 V_1$

Chamber 2: $\hat{U}_1^{II} = \hat{U}(T = 600$ K, $P = 0.5$ MPa$) = 2845.9$ kJ/kg;

$\hat{V}_1^{II} = 0.5483$ m^3/kg; $M^{II} = 1.824 V_1 = V_1 / \hat{V}_1^{II}$

Thus, $\hat{V}_2 = \dfrac{2V_1}{M^I + M^{II}} = \dfrac{2V_1}{4.537 V_1 + 1.824 V_1} = 0.3144$ m^3/kg;

$\hat{U}_2 = \left(M^I \hat{U}_1^I + M^{II} \hat{U}_1^{II} \right) / \left(M_1^I + M_1^{II} \right) = 2720.0$ kJ/kg

By trial and error: $T_2 \sim 302°C$ (575 K) and $P \sim 0.76$ MPa.

2.16 System: contents of the turbine (open, steady state)

(a) adiabatic

mass balance: $\dfrac{dM}{dt} = 0 = \dot{M}_1 + \dot{M}_2 \Rightarrow \dot{M}_2 = -\dot{M}_1$

energy balance: $\dfrac{dU}{dt} = 0 = \dot{M}_1 \hat{H}_1 + \dot{M}_2 \hat{H}_2 + \cancel{\dot{Q}}^0 + \dot{W}_s - P \cancel{\dfrac{dV}{dt}}^0$

$\Rightarrow \dot{W}_s = -\dot{M}_1 \left(\hat{H}_1 - \hat{H}_2 \right) = -\dot{M}_1 (3450.9 - 2865.6)$ kJ/kg

$= -\dot{M}_1 \left(5.853 \times 10^5 \right)$ J/kg

But $\dot{W}_s = -7.5 \times 10^5$ watt $= -7.5 \times 10^5$ J/s

$\dot{M}_1 = \dfrac{-7.50 \times 10^5 \text{ J/s}}{-5.853 \times 10^5 \text{ J/kg}} = 1.281$ kg/s $= 4.613 \times 10^3$ kg/h

(b) Energy balance is

$\dfrac{dU}{dt} = 0 = \dot{M}_1 \hat{H}_1 + \dot{M}_2 \hat{H}_2 + \dot{Q} + \dot{W}_s - P \cancel{\dfrac{dV}{dt}}^0$

$$w\text{here } \dot{Q} = \dot{M}_1(-60 \text{ kJ/kg})$$

$$\hat{H}_2 = \hat{H}(150°\text{C, } 0.3 \text{ MPa}) = 2761.0 \text{ kJ/kg}$$

Thus

$$-\dot{W}_s = 1.281 \text{ kg/s}(3450.9 - 2761.0 - 60) \text{ kJ/kg} = 807 \text{ kJ/s}$$

$$= 8.07 \times 10^5 \text{ watt} = 807 \text{ kW}$$

2.17 System: 1 kg of water (closed system).

Work of vaporization $= \int P dV = P \int dV = P \Delta V$ since P is constant at 1.013 bar.

Also, from Steam Tables

$$\hat{V}^L = 0.001044 \text{ m}^3/\text{kg} \text{ ; } \hat{V}^V = 1.6729 \text{ m}^3/\text{kg} \text{ ; } \Delta \hat{V} = 1.6719 \text{ m}^3/\text{kg}$$

Energy balance for closed system (1 kg):

$$\hat{U}_2 - \hat{U}_1 = Q - \int P dV = Q - 1.013 \times 10^5 \text{ Pa} \times 1.6719 \text{ m}^3/\text{kg}$$

$$= Q - 1.6945 \times 10^5 \text{ J/kg}$$

$$\hat{U}_2 = 2506.5 \text{ kJ/kg} = 2.5065 \times 10^6 \text{ J/kg}$$

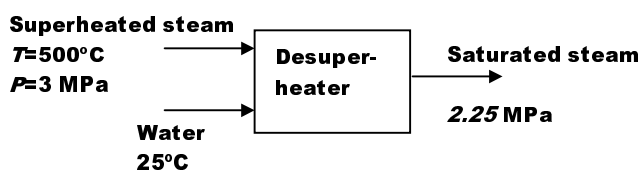$$\hat{U}_1 = 418.94 \text{ kJ/kg} = 4.1894 \times 10^5 \text{ J/kg}$$

Thus

$$Q = \hat{U}_2 - \hat{U}_1 + W = 2.5065 \times 10^6 - 4.1894 \times 10^5 + 1.6945 \times 10^5$$

$$= 2.2570 \times 10^6 \text{ J/kg}$$

$$W = -\int P dV = 1.6945 \times 10^5 \text{ J/kg .}$$

So heat needed to vaporize liquid $= 2.2570 \times 10^6 \text{ J/kg}$ of which 0.16945×10^6 is recovered as work against the atmosphere. The remainder, $2.088 \times 10^6 \text{ kJ/kg}$, goes to increase internal energy.

2.18 System = Contents of desuperheater (open, steady state)

$$\dot{M}_1 = 500 \text{ kg/hr} \text{ ; } \hat{H}_1 = 3456.5 \text{ kJ/kg}$$

$$\dot{M}_2 = ? \text{ ; } \hat{H}_2 = \hat{H}(\text{sat'd liq., } T = 25°\text{C}) = 104.89 \text{ kJ/kg}$$

Mass B: $0 = \dot{M}_1 + \dot{M}_2 + \dot{M}_3$

Energy B: $0 = \dot{M}_1 \hat{H}_1 + \dot{M}_2 \hat{H}_2 + \dot{M}_3 \hat{H}_3 + \cancel{\dot{Q}}^{\,0} + \cancel{\dot{W}_s}^{\,0} - P \cancel{\dfrac{dV}{dt}}^{\,0}$

$\dot{M}_3 = -\left(500 + \dot{M}_2\right)$ kg/hr ; $\hat{H}_3 = \hat{H}(\text{sat'd steam, } P = 2.25 \text{ MPa}) = 2801.7$ kJ/kg

Thus,

$0 = 500 \times 3456.5 + \dot{M}_2 = 104.89 - \left(500 + \dot{M}_2\right) \times 2801.7$

$\Rightarrow \dot{M}_2 = 121.4$ kg/hr

2.19 The process here is identical to that of Illustration 2.5-3, so that we can use the equation

$$T_2 = \frac{P_2}{P_1/T_1 + C_V/C_P\left[(P_2 - P_1)/T_{\text{in}}\right]}$$

developed in the illustration. Here, $P_2 = 2.0$ MPa , $T_{\text{in}} = 120°\text{C} = 393.15$ K , $C_P = 29.3$ J/mol K , $C_V = C_P - R = 20.99$ J/mol K .

Cylinder 1: $P_1 = 0$, $T_2 = \dfrac{C_P}{C_V} T_{\text{in}} = 548.8$ K $= 275.65°\text{C}$

Cylinder 2: $P_1 = 0.1$ MPa , $T_1 = 20°\text{C} = 293.15$ K

$$T_2 = \frac{2.0}{0.1/293.15 + 20.99/29.3\left[(2.0 - 0.1)/393.15\right]} = 525.87 \text{ K} = 252.7°\text{C}$$

Cylinder 3: $P_1 = 1$ MPa , $T_1 = 20°\text{C} = 293.15$ K ; $\Rightarrow T_2 = 382.16$ K $= 109.01°\text{C}$

2.20 System: Gas contained in the cylinder (closed system)

(a) $P = 0.1013 \text{ MPa} + \dfrac{M_{\text{piston}}g}{A} = 1.0133 \times 10^5 + \dfrac{4000 \text{ kg}}{2.5 \text{ m}^2} \times \dfrac{9.8 \text{ m/s}^2}{1 \text{ kgm/Ns}^2}$

$\qquad = 1.1701 \times 10^5 \text{ Pa} = 0.117 \text{ MPa}$

$N = \begin{array}{l}\text{moles of}\\ \text{gas initially}\\ \text{in system}\end{array} = \dfrac{PV}{RT} = \dfrac{1.1701 \times 10^5 \text{ Pa} \times 25 \text{ m}^3}{8.314 \text{ Pa·m}^3/\text{mol K} \times 293.15 \text{ K}}$

$\qquad = 1.200 \times 10^3 \text{ mol} = 1.200 \text{ kmol}$

(b) Energy balance: $U_2 - U_1 = Q - \int P dV = Q - P\Delta V$ since P is constant.

$\Delta V = 3 \text{ m} \times 2.5 \text{ m}^2 = 7.5 \text{ m}^3$; $P\Delta V = 1.1701 \times 10^5 \text{ Pa} \times 7.5 \text{ m}^3 = 8.7758 \times 10^5 \text{ J}$

Final temperature:

$T_2 = \dfrac{PV_2}{NR} = \dfrac{1.1701 \times 10^5 \text{ Pa} \times (25 + 7.5)\text{m}^3}{1.2 \times 10^3 \text{ mol} \times 8.314 \text{ Pam}^3/\text{mol K}} = 381.2 \text{ K} = 108.05°\text{C}$

$U_2 - U_1 = N(\underline{U}_2 - \underline{U}_1) = NC_V(T_2 - T_1)$

$\qquad = 1.2 \times 10^3 \text{ mol} \times (30 - 8.314) \text{ J/mol K} \times (381.2 - 293.15)\text{K}$

$\qquad = 2.291 \times 10^6 \text{ J}$

(c)

$$Q = \underset{\substack{\Delta T \text{ of} \\ \text{gas}}}{\underbrace{\Delta U}} + \underset{\text{work}}{\underbrace{P\Delta V}} = 2.291 \times 10^6 + \underset{\substack{\text{work}=27.7\% \text{ of energy absorbed} \\ \Delta T = 72.3\%}}{8.7758 \times 10^5}$$

$$= 3.169 \times 10^6 \text{ J} = 3.169 \text{ MJ}$$

(d) System: Gas contained within Piston + Cylinder (open system).
[Note: Students tend to assume $dT/dt = 0$. This is true, but not obvious!]

mass balance: $\dfrac{dN}{dt} = \dot{N}$

energy balance: $\dfrac{d}{dt}(N\underline{U}) = \dot{N}\underline{H}_{\text{out}} + \cancelto{0}{\dot{Q}} - P\dfrac{dV}{dt}$

Here (1) P is constant, (2) Ideal Gas Law $V = NRT/P$, (3) T and P of Gas Leaving Cylinder $= T$ and P of gas in the system. Thus,

$$N\frac{d\underline{U}}{dt} + \underline{U}\frac{dN}{dt} = \underline{H}\frac{dN}{dt} - P\frac{d}{dt}\left(\frac{NRT}{P}\right)$$

$$\Rightarrow (\underline{H} - \underline{U})\frac{dN}{dt} = NC_V\frac{dT}{dt} + R\frac{d}{dt}(NT)$$

$$RT\frac{dN}{dt} = NC_V\frac{dT}{dt} + NR\frac{dT}{dt} + RT\frac{dN}{dt} \Rightarrow N(C_V + R)\frac{dT}{dt} = 0$$

$$\Rightarrow \frac{dT}{dt} = 0 \text{ Q.E.D.}$$

Thus $T_3 = T_2 = 381.2$ K

Now going back to

$$N\frac{d\underline{U}}{dt} + \underline{U}\frac{dN}{dt} = \underline{H}\frac{dN}{dt} - P\frac{dV}{dt} \text{ and using } \frac{dT}{dt} = 0 = \frac{d\underline{U}}{dt}$$

$$\Rightarrow (\underline{H} - \underline{U})\frac{dN}{dt} = RT\frac{dN}{dt} = P\frac{dV}{dt} \text{ or } \frac{dN}{dt} = \frac{P}{RT}\frac{dV}{dt} \qquad (**)$$

Since P and T are constants

$$\frac{N_3}{N_2} = \frac{V_3}{V_2} = \frac{25 \text{ m}^3}{25 + 7.5 \text{ m}^3} = 0.7692$$

Thus $N_3 = 0.7692 \times 1200 \text{ mol} = 923 \text{ mol}$;
$\Delta N = -277 \text{ mol} = -0.277 \text{ kmol}$

2.21 (a) System: Gas contained within piston-cylinder (closed system) [neglecting the potential energy change of gas]
energy balance:

$$\frac{d(N\underline{U})}{dt} = N\frac{d\underline{U}}{dt} = \dot{Q} - P\frac{dV}{dt} \; ; \; NC_V\frac{dT}{dt} = \dot{Q} - PA\frac{dh}{dt}$$

But $T = \dfrac{PV}{NR} \Rightarrow \dfrac{dT}{dt} = \dfrac{P}{NR}\left(\dfrac{dV}{dt}\right) = \dfrac{PA}{NR}\dfrac{dh}{dt}$.

Thus

$$Q = \frac{AC_V P}{R}\frac{dh}{dt} + AP\frac{dh}{dt} = PA\left(\frac{C_V}{R}+1\right)\frac{dh}{dt} = \frac{PAC_P}{R}\frac{dh}{dt}$$

$$= \frac{30 \ \text{J/mol K}}{8.314 \ \text{J/mol K}} \times 1.1701 \times 10^5 \ \text{Pa} \times 2.5 \ \text{m}^2 \times 0.2 \ \text{m/s}$$

$$= 2.111 \times 10^5 \ \text{J/s}$$

(b) System: Gas contained within piston and cylinder (open system). Start from result of Part (d), Problem **2.20** (see eqn. (**)) in that illustration)

$$\frac{dN}{dt} = \frac{P}{RT}\frac{dV}{dt} = \frac{PA}{RT}\frac{dh}{dt} \quad \text{with } P \text{ and } T \text{ constant}$$

(See solution to Problem **2.20**)

$$\frac{dN}{dt} = \frac{1.1701 \times 10^5 \ \text{Pa} \times 2.5 \ \text{m}^2}{8.314 \ \text{J/mol K} \times 381.2 \ \text{K}} \times (-0.2 \ \text{m/s}) = -18.46 \ \text{mol/s}$$

$$= -0.01846 \ \text{kmol/s}$$

[check: $-18.46 \ \text{mol/sec} \times 15 \ \text{sec} = -276.9 \ \text{mol}$ compare with part d of Problem **2.20**]

2.22 System: gas contained in the cylinder (open system)
Important observation . . . gas leaving the system (That is, entering the exit valve of the cylinder) has same properties as gas in the cylinder.

mass balance $\dfrac{dN}{dt} = \dot{N}$ ⎫ Note that these are

energy balance $\dfrac{d(N\underline{U})}{dt} = \dot{N}\underline{H}$ ⎬ Eqns. (d) and (e) of Illustration 2.5-5

Proceeding as in that illustration we get Eqn. (f)

$$\left(\frac{T(t)}{T(0)}\right)^{C_P/R} = \left(\frac{P(t)}{P(0)}\right) \quad \text{or} \quad \frac{T(t)}{P(t)^{R/C_P}} = \frac{320}{10^{(8.314/30)}} = 169.05 \ \text{K} \qquad (1)$$

where we have used a slightly different notation. Now using the mass balance we get

$$\frac{dN}{dt} = \frac{d}{dt}\left(\frac{PV}{RT}\right) = \frac{V}{R}\frac{d(P/T)}{dt} = \dot{N}$$

or

$$\frac{d(P/T)}{dt} = \frac{\dot{N}R}{V} = \frac{-(4.5/28) \ \text{mol/s} \times 8.314 \ \text{Pa}\cdot\text{m}^3/\text{mol K}}{0.15 \ \text{m}^3} = -8.908 \ \text{Pa/K}\cdot\text{s}$$

and

$$\left.\frac{P}{T}\right|_t = \left.\frac{P}{T}\right|_{t=0} - 8.908 \times 10^{-5}\,t \quad \text{bar/K}\ \text{ for } P \text{ in bar and } t \text{ in secs.} \tag{2}$$

Using $t = 5$ minutes $= 300$ secs in Eqn. (2) and simultaneously solving Eqns. (1) and (2) yields

$$T(5\ \text{min}) = 152.57\ \text{K}\,,\ \ P(5\ \text{min}) = 0.6907\ \text{bar}$$

Computation of rates of change from mass balance

$$\frac{d}{dt}\left(\frac{P}{T}\right) = \frac{1}{T}\left(\frac{dP}{dt} - \frac{P\,d\ln T}{dt}\right) = \frac{\dot{N}R}{V} \quad \text{or} \quad \frac{d\ln P}{dt} - \frac{d\ln T}{dt} = \frac{\dot{N}RT}{PV} \tag{3}$$

From energy balance (using 2 eqns. above and eqn. (f) in Illustration (2.5-5))

$$\frac{C_V}{R}\frac{d\ln T}{dt} = \frac{d\ln(P/T)}{dt} \quad \text{or} \quad \frac{C_P}{R}\frac{d\ln T}{dt} = \frac{d\ln P}{dt} \tag{4}$$

Now using Eqn. (4) in Eqn. (3). Thus,

$$\frac{C_V}{R}\frac{d\ln T}{dt} = \frac{C_V}{RT}\frac{dT}{dt} = \frac{\dot{N}RT}{PV} \quad \text{or}$$

$$\left.\frac{dT}{dt}\right|_{t=5\,\text{min}} = \left.\frac{\dot{N}(RT)^2}{PVC_V}\right|_{t=5\,\text{min}} = -1.151\ \text{K/sec}$$

and

$$\left.\frac{dP}{dt}\right|_{5\,\text{min}} = \left.\frac{C_P P}{RT}\frac{dT}{dt}\right|_{5\,\text{min}} = -0.0188\ \text{bar/s}$$

2.23 Consider a fixed mass of gas as the (closed) system for this problem. The energy balance is:

$$\frac{d(N\underline{U})}{dt} = N\frac{d\underline{U}}{dt} = NC_V\frac{dT}{dt} = -P\frac{dV}{dt}$$

From the ideal gas law we have $P = NRT/V$. Thus

$$C_V N\frac{dT}{dt} = \frac{-NRT}{V}\frac{dV}{dt} \Rightarrow \frac{C_V}{R}\frac{d\ln T}{dt} = \frac{-d\ln V}{dt}$$

or

$$\frac{C_V}{R}\ln\frac{T_2}{T_1} = -\ln\frac{V_2}{V_1} \Rightarrow \left(\frac{T_2}{T_1}\right)^{C_V/R} = \left(\frac{V_1}{V_2}\right) \tag{*}$$

or

$$V_2 T_2{}^{C_V/R} = V_1 T_1{}^{C_V/R} = VT^{C_V/R} = \text{constant}$$

Substituting the ideal gas law gives $PV^{C_P/C_V} = PV^{\gamma} = \text{constant}$. Note that the heat capacity must be independent of temperature to do the integration in Eqn. (*) as indicated.

2.24 System: Contents of the tank (at any time)

(a) Final temperature $(T = 330 \text{ K})$ and pressure $\left(P = 1.013 \times 10^5 \text{ Pa}\right)$ are known. Thus, there is no need to use balance equations.

$$N_f = \frac{PV}{RT} = \frac{1.013 \times 10^5 \text{ Pa} \times 0.3 \text{ m}^3}{8.314 \text{ J/mol K} \cdot 330 \text{ K}} = 11.08 \text{ mol} = 0.01108 \text{ kmol}$$

(b) Assume, as usual, that enthalpy of gas leaving the cylinder is the same as gas in the cylinder . . . See Illustration 2.5-5. From Eqn. (f) of that illustration we have

$$\frac{P_f}{P_i} = \left(\frac{T_f}{T_i}\right)^{C_P/R} \quad \text{or} \quad \frac{T_f}{T_i} = \left(\frac{P_f}{P_i}\right)^{R/C_P} = \left(\frac{1.0133 \times 10^5}{1.0 \times 10^6}\right)^{8.314/29} = 0.5187$$

Thus $\quad T_f = 0.5187 \times 330 \text{ K} = 171.19 \text{ K}, \qquad P_f = 1.013 \text{ bar}, \qquad$ and $N_f = 21.36 \text{ mol} = 0.02136 \text{ kmol}$.

2.25 Except for the fact that the two cylinders have different volumes, this problem is just like Illustration 2.5-5. Following that illustration we obtain

$$\frac{2P_1^i}{T_1^i} = \frac{2P_1^f}{T_1^f} + \frac{P_2^f}{T_2^f} \qquad\qquad \text{for Eqn. (a')}$$

$$2P_1^i = 2P_1^f + P_2^f \quad \text{or} \quad P^f = \frac{2}{3}P_1^i \qquad\qquad \text{for Eqn. (c')}$$

and again get Eqn. (f)

$$\left(\frac{T_1^f}{T_1^i}\right)^{C_P/R} = \left(\frac{P_1^f}{P_1^i}\right)$$

Then we obtain $P^f = 133.3 \text{ bar}$, $T_1^f = 223.4 \text{ K}$, and $T_2^f = 328.01 \text{ K}$.

2.26 From problem statement $P_1^f = P_2^f = P^f$ and $T_1^f = T_2^f = T^f$.

Mass balance on the composite system of two cylinders

$$N_1^f + N_2^f = N_1^i \quad \text{or} \quad \frac{2P_1^f}{T_1^f} + \frac{P_2^f}{T_2^f} = \frac{3P^f}{T^f} = \frac{2P^i}{T^i}$$

Energy balance on composite system

$$N_1^i \underline{U}_1^i = N_1^f \underline{U}_1^f + N_2^f \underline{U}_2^f \Rightarrow P^f = \frac{2P^i}{3} = \frac{2 \times 200 \text{ bar}}{3} = 133.3 \text{ bar} \quad \text{(as before)}$$

and $T^f = \dfrac{3P^f}{2P_1^i} T_1^i = \dfrac{3}{2}\left(\dfrac{2}{3}\right) T_1^i = T_1^i = 250 \text{ K}$.

2.27 Even though the second cylinder is not initially evacuated, this problem still bears many similarities to Illustration 2.5-5). Proceeding as in that illustration, we obtain

$$\frac{2P_1^i}{T_1^i} + \frac{P_2^i}{T_2^i} = \frac{2P_1^f}{T_1^f} + \frac{P_2^f}{T_2^f} \quad \text{instead of Eqn (a')}$$

$$2P_1^i + P_2^i = 2P_1^f + P_2^f = 3P^f \quad \text{instead of Eqn. (c)}$$

[Thus, $P^f = (2 \times 200 + 1 \times 20)/3 = 140 \text{ bar}$] and again recover Eqn. (f) for Cylinder 1

$$\left(\frac{T_1^f}{T_1^i}\right)^{C_P/R} = \left(\frac{P_1^f}{P_1^i}\right) \qquad\qquad \text{Eqn. (f)}$$

Solution is $P_1^f = P_2^f = 140 \text{ bar}$, $T_1^f = 226.47 \text{ K}$, $T_2^f = 286.51 \text{ K}$.

2.28 (a) System = Gas contained in room (open system)

mass balance: $\dfrac{dN}{dt} = \dot{N}$

energy balance: $\dfrac{d(N\underline{U})}{dt} = \dot{N}\underline{H} + \dot{Q} = \underline{H}\dfrac{dN}{dt} + \dot{Q}$

Thus,

$$\dot{Q} = \frac{d(N\underline{U})}{dt} - \underline{H}\frac{dN}{dt} = (\underline{U} - \underline{H})\frac{dN}{dt} + N\frac{d\underline{U}}{dt}$$

For the ideal gas, $\underline{H} - \underline{U} = P\underline{V} = RT$; $\dfrac{dN}{dt} = \dfrac{d}{dt}\left(\dfrac{PV}{RT}\right) = \dfrac{V}{R}\dfrac{d}{dt}\left(\dfrac{P}{T}\right)$

$$\dot{Q} = -RT\left(\frac{V}{R}\right)\frac{d}{dt}\left(\frac{P}{T}\right) + NC_V\frac{dT}{dt} = -RT\cdot\frac{NT}{P}\frac{d}{dt}\left(\frac{P}{T}\right) + NC_V\frac{dT}{dt}$$

$$\dot{Q} = \frac{-NRT}{P}\frac{dP}{dt} + NR\frac{dT}{dt} + NC_V\frac{dT}{dt}$$

Since $P = \text{constant}$, $\dfrac{dP}{dt} = 0$, $\dot{Q} = \dfrac{NC_P dT}{dt}$ or

$$\frac{dT}{dt} = \frac{\dot{Q}}{C_P}\frac{RT}{PV} = \frac{1.5\times10^3 \ \text{W}\cdot 8.314 \ \text{J/mol K}\cdot 283.15 \ \text{K}}{29 \ \text{J/mol K}\cdot 1.0133\times10^5 \ \text{Pa}\cdot(3.5\times5\times3) \ \text{m}^3}$$

$$= 0.0229 \ \text{K/s} = 1.37 \ \text{K/min}$$

(b) System = Gas contained in sealed room (closed system) $\dot{N} = 0$

Energy balance: $\dfrac{d(N\underline{U})}{dt} = N\dfrac{d\underline{U}}{dt} = NC_v\dfrac{dT}{dt} = \dot{Q}$

$$\left.\frac{dT}{dt}\right|_{\substack{\text{sealed}\\\text{room}}} = \frac{\dot{Q}}{NC_V} = \frac{C_P}{C_V}\left.\frac{dT}{dt}\right|_{\substack{\text{unsealed}\\\text{room}}} = \frac{29}{29-8.314}\times1.37 \ \text{K/min}$$

$$= 1.925 \ \text{K/min}$$

2.29 In each case we must do work to get the weights on the piston, either by pushing the piston down to where it can accept the weights, or by lifting the weights to the location of the piston. We will consider both alternatives here. First, note that choosing the gas contained within piston and cylinder as the system, $\Delta U = Q + W$. But $\Delta U = 0$, since the gas is ideal and $T = \text{constant}$. Also $W = -\int P dV = -NRT\ln(V_f/V_i)$, for the same reasons. Thus, in each case, we have that the net heat and work flows to the gas are

$$W(\text{work done on gas}) = -NRT\ln\left(\frac{V_f}{V_i}\right) = -2479\ln\frac{1.213\times10^{-2}}{2.334\times10^{-2}} = 1622.5 \ \text{J}$$

$$\text{and } Q = -W = -1622.5 \ \text{J} \ (\text{removed from gas})$$

If more work is delivered to the piston, the piston will oscillate eventually dissipating the addition work as heat. Thus, more heat will be removed from the gas + piston and cylinder than if only the minimum work necessary had been used.
    Note that in each case the atmosphere will provide

$$W_{\text{atm}} = P\Delta V = 1.013\times10^5 \ \text{kPa}\times(2.334-1.213)\times10^{-2} \ \text{m}^3 = 1135.6 \ \text{J}$$

and the change in potential energy of piston

$$mg\Delta h = 5 \ \text{kg}\times9.8 \ \text{m/s}^2\times\frac{(2.334-1.213)\times10^{-2} \ \text{m}^3}{1\times10^{-2} \ \text{m}} = 54.9 \ \text{J}$$

The remainder $1622.5 - 1135.6 - 54.9 = 432.0$ J must be supplied from other sources, as a minimum.

(a) One 100 kg weight.
    An efficient way of returning the system to its original state is to slowly (i.e., at zero velocity) force the piston down by supplying 432.0 J of energy. When the piston is down to its original location, the 100 kg is slid sideways, onto the piston, with no energy expenditure.

    An inefficient process would be to lift the 100 kg weight up to the present location of the piston and then put the weight on the piston. In this case we would supply

$$Mg\Delta h = Mg\frac{\Delta V}{A} = 100 \text{ kg} \times 9.8 \ \frac{\text{m}}{\text{s}^2} \times \frac{\left(2.334 \times 10^{-2} - 1.213 \times 10^{-2}\right) \text{m}^3}{1 \times 10^{-2} \text{ m}^2}$$
$$= 1098.6 \ \text{kg m}^2/\text{s}^2 = 1098.6 \text{ J}$$

This energy would be transmitted to the gas as the piston moved down. Thus

$$W(\text{on gas}) = \underset{\text{(atmosphere)}}{1135.6 \text{ J}} + \underset{\text{(PE of piston)}}{54.9 \text{ J}} + \underset{\text{(PE of weight)}}{1098.6 \text{ J}} = 2289.1$$

$$W(\text{J}) = -Q(\text{J}) \quad W_{\text{cycle}} = -Q_{\text{cycle}}$$

	$W(\text{J}) = -Q(\text{J})$	$W_{\text{cycle}} = -Q_{\text{cycle}}$
Efficient	1622.5	$1622.5 - 1190.5 = 432.0$
Inefficient	2289.1	$2289.1 - 1190.5 = 1098.6$

(b) Two 50 kg weights
    In this case we also recover the potential energy of the topmost weight.

$$mg\Delta h = 50 \text{ kg} \times 9.8 \ \frac{\text{m}}{\text{s}^2} \times \frac{(1.597 - 1.213) \times 10^{-2} \text{ m}^3}{0.01 \text{ m}^2} = 188.2 \text{ J}$$

Thus in an efficient process we need supply only

$$1622.5 - 1135.6 - 54.9 - 188.2 = 243.8 \text{ J}$$

An efficient process would be to move the lowest weight up to the position of the piston, by supplying

$$50 \text{ kg} \times 9.8 \ \frac{\text{m}}{\text{s}^2} \times \frac{(2.334 - 1.213) \times 10^{-2} \text{ m}^3}{1 \times 10^{-2} \text{ m}^2} = 549.3 \text{ J}$$

Slide this weight onto the piston and let go. The total work done in this case is

$$\underset{\text{(atmosphere)}}{1135.6} + \underset{\Delta \text{PE of piston}}{54.9} + \underset{\Delta \text{PE of weight}}{243.8} + \underset{\text{supplied by us}}{549.3} = 1983.6 \text{ J}$$

Therefore

$$W(\text{J}) = -Q \quad W_{\text{cycle}} = -Q_{\text{cycle}}$$

Efficient	1622.5	$1622.5 - 1378.7 = 243.8$ J
Inefficient	1983.6	$1983.6 - 1378.7 = 604.9$ J

(c) Four 25 kg weights.
In this case the recovered potential energy of weights is

$$25 \text{ kg} \times 9.8 \text{ m/s}^2 \times \left(\frac{[(1.897 - 1.213) + (1.597 - 1.213) + (1.379 - 1.213)] \times 10^{-2}}{1 \times 10^{-2}} \right) \text{m}$$

$$= 302.3 \text{ J}$$

Thus in an efficient process we need supply only

$$1622.5 - 1135.6 - 54.9 - 302.3 = 129.7 \text{ J}$$

An inefficient process would be to raise the lowest weight up to the piston, expending

$$25 \text{ kg} \times 9.8 \text{ m/s}^2 \times \frac{(2.334 - 1.213) \times 10^{-2} \text{ m}^3}{1 \times 10^{-2} \text{ m}} = 274.6 \text{ J}$$

Thus the total work done is

$$1135.6 + 54.9 + 302.3 + 274.6 = 1767.4 \text{ J}$$

and

$$W = -Q \quad W_{\text{cycle}} = -Q_{\text{cycle}}$$

Efficient	1622.5	$1622.5 - 1493.0 = -129.5$
Inefficient	1767.4	$1767.4 - 1493.0 = -274.4$

(d) Grains of sand
Same analysis as above, except that since one grain of sand has essentially zero weight $W = 1622.5$ J, $Q = -1622.5$ J, $W_{\text{cycle}} = -Q_{\text{cycle}} = 0$.

2.30 System = Gas contained in the cylinder (closed system)
energy balance: $\dfrac{d(N\underline{U})}{dt} = N\dfrac{d\underline{U}}{dt} = NC_V\dfrac{dT}{dt} = -P\dfrac{dV}{dt} = \dfrac{-NRT}{V}\dfrac{dV}{dt}$ {Using the ideal gas equation of state}
Since C_V and C_P are constant

$$\frac{C_V}{R}\frac{1}{T}\frac{dT}{dt} = -\frac{1}{V}\frac{dV}{dt} \quad \text{or} \quad \left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{R/C_V} = \left(\frac{L_1}{L_2}\right)^{R/C_V}$$

$$\Rightarrow T_2 = (25 + 273.15) \times \left(\frac{0.03 \text{ m}^3}{0.03 + 0.6 \times 0.05 \text{ m}^3}\right)^{8.314/(30 - 8.314)}$$

$$= 228.57 \text{ K} = -44.58^\circ\text{C and}$$

$$P_2 = P_1\left(\frac{V_1}{V_2}\right)\left(\frac{T_2}{T_1}\right) = 20 \times \frac{1}{2} \times \frac{228.57}{298.15} = 7.666 \text{ bar}$$

From the difference (change of state) form of energy balance

$$\Delta U = \cancel{Q}^{\,0} + W = NC_V(T_2 - T_1) = -\int PdV$$

and $N = \dfrac{PV}{RT} = \dfrac{20 \text{ bar} \times 0.03 \text{ m}^3 \text{ kmol} \cdot \text{K}}{298.15 \text{ K} \times 8.314 \times 10^{-2} \text{ bar} \cdot \text{m}^3} = 0.0242 \text{ kmol}$

$\Rightarrow W = \Delta U = -0.0242 \text{ kmol} \times (30 - 8.314) \text{ kJ/kmol} \cdot \text{K} \cdot (298.15 - 228.57)\text{K}$

$\quad = -36.52 \text{ kJ}$

Where has this work gone?

(a) To increase potential energy of piston
(b) To increase kinetic energy of piston
(c) To push back atmosphere so system can expand
(d) Work done against friction (and converted to heat).

To see this, write Newton's 2nd Law of Motion for the piston
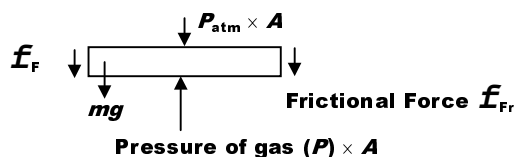
$$f = MA \Rightarrow (PA - P_{atm}A - mg - f_{fr}) = m\frac{dv}{dt}; \ v = \text{velocity of piston}$$

Thus, $P = \dfrac{m}{A}\dfrac{dv}{dt} + P_{atm} + \dfrac{mg}{A} + \dfrac{f_{fr}}{A}$

$$-\Delta U = 36,520 \text{ J} = +\int PdV$$

$$= +\int P_{atm}dV + \frac{m}{A}\int \frac{dv}{dt}\frac{dV}{dt}dt + \frac{mg}{A}\int dV + \frac{1}{A}\int f_{fr}\frac{dv}{dt}dt \qquad (1)$$

Now $\dfrac{1}{A}\dfrac{dV}{dt} = \dfrac{dh}{dt} = v$ ($h = $ piston height) and $v\dfrac{dv}{dt} = \dfrac{1}{2}\dfrac{d}{dt}(v^2)$

$$36,520 \text{ J} = \underset{\substack{3000 \text{ J} \\ \text{Work against} \\ \text{atmosphere}}}{P_{atm}\Delta V} + \underset{\substack{\text{since} \\ v_{initial}=0}}{\frac{mv^2}{2}} + \underset{\substack{1760 \text{ J} \\ \text{Work used to} \\ \text{increase potential} \\ \text{energy of piston}}}{mg\Delta h} + \int f_{fr}vdt$$

Thus $36,520 \text{ J} = 3000 + \dfrac{mv^2}{2} + 1760 + \int f_{fr}vdt$.

(a) If there is no friction $f_{fr} = 0$ then

$$v^2 = \frac{(36520 - 3000 - 1760)\text{J} \times 2}{300 \text{ kg}} = 211.7 \text{ m}^2/\text{s}^2 \Rightarrow v = 14.55 \text{ m/s}$$

(b) If we assume only sliding friction, $f_{fr} = kv$

$$\int f_{fr} v\, dv = k \int v^2 dt \Rightarrow (36520 - 3000 - 1760) = \frac{m}{2} v^2 + k \int v^2 dt$$

In order to determine the velocity now we need to know the coefficient of sliding friction k, and then would have to solve the integral equation above (or integrate successively over small time steps). It is clear, however, that
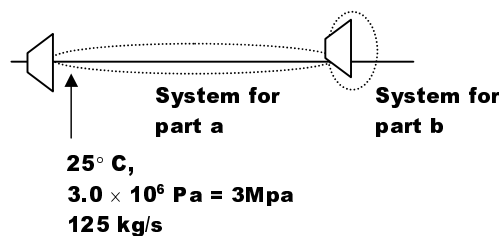
$$v(\text{with friction}) < v(\text{without friction}) = 14.55 \text{ m/s}$$

2.31 $25°C, \ 3.0 \times 10^6 \text{ Pa} = 3 \text{ MPa}$
  125 kg/s

  (a) mass balance (steady-state)

  $0 = \dot{M}_1 + \dot{M}_2$

  $\Rightarrow \dot{M}_1 = -\dot{M}_2 = 125 \text{ kg/s}$

System for part a   **System for part b**

25° C,
3.0×10^6 Pa = 3Mpa
125 kg/s

Energy balance (neglecting PE terms)

$$0 = \dot{M}_1\left(\hat{H}_1 + \frac{v_1^2}{2}\right) + \dot{M}_2\left(\hat{H}_2 + \frac{v_2^2}{2}\right)$$

$\dot{M} = \rho v A = m n v A$; $\rho = $ mass density, $n = $ molar density,
$v = $ velocity, $A = $ pipe area, $m = $ molecular weight.

$$\frac{\dot{M}}{m} = \frac{P}{RT} v A$$

$$\Rightarrow \frac{125 \text{ kg/s}}{16 \text{ kg/kmol}} = \frac{3.0 \times 10^6 \text{ Pa}}{298.15 \text{ K} \times 8.314 \times 10^3 \text{ Pa} \cdot \text{m}^3} \times v(\text{m/s}) \times \pi \times 0.09 \text{ m}^2$$

$$\Rightarrow v = 22.83 \text{ m/s}$$

$$\frac{mv^2}{2} = \frac{16 \text{ kg/kmol} \times (22.83 \text{ m/s})^2}{2 \times 1 \text{ kg} \cdot \text{m}/\text{Ns}^2} = 4.170 \times 10^3 \text{ J/kmol} = 4.17 \text{ kJ/kmol}$$

Back to energy balance, now on a molar basis

$$\underline{H}_1 - \underline{H}_2 = \frac{mv_2^2}{2} - \frac{mv_1^2}{2} = C_p(T_1 - T_2)$$

As a first guess, neglect kinetic energy terms . . .

$$C_p(T_1 - T_2) = 0 \Rightarrow T_1 = T_2 = 25°C$$

Now check this assumption

$$v_2 = \frac{n_1 v_1}{n_2} = \frac{P_1 v_1}{P_2} = \frac{3.0 \times 10^6 v_1}{2.0 \times 10^6} = 34.24 \text{ m/s}$$

Recalculate including the kinetic energy terms

$$C_p(T_1 - T_2) = \frac{m}{2}\left(v_1^2 - v_2^2\right) = \frac{16}{2}\left(34.24^2 - 22.83^2\right) = 5209 \text{ J/kmol}$$

$$T_2 = T_1 - \frac{5209 \text{ J/kmol}}{36.8 \text{ J/mol} \times 1000 \text{ mol/kmol}} = T_1 - 0.14°\text{C}$$

Thus the kinetic energy term makes such a small contribution, we can safely ignore it.

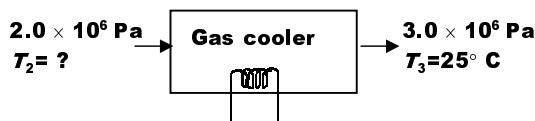(b)   Mass balance on compressor (steady-state) $0 = \dot{N}_1 + \dot{N}_2$

Energy balance on compressor, which is in steady-state operation

$$0 = \dot{N}_1\underline{H}_1 + \dot{N}_2\underline{H}_2 + \cancel{\dot{Q}}^{\,0} + \dot{W}_s \Rightarrow \dot{W}_s = \dot{N}_1 C_p\underset{=25°C}{(T_2 - T_1)}$$
adiabatic compressor

Can compute $\dot{W}_s$ if T_2 is known or vice versa. However, can not compute both without further information.

Analysis as above except that $\dot{Q} \neq 0$ but $\dot{W} = 0$.

Here we get $\begin{cases} 0 = \dot{N}_2 + \dot{N}_3 \\ \dot{Q} = \dot{N}_1 C_p\underset{=25°C}{(T_3 - T_2)} \end{cases}$

Can not compute $\dot{Q}$ until T_2 is known.

See solution to Problem **3.10**.

2.32 a) Define the system to be the nitrogen gas. Since a Joule-Thomson expansion is isenthalpic, $\hat{H}(T_1, P_1) = \hat{H}(T_2, P_2)$. Using the pressure enthalpy diagram for nitrogen, Figure 2.4-3, we have
$\hat{H}(135 \text{ K}, 20 \text{ MPa}) = 153 \text{ kJ / kg}$ and then $T_2 = T(P_2 = 0.4 \text{ MPa}, \hat{H} = 153 \text{ kJ / kg})$

From which we find that $T = 90$ K, with approximately 55% of the nitrogen as vapor, and 45% as liquid.
b) Assuming nitrogen to be an ideal gas (poor assumption), then the enthalpy depends only on temperature. Since a Joule-Thomson expansion is isenthalpic, this implies that the temperature is unchanged, so that the final state will be all vapor.

2.33 Plant produces 1.36×10^9 kwh of energy per year
$\Rightarrow$ Plant uses $1.36 \times 10^9 \times 4 = 5.44 \times 10^9$ kwh of heat

$1 \text{ kwh} = 3.6 \times 10^6 \text{ J}$

$\Rightarrow$ Plant uses $3.6 \times 10^6 \dfrac{\text{J/year}}{\text{kwh}} \times 5.44 \times 10^9 \text{ kwh} = 19.584 \times 10^{15} \text{ J/year}$

ΔH of rock (total) $= M \cdot \hat{C}_p (T_f - T_i)$

$\qquad\qquad\qquad = 10^{12} \text{ kg} \times 1 \text{ J/g K} \times 1000 \text{ g/kg} \times (110 - 600) \text{ K}$

$\qquad\qquad\qquad = -490 \times 10^{15} \text{ J}$

$\Rightarrow 19.58 \times 10^{15} \text{ J/year} \times x \text{ years} = 490 \times 10^{15} \text{ J}$

$x = 25.02 \text{ years}$

3

3.1 (a) System = Ball (1) + Water (2)

Energy balance: $M_1\hat{U}_1^f + M_2\hat{U}_2^f - M_1\hat{U}_1^i - M_2\hat{U}_2^i = 0$

$\Rightarrow M_1 C_{V,1}\left(T_1^f - T_1^i\right) + M_2 C_{V,2}\left(T_2^f - T_2^i\right) = 0$; also $T_1^f - T_2^f$. Thus

$$T^f = \frac{M_1 C_{V,1} T_1^i + M_2 C_{V,2} T_2^i}{M_1 C_{V,1} + M_2 C_{V,2}} = \frac{5 \times 10^3 \times 0.5 \times 75 + 12 \times 10^3 \times 4.2 \times 5}{5 \times 10^3 \times 0.5 + 12 \times 10^3 \times 4.2}$$

$= 8.31°C$

[Note: Since only ΔT's are involved, °C were used instead of K)].

(b) For solids and liquids we have (eqn. 3.4-6). That $\Delta S = M \int C_P \dfrac{dT}{T} = MC_P \ln \dfrac{T_2}{T_1}$ for the case in

which C_P is a constant. Thus

Ball: $\Delta S = 5 \times 10^3 \text{ g} \times 0.5 \dfrac{\text{J}}{\text{g} \cdot \text{K}} \times \ln\left\{\dfrac{8.31 + 273.15}{75 + 273.15}\right\} = -531.61 \dfrac{\text{J}}{\text{K}}$

$= -531.61 \text{ s}$

Water: $\Delta S = 12 \times 10^3 \text{ g} \times 4.2 \dfrac{\text{J}}{\text{g} \cdot \text{K}} \times \ln\left\{\dfrac{8.31 + 273.15}{5 + 273.15}\right\} = +596.22 \dfrac{\text{J}}{\text{K}}$

and

$\Delta S(\text{Ball} + \text{Water}) = 596.22 - 531.61 \dfrac{\text{J}}{\text{K}} = 64.61 \dfrac{\text{J}}{\text{K}}$

Note that the system Ball + Water is isolated. Therefore

$$\Delta S = S_{\text{gen}} = 64.61 \dfrac{\text{J}}{\text{K}}$$

3.2 Energy balance on the combined system of casting and the oil bath

$M_c C_{V,c}\left(T^f - T_c^i\right) + M_o C_{V,o}\left(T^f - T_o^i\right) = 0$ since there is a common final temperature.

$20 \text{ kg} \times 0.5 \dfrac{\text{kJ}}{\text{kg} \cdot \text{K}}\left(T^f - 450\right)\text{K} + 150 \text{ kg} \times 2.6 \dfrac{\text{kJ}}{\text{kg} \cdot \text{K}}\left(T^f - 450\right)\text{K} = 0$

This has the solution $T^f = 60°C = 313.15 \text{ K}$

Since the final temperature is known, the change in entropy of this system can be calculated

from $\Delta S = 20 \times 0.5 \times \ln\left(\dfrac{273.15 + 60}{273.15 + 450}\right) + 150 \times 2.6 \times \ln\left(\dfrac{273.15 + 60}{273.15 + 50}\right) = 4.135 \dfrac{\text{kJ}}{\text{K}}$

3.3 Closed system energy and entropy balances

$$\frac{dU}{dt} = \dot{Q} + \dot{W}_s - P\frac{dV}{dt}; \quad \frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{S}_{\text{gen}};$$

Thus, in general $\dot{Q} = T\dfrac{dS}{dt} - T\dot{S}_{\text{gen}}$ **and**

$$\dot{W}_s = \frac{dU}{dt} - \dot{Q} + P\frac{dV}{dt} = \frac{dU}{dt} - T\frac{dS}{dt} + T\dot{S}_{gen} + P\frac{dV}{dt}$$

Reversible work: $\dot{W}_s^{\text{Rev}} = \dot{W}_s^{\text{Rev}}\left(\dot{S}_{gen} = 0\right) = \frac{dU}{dt} - T\frac{dS}{dt} + P\frac{dV}{dt}$

(a) System at constant U & $V \Rightarrow \frac{dU}{dt} = 0$ and $\frac{dV}{dt} = 0$

$$\dot{W}_s\left(\dot{S}_{gen} = 0\right) = \dot{W}_s^{\text{Rev}} = -T\frac{dS}{dt}$$

(b) System at constant S & $P \Rightarrow \frac{dS}{dt} = 0$ and $\frac{dP}{dt} = 0 \Rightarrow P\frac{dV}{dt} = \frac{d}{dt}(PV)$

so that

$$\dot{W}_s\left(\dot{S}_{gen} = 0\right) = \dot{W}_s^{\text{rev}} = \frac{dU}{dt} + \frac{d}{dt}(PV) = \frac{d}{dt}(U + PV) = \frac{dH}{dt}$$

3.4

700 bar, 600°C $\quad\longrightarrow\; \boxed{\bigcirc} \;\longrightarrow\quad$ 10 bar, $T = ?$

Steady-state balance equations

$$\frac{dM}{dt} = 0 = \dot{M}_1 + \dot{M}_2$$

$$\frac{dU}{dt} = 0 = \dot{M}_1\hat{H}_1 + \dot{M}_2\hat{H}_2 + \cancel{\dot{Q}}^{\,0} + \cancel{\dot{W}_s}^{\,0} - P\cancel{\frac{dV}{dt}}^{\,0} = \dot{M}_1\hat{H}_1 + \dot{M}_2\hat{H}_2$$

or $\hat{H}_1 = \hat{H}_2$

Drawing a line of constant enthalpy on Mollier Diagram we find, at $P = 10$ bar, $T \cong 308°C$

At 700 bar and 600°C $\qquad$ At 10 bar and 308°C
$\hat{V} = 0.003973 \text{ m}^3/\text{kg}$ $\qquad \hat{V} \approx 0.2618 \text{ m}^3/\text{kg}$
$\hat{H} = 3063 \text{ kJ/kg}$ $\qquad\quad \hat{H} \approx 3063 \text{ kJ/kg}$
$\hat{S} = 5.522 \text{ kJ/kg K}$ $\qquad \hat{S} = 7.145 \text{ kJ/kg K}$

Also

$$\frac{dS}{dt} = 0 = \dot{M}_1\hat{S}_1 + \dot{M}_2\hat{S}_2 + \cancel{\frac{\dot{Q}}{T}}^{\,0} + \dot{S}_{gen} = 0$$

$$\Rightarrow \dot{S}_{gen} = \dot{M}_1\left(\hat{S}_2 - \hat{S}_1\right) \text{ or } \frac{\dot{S}_{gen}}{\dot{M}_1} = \hat{S}_2 - \hat{S}_1 = 7.145 - 5.522 = 1.623\frac{\text{kJ}}{\text{kg}\cdot\text{K}}$$

3.5

System $\qquad\qquad \boxed{\text{1} \!-\!\!\circ\!\!-\! \text{2}}$

$\qquad\qquad\qquad\qquad\quad \text{W}_s$
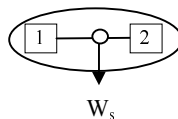
Energy balance

$$\Delta U = \left(U_2^f - U_2^i\right) + \left(U_1^f - U_1^i\right) = \cancel{\dot{Q}}^{\text{ adiabatic}} + W_S - \cancel{\int P dV}^{\text{constant volume}}$$

$$W_s = MC_p\left(T_2^f - T_2^i\right) + MC_p\left(T_1^f - T_1^i\right) = MC_p\left[\left(T_2^f - T_2^i\right) + \left(T_1^f - T_1^i\right)\right]$$

but $T_1^f = T_2^f = T^f \Rightarrow \dfrac{W_s}{MC_p} = \left[2T^f - T_1^i - T_2^i\right]$

Entropy balance

$$\Delta S = \left(S_2^f - S_2^i\right) + \left(S_1^f - S_1^i\right) = \overset{\text{adiabatic}}{\cancelto{0}{\int \frac{\dot{Q}}{T}dt}} + \cancel{\dot{S}}_{\text{gen}}$$

0 for maximum work

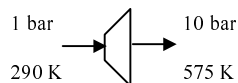$$\left(S_2^f - S_2^i\right) + \left(S_1^f - S_1^i\right) = 0 = MC_p \ln\frac{T_2^f}{T_2^i} + MC_p \ln\frac{T_1^f}{T_1^i}$$

or $\ln\left\{\dfrac{T_2^f\,T_1^f}{T_2^i\,T_1^i}\right\} = 0$; $T_1^f\,T_2^f = T_1^i\,T_2^i$; but $T_1^f = T_2^f = T^f$

$\Rightarrow \left(T^f\right)^2 = \left(T_1^i\,T_2^i\right)$ or $T^f = \sqrt{T_1^i\,T_2^i}$ and

$$\frac{W_s}{MC_p} = \left[2T^f - T_1^i - T_2^i\right] = \left[2\sqrt{T_1^i\,T_2^i} - T_1^i - T_2^i\right]$$

3.6

1 bar   10 bar

290 K   575 K

(a) Entropy change per mole of gas

$\Delta \underline{S} = C_p \ln\dfrac{T_2}{T_1} - R\ln\dfrac{P_2}{P_1}$ **eqn. (3.4-3)**

Thus $\Delta S = 29.3\dfrac{\text{J}}{\text{mol K}}\ln\dfrac{575}{290} - 8.314\dfrac{\text{J}}{\text{mol K}}\ln\dfrac{10}{1} = 0.9118\dfrac{\text{J}}{\text{mol K}}$

(b) System = contents of turbine (steady-state system)

Mass balance $\dfrac{dN}{dt} = 0 = \dot{N}_1 + \dot{N}_2 \Rightarrow -\dot{N}_2 = \dot{N}_1 = \dot{N}$

Energy balance $\dfrac{dU}{dt} = 0 = \dot{N}_1\underline{H}_1 + \dot{N}_2\underline{H}_2 + \cancelto{0}{\dot{Q}} + \dot{W}_s - P\cancelto{0}{\dfrac{dV}{dt}}$

$\dot{W}_s = \dot{N}(\underline{H}_2 - \underline{H}_1) = \dot{N}C_p(T_2 - T_1)$

$W = \dfrac{\dot{W}_s}{\dot{N}} = C_p(T_2 - T_1) = 29.3\dfrac{\text{J}}{\text{mol K}} \times (575 - 290)\text{K}$

$= 8350.5\dfrac{\text{J}}{\text{mol}}$

(c) In Illustration 3.5-1, $W = 7834.8$ J/mol because of irreversiblitities $(\Delta S \neq 0)$, more work is done on the gas here. What happens to this additional energy input? It appears as an increase of the internal energy (temperature) of the gas.

3.7 Heat loss from metal block

$$\frac{dU}{dt} = C_p\frac{dT}{dt} = \dot{Q}$$

$$-\dot{W} = \frac{T - T_2}{T}\dot{Q}(-1)\begin{cases}\dot{Q} = \text{heat out of metal} \\ -\dot{Q} = \text{heat into heat engine}\end{cases}$$
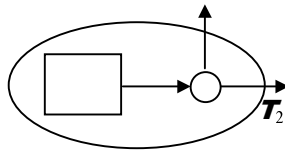
$$C_P\frac{dT}{dt}\frac{(T - T_2)}{T} = -\dot{W} \Rightarrow -\int_0^t \dot{W}dt = C_P\int_{T_1}^{T_2}\left(1 - \frac{T_2}{T}\right)dT$$

$$-W = C_P(T_2 - T_1) - C_P \cdot T_2 \ln\frac{T_2}{T_1} = C_P\left[(T_2 - T_1) - T_2 \ln\frac{T_2}{T_1}\right]$$

$$-W = C_P T_2\left[\left(1 - \frac{T_1}{T_2}\right) - \ln\frac{T_2}{T_1}\right]$$

$$Q = \int_{T_1}^{T_2} C_P dT = C_P(T_2 - T_1) = C_P T_2\left(1 - \frac{T_1}{T_2}\right)$$

Alternate way to solve the problem

System is the metal block + heat engine (closed)

E.B.: $\dfrac{dU}{dt} = C_P\dfrac{dT}{dt} = \dot{Q} + \dot{W}$

S.B.: $\dfrac{dS}{dt} = \dfrac{\dot{Q}}{T^2} + \cancel{S_{gen}}$

$\qquad\qquad\qquad$ 0 for maximum wor

$$\dot{Q} = T_2\frac{dS}{dt} ; \quad \frac{dU}{dt} = T_2\frac{dS}{dt} + \dot{W} ; \quad dU = C_P dT ; \quad dS = \frac{C_P}{T}dT$$

$$\dot{W} = \frac{dU}{dt} - T_2\frac{dS}{dt} = C_P dT - T_2\frac{C_P}{T}dT = C_P\left(1 - \frac{T_2}{T}\right)dT$$

$$W = \int \dot{W}dt = \int_{T_1}^{T_2} C_P\left(1 - \frac{T_2}{T}\right)dT = C_P\int_{T_1}^{T_2}\left(1 - \frac{T_2}{T}\right)dT$$

$$W = C_P(T_2 - T_1) - T_2 C_P \ln\frac{T_2}{T_1} = C_P T_2\left[\left(1 - \frac{T_1}{T_2}\right) - \ln\frac{T_2}{T_1}\right]$$

3.8 This problem is not well posed since we do not know exactly what is happening. There are several possibilities:

(1) Water contact is very short so neither stream changes T very much. In this case we have the Carnot efficiency

$$\eta = \frac{-W}{Q} = \frac{T_{high} - T_{low}}{T_{high}} = \frac{22}{27 + 273} = \frac{22}{300} = 0.0733 = 7.33\%$$

(2) Both warm surface water (27°C) and cold deep water (5°C) enter work producing device, and they leave at a common temperature.
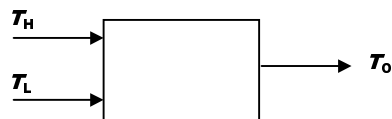
M.B.: $\dfrac{dM}{dt} = 0 = \dot{M}_H + \dot{M}_L + \dot{M}_0 \Rightarrow \dot{M}_0 = -\left(\dot{M}_H + \dot{M}_L\right)$

E.B.: $\dfrac{dU}{dt} = 0 = \dot{M}_H \hat{H}_H + \dot{M}_L \hat{H}_L + \dot{M}_0 \hat{H}_0 + \dot{W} = 0$

$\begin{aligned}
\dot{W} &= -\dot{M}_H \hat{H}_H - \dot{M}_L \hat{H}_L + \left(\dot{M}_H + \dot{M}_L\right)\hat{H}_0 \\
&= \dot{M}_H\left(\hat{H}_0 - \hat{H}_H\right) + \dot{M}_L\left(\hat{H}_0 - \hat{H}_L\right) \\
&= \dot{M}_H C_P\left(T_0 - T_H\right) + \dot{M}_L C_P\left(T_0 - T_L\right)
\end{aligned}$

S.B.: $\dfrac{dS}{dt} = 0 = \dot{M}_H \hat{S}_H + \dot{M}_L \hat{S}_L + M_0 \hat{S}_0 + \cancelto{0}{\dfrac{\dot{Q}}{T}} + \cancelto{0}{\dot{S}_{gen}}$

$\dot{M}_H \hat{S}_H + \dot{M}_L \hat{S}_L - \left(\dot{M}_H + \dot{M}_L\right)\hat{S}_0 = 0$

$\dot{M}_H\left(\hat{S}_H - \hat{S}_0\right) + \dot{M}_L\left(\hat{S}_L - \hat{S}_0\right) = 0 \Rightarrow \dot{M}_H C_P \ln\dfrac{T_H}{T_0} + \dot{M}_L C_P \ln\dfrac{T_L}{T_0} = 0$

$\left(\dfrac{T_H}{T_0}\right)^{\dot{M}_H}\left(\dfrac{T_L}{T_0}\right)^{\dot{M}_L} = 1$ or $T_H^{\dot{M}_H} T_L^{\dot{M}_L} = T_0^{\dot{M}_H + \dot{M}_L}$

$T_0 = T_H^{\dot{M}_H/\left(\dot{M}_H + \dot{M}_L\right)} T_L^{\dot{M}_L/\left(\dot{M}_H + \dot{M}_L\right)}$

From this can calculate T_0. Then

$$\dot{W} = \dot{M}_H C_P\left(T_0 - T_H\right) + \dot{M}_L C_P\left(T_0 - T_L\right)$$

This can be used for any flowrate ratio.

(3) Suppose very large amount of surface water is contacted with a small amount of deep water, i.e., $\dot{M}_H \gg \dot{M}_L$. Then $T_0 \sim T_H$

$\dot{W} = \dot{M}_H C_P\left(T_H - T_H\right) + \dot{M}_L C_P\left(T_H - T_L\right) \sim \dot{M}_L C_P\left(T_H - T_L\right)$

(4) Suppose very large amount of deep water is contacted with a small amount of surface water, i.e., $\dot{M}_H \ll \dot{M}_L$, $T_0 \sim T_L$.

$\dot{W} = \dot{M}_H C_P\left(T_L - T_H\right) + \dot{M}_L C_P\left(T_L - T_L\right) \sim \dot{M}_H C_P\left(T_L - T_H\right)$

3.9 System = contents of the turbine. This is a steady-state, adiabatic, constant volume system.

(a) Mass balance $\dfrac{dM}{dt} = 0 = \dot{M}_1 + \dot{M}_2$ or $\dot{M}_2 = -\dot{M}_1$

Energy balance

$$\dfrac{dU}{dt} = 0 = \dot{M}_1 \hat{H}_1 + \dot{M}_2 \hat{H}_2 + \cancelto{adiabatic}{\dot{Q}} + \dot{W}_s - P\cancelto{constant\ volume}{\dfrac{dV}{dt}}$$

Entropy balance

$$\dfrac{dS}{dt} = 0 = \dot{M}_1 \hat{S}_1 + \dot{M}_2 \hat{S}_2 + \cancelto{}{\dfrac{\dot{Q}}{T}} + \cancelto{0,\ \text{by problem statement}}{\dot{S}_{gen}}$$

Thus

$\dot{M}_2 = -\dot{M}_1 = -4500\,\text{kg/h}$ M.B.

$\dot{W}_S = -\dot{M}_1\left(\hat{H}_1 - \hat{H}_2\right)$ E.B.

$\hat{S}_2 = \hat{S}_1$ S.B.

State 1 $T_1 = 500°\text{C}$ $\xrightarrow[\text{Tables}]{\text{Steam}}$ $\hat{H}_1 = 3422.2$ kJ/kg
    $P_1 = 60$ bar $\hat{S}_1 = 6.8803$ kJ/kg

State 2 $P_2 = 10$ bar $\xrightarrow[\text{Tables}]{\text{Steam}}$ $T_2 \cong 240.4°\text{C}$

$\hat{S}_2 = \hat{S}_1 = 6.8803 \dfrac{\text{kJ}}{\text{kgK}}$ $\hat{H}_2 \approx 2920.5$ kJ/kg

$$\dot{W}_s = 4500 \frac{\text{kg}}{\text{h}} \times (2920.5 - 3422.2)\frac{\text{kJ}}{\text{kg}} = -2257650 \frac{\text{kJ}}{\text{h}} = -627.1 \text{ kW}$$

(b) Same exit pressure $(P_2 = 10 \text{ bar})$, and still adiabatic

$$\Rightarrow \dot{W}_s = -\dot{M}_1(\hat{H}_1 - \hat{H}_2).$$

Here, however,

$$\dot{W}_s = 0.8\dot{W}_s(\text{Part a}) = 0.8(-2.258 \times 10^6)\frac{\text{kJ}}{\text{h}} = 4500(\hat{H}_2 - 3422.2)\frac{\text{kJ}}{\text{h}}$$

$\Rightarrow \quad \hat{H}_2 = 3020.8$ kJ/kg $\xrightarrow[\text{Tables}]{\text{Steam}}$ $T_2 \cong 286.7$ K
     $P = 10$ bar $\hat{S}_2 \approx 7.0677$ kJ/kg K

Thus

$$\dot{S}_{\text{gen}} = -\dot{M}_1(\hat{S}_1 - \hat{S}_2) = -4500\frac{\text{kg}}{\text{h}} \times (6.8803 - 7.0677)\frac{\text{kJ}}{\text{kg K}} = 843.3 \frac{\text{kJ}}{\text{K} \cdot \text{h}}$$

(c) Flow across valve is a Joule-Thompson (isenthalpic expansion) ... See Illustration 2.3-3. Thus, $\hat{H}_{\text{into valve}} = \hat{H}_{\text{out of valve}}$, and the inlet conditions to the turbine are

$$\hat{H}_1 = \hat{H}_{\text{out of valve}} = \hat{H}_{\text{into valve}} = 3422.2 \text{ kJ/kg}$$
$$P_1 = 30 \text{ bar}$$

$$\xrightarrow[\text{Tables}]{\text{Steam}} \qquad \begin{matrix} T_1 \approx 484.8°\text{C} \\ S_1 \approx 7.1874 \text{ kJ/kg K} \end{matrix}$$

Flow across turbine is isentropic, as in part (a)

$\hat{S}_2 = \hat{S}_1 = 7.1874$ kJ/kg K $\xrightarrow[\text{Tables}]{\text{Steam}}$ $T_2 \cong 318.1°\text{C}$
$P_2 = 10$ bar $\hat{H}_2 \approx 3090.4$ kJ/kg

$$\dot{W}_s = 4500\frac{\text{kg}}{\text{h}} \times (3090.4 - 3422.2)\frac{\text{kJ}}{\text{kg}} = -1.493 \times 10^6 \frac{\text{kJ}}{\text{h}} = -414.8 \text{ kW}$$

3.10 Since compression is isentropic, and gas is ideal with constant heat capacity, we have

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{P_2}{P_1}\right)^{R/C_P}$$

So that $T_2 = T_1\left(\dfrac{P_2}{P_1}\right)^{R/C_P} = 298.15\left(\dfrac{3 \times 10^6}{2 \times 10^6}\right)^{8.314/36.8} = 326.75 \text{ K}$. Now using, from solution to

Problem 2.31, that $\dot{W}_s = \dot{N}C_P(T_2 - T_1)$

$$\dot{W}_s = 125\frac{\text{kg}}{\text{s}} \times \frac{1 \text{ mol}}{16 \text{ g}} \times 36.8\frac{\text{J}}{\text{mol K}} \times (326.75 - 298.15)\text{K} \times \frac{1000 \text{ g}}{\text{kg}}$$

$$= 8.23 \times 10^6 \text{ J/s}$$

The load on the gas cooler is, from Problem 2.31,

$$\dot{Q} = \dot{N}C_{\text{p}}(T_3 - T_2)$$

$$= \frac{125 \text{ kg/s} \times 1000 \text{ g/kg}}{16 \text{ g/mol}} \times 36.8\frac{\text{J}}{\text{mol K}} \times (298.15 - 326.75)K$$

$$= -8.23 \times 10^{+6} \text{ J/s}$$

3.11 (a) This is a Joule-Thomson expansion

$$\Rightarrow \hat{H}(70 \text{ bar}, T = ?) = \hat{H}(1.0133 \text{ bar}, T = 400°\text{C}) \approx \hat{H}(1 \text{ bar}, T = 400°\text{C})$$
$$= 3278.2 \text{ kJ/kg}$$
$$\text{and } T = 447°\text{C}, \ \hat{S} = 6.619 \text{ kJ/kg K}$$

(b) If turbine is adiabatic and reversible $\left(\dot{S}_{\text{gen}} = 0\right)$, then $\hat{S}_{\text{out}} = \hat{S}_{\text{in}} = 6.619$ kJ/kg K and $P = 1.013$ bar. This suggests that a two-phase mixture is leaving the turbine

Let x = fraction vapor
$$\hat{S}^{\text{V}} = 7.3594 \text{ kJ/kg K}$$
$$\hat{S}^{\text{L}} = 1.3026 \text{ kJ/kg K}$$

Then $x(7.3594) + (1-x)(1.3026) = 6.619$ kJ/kg K or $x = 0.8778$. Therefore the enthalpy of fluid leaving turbine is

$$\hat{H} = 0.8788 \times \underset{\hat{H}^{\text{V}} \text{ (sat'd, 1 bar)}}{2675.5} + (1-0.8778) \times \underset{\hat{H}^{\text{L}} \text{ (sat'd, 1 bar)}}{417.46} = 2399.6 \frac{\text{kJ}}{\text{kg}}$$

Energy balance

$$0 = \dot{M}_{\text{in}}\hat{H}_{\text{in}} + \dot{M}_{\text{out}}\hat{H}_{\text{out}} + \cancelto{0}{\dot{Q}} + \dot{W}_s - P\cancelto{0}{\frac{dV}{dt}}$$

but $\dot{M}_{\text{in}} = -\dot{M}_{\text{out}}$

$$\Rightarrow -\frac{\dot{W}_s}{\dot{M}_{\text{in}}} = 3278.2 - 2399.6 = 878.6 \frac{\text{kJ}}{\text{kg}}$$

(c) Saturated vapor at 1 bar

$$\hat{S} = 7.3594 \text{ kJ/kg K}; \ \hat{H} = 2675.5 \text{ kJ/kg}$$

$$-\frac{\dot{W}_s}{\dot{M}_{\text{in}}}\Bigg|_{\text{Actual}} = 3278.2 - 2675.5 = 602.7 \text{ kJ/kg}$$

$$\text{Efficiency (\%)} = \frac{602.7 \times 100}{878.6} = 68.6\%$$

$$\frac{\dot{S}_{\text{gen}}}{\dot{M}_{\text{in}}} = 7.3594 - 6.619 = 0.740 \text{ kJ/Kh}$$

(d)
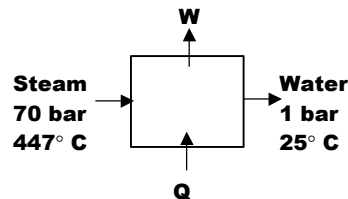
$$0 = \dot{M}_1 + \dot{M}_2 \Rightarrow \dot{M}_2 = -\dot{M}_1$$
$$0 = \dot{M}_1\left(\hat{H}_1 - \hat{H}_2\right) + \dot{W}_s + \dot{Q} - P\frac{dV}{dt}$$
$$0 = \dot{M}_1\left(\hat{S}_1 - \hat{S}_2\right) + \frac{\dot{Q}}{T} + \dot{S}_{\text{gen}}$$

Simplifications to balance equations

$\dot{S}_{\text{gen}} = 0$ (for maximum work); $P\dfrac{dV}{dt} = 0$ (constant volume)

$\dfrac{\dot{Q}}{T} = \dfrac{\dot{Q}}{T_0}$ where $T_0 = 25°\text{C}$ (all heat transfer at ambient temperature)

$$\hat{H} \text{ (sat'd liq, } 25°C) = 104.89 \frac{kJ}{kg}; \quad \hat{S} \text{ (sat'd liq, } T = 25°C) = 0.3674 \frac{kJ}{kg \ K}$$

$$\frac{\dot{Q}}{\dot{M}} = T_0(\hat{S}_2 - \hat{S}_1); \quad \left.\frac{-\dot{W}_s}{\dot{M}}\right|_{max} = \hat{H}_1 - \hat{H}_2 + T_0(\hat{S}_2 - \hat{S}_1) = (\hat{H}_1 - T_0\hat{S}_1) - (\hat{H}_2 - T_0\hat{S}_2)$$

$$\left.\frac{-\dot{W}_s}{\dot{M}}\right|_{max} = [3278.2 - 298.15 \times 6.619] - [104.89 - 298.15 \times 0.3674]$$

$$= 1304.75 + 4.65 = 1309.4 \ kJ/kg$$

3.12 Take that portion of the methane initially in the tank that is also in the tank finally to be in the system. This system is isentropic $S_f = S_i$.

(a) The ideal gas solution

$$\underline{S}_f = \underline{S}_i \Rightarrow T_f = T_i \left(\frac{P_f}{P_i}\right)^{R/C_p} = 300 \left(\frac{35}{70}\right)^{8.314/36} = 150.2 \ K$$

$$N = \frac{PV}{RT} \Rightarrow N_i = \frac{P_i V}{RT_i} = 1964.6 \ mol; \ N_f = \frac{P_f V}{RT_f} = 196.2 \ mol$$

$$\Delta N = N_f - N_i = -1768.4 \ mol$$

(b) Using Figure 2.4-2.

70 bar ≈ 7 MPa, $T = 300$ K $\hat{S}_i = 5.05 \ kJ/kg \ K = \hat{S}_f$

$$\hat{V}_i = 0.0195 \frac{m^3}{kg}, \text{ so that } m_i = \frac{0.7 m^3}{0.0195 \frac{m^3}{kg}} = 35.90 \ kg.$$

$$N_i = \frac{35.90 \ kg \times 1000 \frac{g}{kg}}{28 \frac{g}{mol}} = 1282 \ mol$$

At 3.5 bar = 0.35 MPa and $\hat{S}_f = 5.05 \ kJ/kg \ K \Rightarrow T \approx 138$ K. Also,

$$\hat{V}_f = 0.192 \frac{m^3}{kg}, \text{ so that } m_f = \frac{0.7 m^3}{0.192 \frac{m^3}{kg}} = 3.646 \ kg.$$

$$N_f = \frac{3.646 \ kg \times 1000 \frac{g}{kg}}{28 \frac{g}{mol}} = 130.2 \ mol$$

$$\Delta N = N_f - N_i = 130.2 - 1282 = -1151.8 \ mol$$

3.13 $d\underline{S} = C \dfrac{dT}{T} + R \dfrac{dV}{\underline{V}}$ eqn. (3.4-1)

$$\Delta S = \int \left[(a - R) + bT + cT^2 + dT^3 + \frac{e}{T^2} \right] \frac{dT}{T} + R \int \frac{dV}{\underline{V}}$$

so that

$$\underline{S}(T_2, \underline{V}_2) - \underline{S}(T_1, \underline{V}_1) = (a - R)\ln\frac{T_2}{T_1} + b(T_2 - T_1) + \frac{c}{2}\left(T_2^2 - T_1^2\right)$$

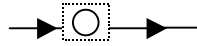$$+ \frac{d}{3}\left(T_2^3 - T_1^3\right) - \frac{e}{2}\left(T_2^{-2} - T_1^{-2}\right) + R\ln\frac{\underline{V}_2}{\underline{V}_1}$$

Now using

$$P\underline{V} = RT \Rightarrow \frac{\underline{V}_2}{\underline{V}_1} = \frac{T_2}{T_1}\cdot\frac{P_1}{P_2} \Rightarrow$$

$$\underline{S}(T_2, P_2) - S(T_1, P_1) = a\ln\frac{T_2}{T_1} + b(T_2 - T_1) + \frac{c}{2}\left(T_2^2 - T_1^2\right)$$

$$+ \frac{d}{3}\left(T_2^3 - T_1^3\right) - \frac{e}{2}\left(T_2^{-2} - T_1^{-2}\right) - R\ln\frac{P_2}{P_1}$$

Finally, eliminating T_2 using $T_2 = T_1 P_2 \underline{V}_2 / P_1 \underline{V}_1$ yields

$$\underline{S}(P_2,\underline{V}_2) - \underline{S}(P_1,\underline{V}_1) = a\ln\left(\frac{P_2\underline{V}_2}{P_1\underline{V}_1}\right) + \frac{b}{R}(P_2\underline{V}_2 - P_1\underline{V}_1)$$

$$+ \frac{c}{2R^2}\left[(P_2\underline{V}_2)^2 - (P_1\underline{V}_1)^2\right]$$

$$+ \frac{d}{3R^3}\left[(P_2\underline{V}_2)^3 - (P_1\underline{V}_1)^3\right]$$

$$- \frac{eR^2}{2}\left[\left(P_2\underline{V}_2^{-2}\right) - \left(P_1\underline{V}_1^{-2}\right)\right] - R\ln\frac{P_2}{P_1}$$

3.14   System: contents of valve (steady-state, adiabatic, constant volume system)

Mass balance $0 = \dot{N}_1 + \dot{N}_2$

Energy balance $0 = \dot{N}_1\underline{H}_1 + \dot{N}_2\underline{H}_2 + \cancelto{0}{\dot{Q}} + \cancelto{0}{\dot{W}_s} - P\cancelto{0}{\frac{dV}{dt}}$

$$\Rightarrow \underline{H}_1 = \underline{H}_2$$

Entropy balance $0 = \dot{N}_1\underline{S}_1 + \dot{N}_2\underline{S}_2 + \dot{S}_{gen} + \cancelto{0}{\frac{\dot{Q}}{T}}$

$$\Rightarrow \Delta\underline{S} = \underline{S}_2 - \underline{S}_1 = \frac{\dot{S}_{gen}}{\dot{N}}$$

(a) Using the Mollier Diagram for steam (Fig. 2.4-1a) or the Steam Tables

$$\begin{array}{ll} T_1 = 600\text{ K} & P_2 = 7\text{ bar} \\ P_1 = 35\text{ bar} & \hat{H}_2 = 3045.3\text{ J/g} \end{array} \Rightarrow \begin{array}{l} T_2 \approx 293°\text{C} \\ \hat{S}_2 = 7.277\text{ J/g K} \end{array}$$

$\hat{H}_1 = \hat{H}_2 = 3045.3$ J/g . Thus $\hat{S}_1 = 6.5598$ J/g K; $T_{exit} = 293°$C

$\Delta\hat{S} = \hat{S}_2 - \hat{S}_1 = 0.717$ J/g K

(b) For the ideal gas, $\underline{H}_1 = \underline{H}_2 \Rightarrow T_1 = T_2 = 600$ K

$$\Delta \underline{S} = \underline{S}(T_2, P_2) - \underline{S}(T_1, P_1) = C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

$$= -R \ln \frac{P_2}{P_1} = 13.38 \text{ J/mol K} \Rightarrow$$

$$\Delta \hat{S} = 0.743 \text{ J/mol K}$$

3.15 From the Steam Tables

$$P = 1.5538 \text{ MPa}$$

At 200°C,

$$\hat{V}^L = 0.001157 \text{ m}^3 / \text{kg} \quad \hat{V}^V = 0.12736 \text{ m}^3 / \text{kg}$$

$$\hat{U}^L = 850.65 \text{ kJ} / \text{kg} \quad \hat{U}^V = 2595.3 \text{ kJ} / \text{kg}$$

$$\hat{H}^L = 852.45 \text{ kJ} / \text{kg} \quad \hat{H}^L = 2793.2 \text{ kJ} / \text{kg}$$

$$\hat{S}^L = 2.3309 \text{ kJ} / \text{kg} \cdot \text{K} \quad \hat{S}^V = 6.4323 \text{ kJ} / \text{kg} \cdot \text{K}$$

$$\Delta \hat{H}^{\text{vap}} = 1940.7 \text{ kJ} / \text{kg} \quad \Delta \hat{S}^{\text{vap}} = 4.1014 \text{ kJ} / \text{kg} \cdot \text{K}$$

(a) Now assuming that there will be a vapor-liquid mixture in the tank at the end, the properties of the steam and water will be

$$P = 0.4578 \text{ MPa}$$

At 150°C,

$$\hat{V}^L = 0.001091 \text{ m}^3 / \text{kg} \quad \hat{V}^V = 0.3928 \text{ m}^3 / \text{kg}$$

$$\hat{U}^L = 631.68 \text{ kJ} / \text{kg} \quad \hat{U}^V = 2559.5 \text{ kJ} / \text{kg}$$

$$\hat{H}^L = 632.20 \text{ kJ} / \text{kg} \quad \hat{H}^V = 2746.5 \text{ kJ} / \text{kg}$$

$$\hat{S}^L = 1.8418 \text{ kJ} / \text{kg} \cdot \text{K} \quad \hat{S}^V = 6.8379 \text{ kJ} / \text{kg} \cdot \text{K}$$

$$\Delta \hat{H}^{\text{vap}} = 2114.3 \text{ kJ} / \text{kg} \quad \Delta \hat{S}^{\text{vap}} = 4.9960 \text{ kJ} / \text{kg} \cdot \text{K}$$

(b) For simplicity of calculations, assume 1 m³ volume of tank. Then

$$\text{Mass steam initially} = \frac{0.8 \text{ m}^3}{0.12736 \text{ m}^3 / \text{kg}} = 6.2814 \text{ kg}$$

$$\text{Mass water initially} = \frac{0.2 \text{ m}^3}{0.001157 \text{ m}^3 / \text{kg}} = 172.86 \text{ kg}$$

$$\text{Weight fraction of steam initially} = \frac{6.2814}{179.14} = 0.03506$$

$$\text{Weight fraction of water initially} = \frac{6.2814}{179.14} = 0.96494$$

The mass, energy and entropy balances on the liquid in the tank (open system) at any time yields

$$\frac{dM^L}{dt} = \dot{M}^L; \quad \frac{dM^L \hat{U}^L}{dt} = \dot{M}^L \hat{H}^V; \text{ and } \frac{dM^L \hat{S}^L}{dt} = \dot{M}^L \hat{S}^V$$

or $$M^L \frac{d\hat{U}^L}{dt} + \hat{U}^L \frac{dM^L}{dt} = \dot{M}^L \hat{H}^V = \hat{H}^V \frac{dM^L}{dt}$$

$$M^L \frac{d\hat{U}^L}{dt} = \frac{dM^L}{dt} \left(\hat{H}^V - \hat{U}^L \right)$$

Also, in a similar fashion, from the entropy balance be obtain

$$M^L \frac{d\hat{S}^L}{dt} = \frac{dM^L}{dt} \left(\hat{S}^V - \hat{S}^L \right) = \frac{dM^L}{dt} \Delta \hat{S}^{\text{vap}}$$

There are now several ways to proceed. The most correct is to use the steam tables, and to use either the energy balance or the entropy balance and do the integrals numerically (since the internal energy, enthalpy, entropy, and the changes on vaporization depend on temperature. This is the method we will use first. Then a simpler method will be considered.

Using the energy balance, we have

$$\frac{dM^L}{M^L} = \frac{d\hat{U}^L}{\hat{H}^V - \hat{U}^L}, \quad \text{or replacing the derivatives by finite differences}$$

$$\frac{M_{i+1}^L - M_i^L}{M_i^L} = \frac{\hat{U}_{i+1}^L - \hat{U}_i^L}{\hat{H}_i^V - \hat{U}_i^L} \quad \text{or finally} \quad M_{i+1}^L = M_i^L\left(1 + \frac{\hat{U}_{i+1}^L - \hat{U}_i^L}{\hat{H}_i^V - \hat{U}_i^L}\right)$$

So we can start with the known initial mass of water, then using the Steam Tables and the data at every 5°C do a finite difference calculation to obtain the results below.

i	T (°C)	$\hat{U}_i^L$ (kJ/kg K)	$\hat{H}_i^V$ (kJ/kg K)	M_i^L (kg)
1	200	850.65	2793.2	172.86
2	195	828.37	2790.0	170.88
3	190	806.19	2786.4	168.95
4	185	784.10	2782.4	167.06
5	180	762.09	2778.2	165.22
6	175	740.17	2773.6	163.42
7	170	718.33	2768.7	161.67
8	165	696.56	2763.5	159.95
9	160	674.87	2758.1	158.27
10	155	653.24	2752.4	156.63
11	150	631.68	2746.5	155.02

So the final total mass of water is 155.02 kg; using the specific volume of liquid water at 150°C listed at the beginning of the problem, we have that the water occupies 0.1691 m³ leaving 0.8309 m³ for the steam. Using its specific volume, the final mass of steam is found to be 2.12 kg. Using these results, we find that the final volume fraction of steam is 83.09%, the final volume fraction of water is 16.91%, and the fraction of the initial steam + water that has been withdrawn is (172.86+6.28-155.02-2.12)/(172.86+6.28) = 0.1228 or 12.28%. A total of 22.00 kg of steam has withdrawn, and 87.7% of the original mass of steam and water remain in the tank.

For comparison, using the entropy balance, we have

$$\frac{dM^L}{M^L} = \frac{d\hat{S}^L}{\hat{S}^V - \hat{S}^L}, \quad \text{or replacing the derivatives by finite differences}$$

$$\frac{M_{i+1}^L - M_i^L}{M_i^L} = \frac{\hat{S}_{i+1}^L - \hat{S}_i^L}{\Delta\hat{S}_i^{vap}} \quad \text{of finally} \quad M_{i+1}^L = M_i^L\left(1 + \frac{\hat{S}_{i+1}^L - \hat{S}_i^L}{\Delta\hat{S}_i^{vap}}\right)$$

So again we can start with the known initial mass of water, then using the Steam Tables and the data at every 5°C do a finite difference calculation to obtain the results below.

i	T (°C)	$\hat{S}_i^L$ (kJ/kg K)	$\hat{S}_i^L$ (kJ/kg K)	M_i^L (kg)
1	200	2.3309	6.4323	172.86
2	195	2.2835	6.4698	170.86
3	190	2.2359	6.5079	168.92
4	185	2.1879	6.5465	167.02
5	180	2.1396	6.5857	165.17
6	175	2.0909	6.6256	163.36
7	170	2.0419	6.6663	161.60
8	165	1.9925	6.7078	159.87
9	160	1.9427	6.7502	158.18

| 10 | 155 | 1.8925 | 6.7935 | 156.53 |
| 11 | 150 | 1.8418 | 6.8379 | 154.91 |

So the final total mass of water is 154.91 kg; using the specific volume of liquid water at 150°C listed at the beginning of the problem, we have that the water occupies 0.1690 m³ leaving 0.8310 m³ for the steam. Using its specific volume, the final mass of steam is found to be 2.12 kg. Using these results, we find that the final volume fraction of steam is 83.10%, the final volume fraction of water is 16.90%, and the fraction of the initial steam + water that has been withdrawn is
(172.86+6.28-154.91-2.12)/(172.86+6.28) = 0.1234 or 12.34%. A total of 22.11 kg of steam has withdrawn, and 87.7% of the original mass of steam and water remain in the tank.

These results are similar to that from the energy balance. The differences are the result of round off errors in the simple finite difference calculation scheme used here (i.e., more complicated predictor-corrector methods would yield more accurate results.).

A simpler method of doing the calculation, avoiding numerical integration, is to assume that the heat capacity and change on vaporization of liquid water are independent of temperature. Since liquid water is a condensed phase and the pressure change is small, we can make the following assumptions

$$\hat{U}^L \approx \hat{H}^L \quad \text{and} \quad \hat{H}^V - \hat{H}^L = \Delta \hat{H}^{vap}$$

$$\frac{d\hat{U}^L}{dt} \approx \frac{d\hat{H}^L}{dt} \approx C_P^L \frac{dT^L}{dt}; \quad \text{and} \quad \frac{d\hat{S}^L}{dt} \approx \frac{C_P^L}{T} \frac{dT^L}{dt}$$

With these substitutions and approximations, we obtain from the energy balance

$$M^L \frac{d\hat{U}^L}{dt} = \frac{dM^L}{dt}\left(\hat{H}^V - \hat{U}^L\right) \quad \rightarrow \quad M^L \frac{d\hat{H}^L}{dt} = \frac{dM^L}{dt}\Delta \hat{H}^{vap}$$

$$M^L C_P^L \frac{dT}{dt} = \frac{dM^L}{dt}\Delta \hat{H}^{vap}$$

Now using an average value of C_P^L and $\Delta \hat{H}^{vap}$ over the temperature range we obtain

$$\frac{C_P^L}{\Delta \hat{H}^{vap}} \frac{dT}{dt} = \frac{1}{M^L} \frac{dM^L}{dt} \quad \text{or}$$

$$\frac{C_P^L}{\Delta \hat{H}^{vap}}(150 - 200) = \ln\left(\frac{M_f^L}{M_i^L}\right)$$

and from the entropy balance

$$M^L \frac{d\hat{S}^L}{dt} = \frac{dM^L}{dt}\Delta \hat{S}^{vap} \quad \rightarrow \quad M^L \frac{C_P^L}{T} \frac{dT}{dt} = \frac{dM^L}{dt}\Delta \hat{S}^{vap}$$

Now using an average value of C_P^L and $\Delta \hat{S}^{vap}$ over the temperature range we obtain

$$\frac{C_P^L}{T\Delta \hat{S}^{vap}} \frac{dT}{dt} = \frac{1}{M^L} \frac{dM^L}{dt} \quad \text{or}$$

$$\frac{C_P^L}{\Delta \hat{S}^{vap}}\ln\left(\frac{150+273.15}{200+273.15}\right) = \ln\left(\frac{M_f^L}{M_i^L}\right)$$

From the Steam Table data listed above, we obtain the following estimates:

$$C_P^L = \frac{\hat{U}(T=200°C) - \hat{U}(T=150°C)}{200°C - 150°C} = \frac{852.45 - 632.20}{50} = 4.405 \frac{\text{kJ}}{\text{kg} \cdot \text{K}}$$

or using the ln mean value (more appropriate for the entropy calculation) based on

$$C_P^L \ln\left(\frac{T_2}{T_1}\right) = \hat{S}(T_2) - \hat{S}(T_1)$$

$$C_P^L = \frac{\hat{S}(T=200°C) - \hat{S}(T=150°C)}{\ln\left(\frac{200+273.15}{150+273.15}\right)} = \frac{2.3309 - 1.8418}{\ln\left(\frac{473.15}{423.15}\right)} = 4.3793 \frac{\text{kJ}}{\text{kg} \cdot \text{K}}$$

Also, obtaining average values of the property changes on vaporization, yields

$$\Delta\hat{H}^{\text{vap}} = \frac{1}{2} \times \left[\Delta\hat{H}^{\text{vap}}(T=150°C) + \Delta\hat{H}^{\text{vap}}(T=200°C)\right] = \frac{1}{2} \times [2114.3 + 1940.7] = 2027.5 \frac{\text{kJ}}{\text{kg}}$$

$$\Delta\hat{S}^{\text{vap}} = \frac{1}{2} \times \left[\Delta\hat{S}^{\text{vap}}(T=150°C) + \Delta\hat{S}^{\text{vap}}(T=200°C)\right] = \frac{1}{2} \times [4.9960 + 4.1014] = 4.5487 \frac{\text{kJ}}{\text{kg} \cdot \text{K}}$$

With this information, we can now use either the energy of the entropy balance to solve the problem. To compare the results, we will use both (with the linear average C_p in the energy balance and the log mean in the entropy balance. First using the energy balance

$$\frac{C_P^L}{\Delta\hat{H}^{\text{vap}}}(150 - 200) = \ln\left(\frac{M_f^L}{M_i^L}\right) = \frac{-4.405 \times 50}{2027.5} = -0.10863$$

$$\frac{M_f^L}{M_i^L} = \exp(-0.10863) = 0.89706$$

Now using the entropy balance

$$\ln\left(\frac{M_f^L}{M_i^L}\right) = \frac{C_P^L}{\Delta\hat{S}^{\text{vap}}}\ln\left(\frac{150+273.15}{200+273.15}\right) = \frac{4.3793}{4.5487}\ln\left(\frac{423.15}{473.15}\right) = 0.9628\ln\left(\frac{423.15}{473.15}\right)$$

$$\frac{M_f^L}{M_i^L} = \left(\frac{423.15}{473.15}\right)^{0.9628} = 0.89805$$

Given the approximations, the two results are in quite good agreement. For what follows, the energy balance result will be used. Therefore, the mass of water finally present (per m³) is

$$M^L(\text{final}) = 0.897 \times M^L(\text{initial}) = 155.06 \text{ kg}$$

occupying $V = M^L(\text{final}) \times \hat{V}^L(150°C) = 155.06 \times 0.001091 = 0.1692 \text{ m}^3$

Therefore, the steam occupies 0.8308 m³, corresponding to

$$M^V(\text{final}) = \frac{0.8308 \text{ m}^3}{\hat{V}^V(150°C)} = \frac{0.8308 \text{ m}^3}{0.3928 \frac{\text{m}^3}{\text{kg}}} = 2.115 \text{ kg}$$

So the fraction of liquid in the tank by mass at the end is 155.06/(155.06+2.12) = 0.9865, though the fraction by volume is 0.1692. Similarly the fraction of the tank volume that is steam is 0.8308, though steam is only 2.12/(155.06+2.12) = 0.0135 of the mass in the tank.

(c) Initially there was 6.28 + 172.86 = 179.14 kg of combined steam and water, and finally from the simpler calculation above there is 155.06 + 2.12 = 157.18 kg. Therefore, 87.7% of the total amount of steam + water initially in the tank are there finally, or 12.3% has been withdrawn. This corresponds to 21.96 kg being withdrawn. This is in excellent agreement with the more rigorous finite difference calculations done above.

3.16 (a) $\dfrac{dN}{dt} = 0 = \dot{N}_1 + \dot{N}_2;$ or $\dot{N}_2 = -\dot{N}_1$

$$\frac{dU}{dt} = 0 = \dot{N}_1\underline{H}_1 + \dot{N}_2\underline{H}_2 + \dot{W}_S + \dot{Q} - P\frac{dV}{dt} = \dot{W}_S + \dot{N}_1\underline{H}_1 - \dot{N}_1\underline{H}_2 \text{ or } \frac{\dot{W}_S}{\dot{N}_1} = \underline{H}_2 - \underline{H}_1$$

$$\frac{dS}{dt} = 0 = \dot{N}_1\underline{S}_1 - \dot{N}_1\underline{S}_2 + \frac{\dot{Q}}{T_0} + \dot{S}_{gen} \qquad \frac{\dot{S}_{gen}}{\dot{N}_1} = \underline{S}_2 - \underline{S}_1 \qquad C_P = 37.151\frac{J}{mol \cdot K}$$

$$\frac{\dot{W}_S}{\dot{N}_1} = \underline{H}_2 - \underline{H}_1 = \int_{298.15K}^{T_f} C_P dT = C_P \cdot (T_f - 298.15K) \qquad \text{if the heat capacity is independent of}$$

temperature. First consider the reversible case,

$$\underline{S}_2 - \underline{S}_1 = 0 \text{ gives } \int_{T_i}^{T_f} \frac{C_P}{T} dT = R\int_1^{10} \frac{dP}{P} \qquad\qquad \text{The} \qquad \text{solution} \qquad \text{is} \qquad 499.14K. \qquad \text{Then}$$

$$\frac{\dot{W}_S^{rev}}{\dot{N}_1} = C_P \cdot (499.14 - 298.15K) = 7467\frac{J}{mol}. \qquad \text{The} \qquad \text{actual} \qquad \text{work} \qquad \text{is} \qquad 25\% \qquad \text{greater}$$

$$W_{act} = 1.25W_S^{rev} = 9334\frac{J}{mol} = C_P \cdot (T_f - 298.15K)$$

The solultion is $T_f = 549.39K$

(b)   Repeat the calculation with a temperature-dependent heat capacity
$$C_P(T) = 22.243 + 5.977 \cdot 10^{-2}T - 3.499 \cdot 10^{-5}T^2 + 7.464 \cdot 10^{-9}T^3$$

Assuming reversibility T_f = 479.44K. Repeating the calculations above with the temperature-dependent heat capacity we find W_{act} = 9191 J, and T_f=520.92K.
So there is a significant difference between the results for the constant heat capacity and variable heat capacity cases.

3.17 $T_i = 300$ K, $T_f = 800$ K, and $P_i = 1.0$ bar

$$C_P(T) = 29.088 - 0.192 \times 10^{-2}\,T + 0.4 \times 10^{-5}T^2 - 0.870 \times 10^{-9}T^3\,\frac{J}{mol \cdot K}$$

$$\int_{T_i = 300K}^{T_f = 800K} \frac{C_P(T)}{T}dT = P\int_{P_i=1}^{P_f} \frac{dP}{P}$$

Calculated final pressure $P_f = 3.092 \times 10^6$ Pa.

$$W_{rev} = \int_{T_i=300K}^{T_f=800K} C_P(T)dT = 1.458 \times 10^4\,\frac{J}{mol}$$

3.18   Stage 1 is as in the previous problem.
Stage 2
Following the same calculation as above.

Stage 2 allowed pressure $P_{f,2} = 9.563 \times 10^7$ Pa

$$W_{rev} = 1.458 \times 10^{-4}\,\frac{J}{mol} = \text{Stage 2 work}$$

Stage 3

Following the same calculation method

$P_{f,3} = 2.957 \times 10^{-9}$ Pa $=$ Stage 3 allowed pressure.

$W_{rev} = 1.458 \times 10^4 \dfrac{\text{J}}{\text{mol}}$ $=$ Stage 3 work

Question for the student: Why is the calculated work the same for each stage?

3.19 The mass, energy and entropy balances are

$$\frac{dM}{dt} = \dot{M}_1 + \dot{M}_2 = 0, \ \dot{M}_2 = -\dot{M}_1$$

$$\frac{dU}{dt} = 0 = \dot{M}_1 \hat{H}_1 + \dot{M}_2 \hat{H}_2 + \dot{Q} + \dot{W}_s; \ \dot{M}_1\left(\hat{H}_1 - \hat{H}_2\right) + \dot{W}_s = 0;$$

$$\dot{W}_s = +\dot{M}_1\left(\hat{H}_2 - \hat{H}_1\right)$$

$$\frac{dS}{dt} = 0 = \dot{M}_1 \hat{S}_1 + \dot{M}_2 \hat{S}_2 + \frac{\dot{Q}}{T} + \dot{S}_{gen} = \dot{M}_1\left(\hat{S}_1 - \hat{S}_2\right) + \dot{S}_{gen} = 0$$

$$\dot{S}_{gen} = \dot{M}_1\left(\hat{S}_2 - \hat{S}_1\right)$$

300°C, 5 bar = 0.5 MPa $\qquad\qquad$ $\hat{H}_1 = 3064.2$ kJ/kg

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $\hat{S}_1 = 7.4599$ kJ/kg K

100°C, 1 bar = 0.1 MPa $\qquad\qquad$ $\hat{H}_2 = 2676.2$ kJ/kg

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $\hat{S}_2 = 7.3614$ kJ/kg K

$$\frac{\dot{W}_s}{\dot{M}_1} = 2676.2 - 3064.2 = 388 \text{ kJ/kg} \text{ satisfied the energy balance.}$$

$$\frac{\dot{S}_{gen}}{\dot{M}_1} = \hat{S}_2 - \hat{S}_1 = 7.3614 - 7.4599 = -0.0985 \text{ kJ/kg K} \text{ can not be. Therefore the process is impossible.}$$

3.20 Steam 20 bar = 2 MPa and 300°C $\qquad$ $\hat{H} = 3023.5$ kJ/kg

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $\hat{S} = 6.7664$ kJ/kg $\qquad$ (from Steam Tables)

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $\hat{U} = 2772.6$ kJ/kg

Final pressure = 1 bar. For reference saturation conditions are
$P = 0.1$ MPa, $T = 99.63$

$\hat{U}^L = 417.36$ $\qquad\qquad$ $\hat{H}^L = 417.46$ $\qquad$ $\hat{S}^L = 1.3026$
$\hat{U}^V = 2506.1$ $\qquad\qquad$ $\hat{H}^V = 2675.5$ $\qquad$ $\hat{S}^V = 7.3594$

(a) Adiabatic expansion valve $\dot{W} = 0$ and $\dot{Q} = 0$

$\qquad$ M.B.: $\dfrac{dM}{dt} = \dot{M}_1 + \dot{M}_2 = 0$; $\dot{M}_2 = -\dot{M}_1$;

$\qquad$ E.B.: $\dfrac{dU}{dt} = \dot{M}_1 \hat{H}_1 + \dot{M}_2 \hat{H}_2 = 0$; $\hat{H}_2 = \hat{H}_1$

$\qquad$ From Steam Tables

$\qquad\qquad \Rightarrow H_2 = 3023.5$ $\qquad$ $T = 250°C$ $\qquad$ $\hat{H} = 2974.3$ kJ/kg $\qquad$ $\hat{S} = 8.0333$ kJ/kg K

$\qquad\qquad\qquad\qquad\qquad\qquad$ $P = 0.1$ MPa $\qquad$ $T = 300°C$ $\qquad$ $\hat{H} = 3074.3$ kJ/kg $\qquad$ $\hat{S} = 8.2158$ kJ/kg K

$\qquad$ By interpolation $T = 275°C$ gives $\hat{H} = 3023.5$ kJ / kg $\Rightarrow$ all vapor

$\hat{S} = 8.1245$ kJ/kg K

$$\frac{dS}{dt} = \dot{M}\hat{S}_1 + \dot{M}_2\hat{S}_2 + \dot{S}_{gen} = 0$$

$$\frac{\dot{S}_{gen}}{\dot{M}_{gen}} = \hat{S}_2 - \hat{S}_1 = 8.1254 - 6.7664 = 1.359 \text{ kJ/kg K}$$

(b) Well designed, adiabatic turbine

    E.B.: $\dot{M}_1\hat{H}_1 + \dot{M}_2\hat{H}_2 + \dot{W} = 0$; $\dot{W} = \left(\hat{H}_2 - \hat{H}_1\right)$

    S.B.: $\dot{M}_1\hat{S}_1 + \dot{M}_2\hat{S}_2 = 0$; $\hat{S}_2 = \hat{S}_1$; $\hat{S}_2 = 6.7664$ kJ/kg K

    $\Rightarrow$ Two-phase mixture. Solve for fraction of liquid using entropy balance.

    $x \cdot (7.3594) + (1-x) \cdot 1.3026 = 6.7664$

    $x = 0.902$ (not good for turbine!)

    $\hat{H}_2 = 0.902 \times 2675.5 + 0.098 \times 417.46 = 2454.2$ kJ/kg

    $\dfrac{\dot{W}}{\dot{M}} = (2454.2 - 3023.5) = -569.3$ kJ/kg

    $-\dfrac{\dot{W}}{\dot{M}} = 569.3$ kJ/kg

(c) Isorthermal turbine $\Rightarrow$ superheated vapor

    $\left.\begin{array}{l} T = 300°\text{C} \\ P = 0.1 \text{ MPa} \end{array}\right]$ final state $\hat{H} = 3074.3$ kJ/kg

                                         $\hat{S} = 8.2158$ kJ/kg K

    E.B.: $\dot{M}_1\hat{H}_1 + \dot{M}_2\hat{H}_2 + \dot{Q} + \dot{W}_s = 0$

    S.B.: $\dot{M}_1\hat{S}_1 + \dot{M}_2\hat{S}_2 + \dfrac{\dot{Q}}{T} + \cancel{\dot{S}_{gen}}^{\,0} = 0$

        $\dfrac{\dot{Q}}{T} = -\dot{M}_1\hat{S}_1 - \dot{M}_2\hat{S}_2 = \dot{M}_1\left(\hat{S}_2 - \hat{S}_1\right)$

        $\dfrac{\dot{Q}}{\dot{M}} = T\left(\hat{S}_2 - \hat{S}_1\right) = (300 + 273.15)(8.2158 - 6.7664)$ kJ/kg K

             $= 830.7$ kJ/kg

        $-\dfrac{\dot{W}_s}{\dot{M}} = \dfrac{\dot{Q}}{\dot{M}} + \left(\hat{H}_1 - \hat{H}_2\right) = 830.7 + (3023.5 - 3074.3) = 779.9$ kJ/kg

    $\Rightarrow$ get more work out than in adiabatic case, but have to put in heat.

3.21   System = contents of the compressor (steady-state, constant volume). Also, gas is ideal.

(a) Mass balance $0 = \dot{N}_1 + \dot{N}_2 \rightarrow \dot{N}_2 = -\dot{N}_1$

Energy balance $0 = \dot{N}_1\underline{H}_1 + \dot{N}_2\underline{H}_2 + \underbrace{\dot{Q}}_{\text{adiabatic}}{}^{0} + \dot{W}_s - P\,\dfrac{dV}{dt}^{0}$

Entropy balance

$$0 = \dot{N}_1\underline{S}_1 + \dot{N}_2\underline{S}_2 + \underbrace{\dfrac{\dot{Q}}{T}}^{0} + \underbrace{\dot{S}_{\text{gen}}}_{0}^{\overset{\text{reversible}}{\text{compressor}}} \Rightarrow \underline{S}_1 = \underline{S}_2$$

From the energy balance $\dot{W}_s = \dot{N}C_{\mathrm{P}}(T_2 - T_1)$ or $\dfrac{\dot{W}_s}{\dot{N}} = C_{\mathrm{P}}(T_2 - T_1)$

From the entropy balance $\underline{S}_1 = \underline{S}_2 \Rightarrow T_2 = T_1\left(\dfrac{P_2}{P_1}\right)^{R/C_{\mathrm{P}}}$

Thus

$$\frac{\dot{W}_s}{\dot{N}} = C_{\mathrm{P}}T_1\left[\left(\frac{P_2}{P_1}\right)^{R/C_{\mathrm{P}}} - 1\right]$$

(b) Two stage compression, with intercooling, so that gas is returned to initial temperature, before entering 2nd compressor

work in stage 1 $= \dot{W}_s^{I} = NC_{\mathrm{P}}T_1\left[\left(\dfrac{P^*}{P_1}\right)^{R/C_{\mathrm{P}}} - 1\right]$; where P^* = pressure after 1st compressor.

work in stage 2 $= \dot{W}_s^{II} = NC_{\mathrm{P}}T_1\left[\left(\dfrac{P_2}{P^*}\right)^{R/C_{\mathrm{P}}} - 1\right]$

Total work $= \dot{W}_s^{I} + \dot{W}_s^{II} = \dot{N}C_{\mathrm{P}}T_1\left[\left(\dfrac{P^*}{P_1}\right)^{R/C_{\mathrm{P}}} + \left(\dfrac{P_2}{P^*}\right)^{R/C_{\mathrm{P}}} - 2\right] = \dot{W}_s$

To find P^* for minimum work, set $d\dot{W}_s/dP^* = 0$.

$$\frac{d}{dP^*}(\dot{W}_s) = 0 = \dot{N}C_{\mathrm{P}}T_1\left\{\frac{R}{C_{\mathrm{P}}}\left(\frac{P^*}{P_1}\right)^{(R/C_{\mathrm{P}})-1}\frac{1}{P_1} - \frac{R}{C_{\mathrm{P}}}\left(\frac{P_2}{P^*}\right)^{(R/C_{\mathrm{P}})-1}\left(\frac{P_2}{P^{*2}}\right)\right\}$$

$$\Rightarrow (P^*)^{2R/C_{\mathrm{P}}} = (P_1P_2)^{R/C_{\mathrm{P}}}$$

or

$P^* = \sqrt{P_1P_2}$

Students should check that this results in minimum, and ***not*** maximum work.

3.22   System: nitrogen contained in both tanks (closed, adiabatic, constant volume)

Mass balance: $M_1^i = M_1^f + M_2^f$ (1)

Energy balance: $M_1\hat{U}_1 = M_1^f\hat{U}_1^f + M_2^f\hat{U}_2^f$ (2)

Final pressure condition: $P_1^f = P_2^f$ (3)

For the entropy balance, the nitrogen in the first tank that remains in the tank will be taken as the system. Then

$\hat{S}_1^i = \hat{S}_1^f$ (4)

Equation (1) –(4), together with eqn. of state information of the form $\hat{S} = \hat{S}(T,P)$, $\hat{U} = \hat{U}(T,P)$ and $\hat{V} = \hat{V}(T,P)$ which we can get from Fig. 2.4-3 provides 4 eqns. for the 4 unknowns T_1^f, P_1^f, T_2^f and P_2^f. Procedure to be followed in solution

(i)   Guess a final pressure P^f

(ii)   Use eqn. (4) + Fig. 2.4-3 to compute T_1^f, caluculate $\hat{U}_1^f$

(iii)   Use Fig. 2.4-3 to get $\hat{V}_1^f$, compute $M_1^f = \dfrac{V}{\hat{V}_1^f}$

(iv) $M_2^f = M_1^i - M_1^f$, and $\hat{V}_2^f = V / M_2^f$

(v)   Use P^f and $\hat{V}_2^f$ to get T_2^f and $\hat{U}_2^f$

(vi)   See if energy balance, Eqn. (2), is satisfied. If it is, guessed P^f is correct. If it is not, guess new p^f, go back to (ii), and repeat calculation.

Some preliminaries

$T_1^i = 250$ K $\qquad \xrightarrow[\text{2.4 - 3}]{\text{Figure}} \qquad \hat{H}_1^i = 368$ kJ/kg

$P_1^i = 200$ bar $\qquad\qquad\qquad\qquad \hat{V}_1^i \approx 0.0037$ m^3/kg

Thus $M_1^i = V / \hat{V}_1^i = 0.01$ m^3 / 0.0037 m^3/kg $= 2.703$ kg

As a first guess, use ideal gas solution for pressure. (Also try some neighboring pressures.) My solution is

$P_1^f = P_2^f = 133.3$ bar (same as ideal gas solution)

$T_1^f = 226$ K $\left(\text{ideal gas solution: } T_1^f = 222.8 \text{ K}\right)$

$T_2^f = 285$ K $\left(\text{ideal gas solution: } T_2^f = 330.4 \text{ K}\right)$

3.23 (a) Set up just as in Problem 3.22 above. Solution after a number of iterations is $P_1^f = P_2^f \approx 5$ bar .

$T_1^f = 275.6°$C and $T_2^f = 497.7°$C .

(b) Since now there is heat exchange between the two chambers we have $T_1^f = T_2^f$. This equation is used instead of entropy balance. Solution procedure is to guess a final pressure, and then compute final temperature using first the mass balance

$$M_1^i = M_1^f + M_2^f \Rightarrow \frac{V_1}{\hat{V}_1^i} = \frac{V_1}{\hat{V}_1^f} + \frac{V_2}{\hat{V}_2^f} = \frac{V_1 + V_2}{\hat{V}^f} \Rightarrow \hat{V}_f = \frac{V_1 + V_2}{V_1}\hat{V}_1^i \qquad (1)$$

That is, choose T^f until eqn (1) is satisfied. Then compute T^f from energy balance i.e.

$$M_1^i \hat{U}_1^i = M_1^f \hat{U}_1^f + M_2^f \hat{U}_2^f = \left(M_1^f + M_2^f\right)\hat{U}_2^f \Rightarrow \hat{U}_1^i = \hat{U}^f \qquad (2)$$

When guessed P^f is correct, T^f computed from eqns. (1) and (2) using the Steam Tables will be identical. My solution is $P^f = 5$ bar and $T^f \cong 366°$C .

3.24   System = contents of turbine (open, constrant volume, steady-state)

Mass balance: $\dfrac{dN}{dt} = 0 = \dot{N}_1 + \dot{N}_2 \Rightarrow \dot{N}_2 - \dot{N}_1$

Energy balance: $\dfrac{dN}{dt} = 0 = \dot{N}_1\underline{H}_1 + \dot{N}_2\underline{H}_2 + \underset{\text{adiabatic}}{\cancel{\dot{Q}}}^{\,0} + \dot{W}_s - P\underset{\substack{\text{constant}\\\text{volume}}}{\cancel{\dfrac{dV}{dt}}}^{\,0}$

$$\Rightarrow \dot{W}_s = -\dot{N}_1(\underline{H}_1 - \underline{H}_2) = -\dot{N}_1 C_P(T_1 - T_2) \text{ for the ideal gas}$$

Entropy balance: $\dfrac{dN}{dt} = 0 = \dot{N}_1 \underline{S}_1 + \dot{N}_2 \underline{S}_2 + \cancel{\dfrac{\dot{Q}}{T}}^{\,0} + \dot{S}_{gen}$

$$\Rightarrow \dot{S}_{gen} = -\dot{N}_1(\underline{S}_1 - \underline{S}_2) = \dot{N}_1\left\{C_P \ln\left(\dfrac{T_2}{T_1}\right) - R\ln\left(\dfrac{P_2}{P_1}\right)\right\}$$

or

$$T_2 = T_1\left(\dfrac{P_2}{P_1}\right)^{R/C_P} \exp\left[\dfrac{\dot{S}_{gen}}{\dot{N}_1 C_P}\right]$$

(a) For T_2 to be a minimum, since $\dot{S}_{gen} \geq 0$ and $\dot{N}_1 > 0$, $\dot{S}_{gen}$ must be zero. Thus the minimum outlet temperature occurs in reversible operation.

(b) $\dot{W}_s = +\dot{N}_1 C_P(T_2 - T_1)$. Since $T_1 > T_2$, the maximum work occurs when T_2 is a minimum. Thus, $\dot{W}_s$ is a maximum (in magnitude) for a reversible process.

3.25 (a) For any system:

$$\dfrac{dS}{dt} = \left[\dot{M}_i \hat{S}_i + \dfrac{\dot{Q}}{T} + \dot{S}_{gen}\right]$$

depending 0n the process $\dot{Q} \geq 0$ or $\dot{Q} \leq 0$ and $\sum \dot{M}_i \hat{S}_i \geq 0$ or $\sum \dot{M}_i \hat{S}_i \leq 0$. Also, $\dot{S}_{gen} = 0$ or $\dot{S}_{gen} > 0$, depending on whether or not the process is reversible. Thus, dS/dt for a system can be greater than, less than, or equal to zero.

  Since, by definition, the universe contains everything, it must be a closed system and adiabatic, since there is nothing for the universe to exchange mass or heat with. Therefore

$$\dfrac{dS}{dt} = 0 + 0 + \dot{S}_{gen} \Rightarrow \dfrac{dS}{dt} = \dot{S}_{gen} \geq 0$$

Thus the entropy of the universe can not decrease, and the statement is true.

(b) Consider the change from any state 1 to any state 2 in a closed system. The energy and entropy balances for this transformation are:

(1) $\quad U_2 - U_2 = Q + W = W$ $\left\{\right.$Since the process is adiabatic
(2) $\quad S_2 - S_1 = S_{gen}$ $\left.\right.$

If the transformation is possible, then $S_{gen} \geq 0$ now consider the transformation from state 2 to state 1. Here

(3) $\quad U_1 - U_1 = W^*$
(4) $\quad S_1 - S_2 = S^*_{gen}$

Comparing eqns. (1) and (3) we have $W = -W^*$ (This is ok).
Comparing eqns. (2) and (4) we have $S_{gen} = -S^*_{gen}$ $\hspace{2cm}$ (5)

Separately we have, if the processes are possible, that $S_{gen} \geq 0$ and $S^*_{gen} \geq 0$. The only way that all these three equations for S_{gen} and S^*_{gen} can be satisfied is if $S_{gen} = S^*_{gen} = 0$, that is, both processes are reversible. Generally, processes are not reversible. However, eqn. (5) requires that only one of S_{gen} and S^*_{gen} can be greater than zero. Thus,

If $S_{gen} > 0$ $1 \rightarrow 2$ is possible, but $2 \rightarrow 1$ is not possible.

If $S_{gen}^* > 0$ $2 \rightarrow 1$ is possible, but $1 \rightarrow 2$ is not possible.

3.26 This is like Illustration 3.7-2 except that the Rankine rather than vapor compression refrigeration cycle is used. Only properties of point 2, and path from $1 \rightarrow 2$ changes.

Point 2: isentropic $\hat{S} = 1.2622$ kJ/kg K ; $\hat{H} = 279.8$ kJ/kg; $55°C$; $T = 5°C$

$\hat{S}^L(5°C) = 1.0244$; $x =$ fraction vapor; $\hat{S}^V(5°C) = 1.7252$

$1.7252 \cdot x + 1.0244(1 - x) = 1.2622$

$x = 0.3393$

$\hat{H}^L(5°C) = 206.8$ $\qquad \hat{H} = x(401.7) + (1 - x)(206.8)$

$\hat{H}^V(5°C) = 401.7$ $\qquad \hat{H} = 272.9$

$\hat{Q}_B^L = \hat{H}_3 - \hat{H}_2 = 402 - 272.9 = 129.1$

$\hat{W} = \hat{H}_4 - \hat{H}_3 = 432 - 402 = 30$

$C.O.P. = \dfrac{129.1}{30} = 4.303$

If the turbine drives compressor

$\hat{W} = \left(\hat{H}_4 - \hat{H}_3\right) - \left(\hat{H}_1 - \hat{H}_2\right) = (432 - 402) - (280 - 272.9) = 22.9$

$C.O.P. = \dfrac{129.1}{22.9} = 5.64$

Vapor compression cycle with change of T_{low} and T_{high} .

Location	State	Path	$T(°C)$	P (kPa)	$\hat{H}$(kJ/kg)	$\hat{S}$(kJ/kg)
1	Sat'd liq		60	1683	287.9	1.286
		isenthalp				
2	V-L mix		0	293	287.9	
		$P = $ const				
3	Sat'd vap		0	293	398.8	1.728
		isentrope				↓
4	superheated vapor			1683	433.6	1.728
		$P = $ const		↑		
5	Sat'd liq		66	1683	287.9	1.286

Interpolation

$P = 1600$ kPa $\qquad 60°C \qquad \hat{S} = 1.7134 \qquad \hat{H} = 429.3$

$\qquad\qquad\qquad\quad 65°C \qquad \hat{S} = 1.7323 \qquad \hat{H} = 435.6$

$\qquad\qquad\qquad\quad 70°C \qquad \hat{S} = 1.7503 \qquad \hat{H} = 441.7$

$P = 1700$ kPa $\qquad 65°C \qquad \hat{S} = 1.7217 \qquad \hat{H} = 433.3$

$\qquad\qquad\qquad\quad 70°C \qquad \hat{S} = 1.7405 \qquad \hat{H} = 439.7$

at 1700 kPa $\hat{S} = 1.728$ at $65.16°C$ and $\hat{H} = 433.5$

at 1600 kPa $\hat{S} = 1.728$ at $63.84°C$ and $\hat{H} = 434.1$

$\Rightarrow$ at 1683 kPa $T = 64.9°C$ and $\hat{H} = 433.6$

$$\hat{Q}_C = \hat{H}_3 - \hat{H}_2 = 398.8 - 287.9 = 110.9$$

$$\hat{W} = \hat{H}_4 - \hat{H}_3 = 433.6 - 398.8 = 34.8$$

$$\text{C.O.P.} = \frac{110.9}{34.8} = 3.18$$

3.27   General analysis of a heat engine
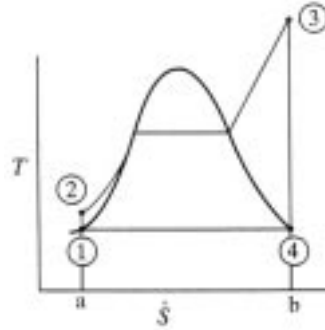
$$\frac{dS}{dt} = \frac{\dot{Q}}{T}; \quad \dot{Q} = T\frac{dS}{dt}; \quad Q_{2-3} = \int_{T_2}^{T_3} TdS = \text{area}(a-1-2-3-4-b-a)$$

$$Q_{4-1} = \int TdS = T(S_1 - S_4) = \text{area}(a-1-4-b-a)$$

Integration around a cycle

$$0 = Q_{2-3} + Q_{4-1} + W_{\text{net}}$$

$$-W_{\text{net}} = +Q_{2-3} + Q_{4-1} = \text{area}(a-1-2-3-4-b-a) - \text{area}(a-1-4-b-a)$$

$$= \text{area}(1-2-3-4-1)$$

$$\eta = \frac{-W_{\text{net}}}{Q_{\text{in}}} = \frac{-W_{\text{net}}}{Q_{2-3}} = \frac{\text{area}(1-2-3-4-1)}{\text{area}(a-1-2-3-4-b-a)}$$

Original cycle   Increasing evaporator T but not pressure
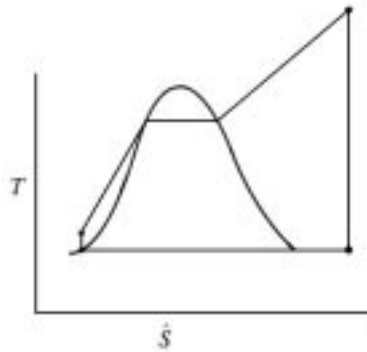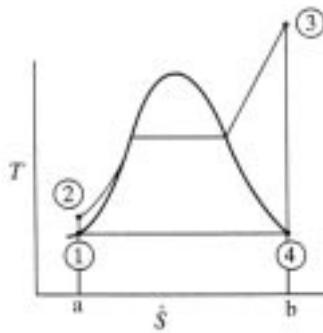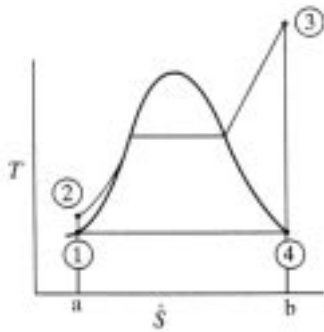
Original cycle   Increasing evaporator T and P
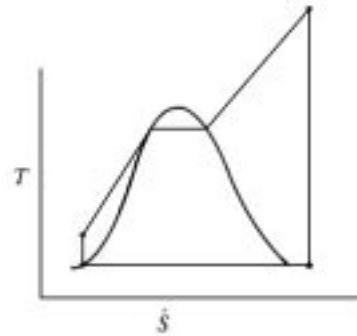
Either way more work is obtained, with only a slight increase in heat rejected
$\Rightarrow$ almost all the additional heat input is converted to work.
$\Rightarrow$ efficiency improves

Decreasing evaporator T
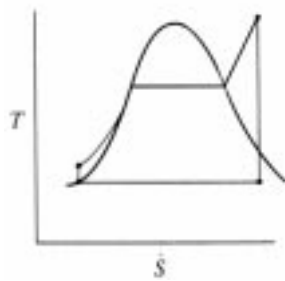
(Note: may get in to 2-phase region)

Again, efficiency will increase due to more work being produced and less heat rejected.

3.28 $a - 1 - 2 - 3' - 4' - b' - a$ without superheat
$a - 1 - 2 - 3 - 4 - b - a$ with superheating.
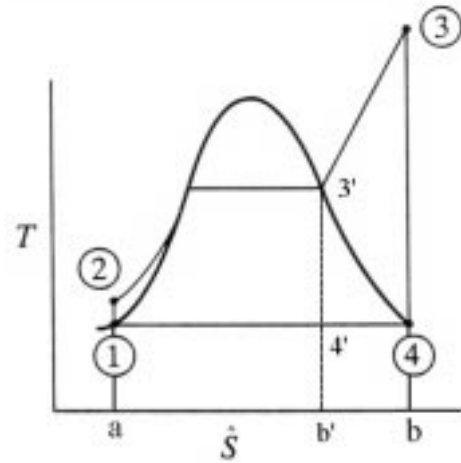
Clearly greater work output and higher efficiency with superheat.

$a-1-2-3-4-b-a$ without subcooling
$a'-1'-2'-3-4-b-a'$ with subcooling
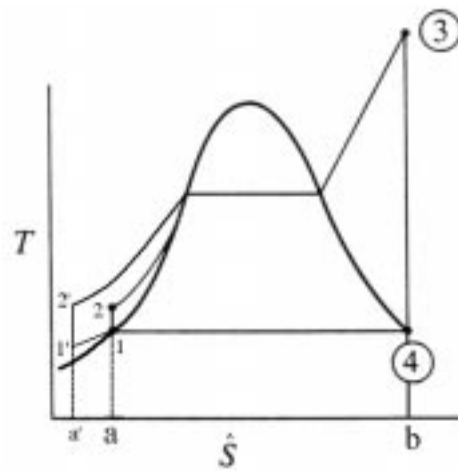
Probably is greater efficiency with subcooling, but is not as evident as with superheating case.

3.29
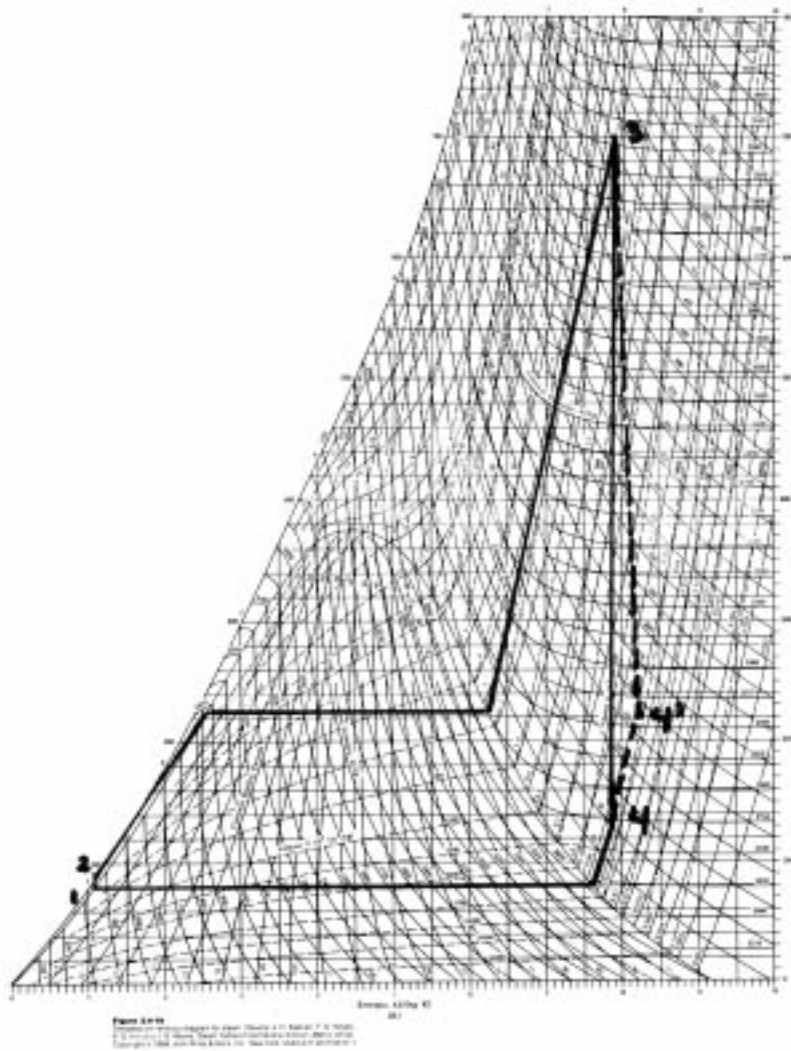
		T	P	$\hat{S}$	$\hat{H}$	$\hat{V}$
1		80°C	47.39 kPa	1.0753	334.91	0.00102
	isentropic					
2			2.5 MPa	1.0753	337.4	
3		700	2.5 MPa	7.8435	3914.5	
4		130.3	47.39	7.8435	2741.8	
1		80°C	47.39			

at $P = 0.050$ MPa(~ 0.04739)

  $T = 100$; $\hat{H} = 2682.5$; $\hat{S} = 7.6947$

$T = 150$; $\hat{H} = 2780.5$; $\hat{S} = 7.9401$

$\Rightarrow T = 130.3$; $\hat{H} = 2741.8$ kJ/kg

$\text{Work}_{1 \to 2} = +\int VdP = 0.001029 \ \text{m}^3/\text{kg} \times (2500 - 47.39)\text{kPa}$

$\qquad = 2.524 \ \text{m}^3/\text{kg} \times 10^3 \ \text{Pa} = 2.524 \times 10^3 \ \text{m}^3/\text{kg} \times \text{J}/\text{m}^3$

$\qquad = 2524 \ \text{kJ/kg}$

$\eta = \dfrac{-W_{net}}{Q_{in}}$ $+W_{net} = (2741.8 - 3914.5) + 2.5 = -1170.2$

$\qquad\qquad Q_{in} = 3914.5 - 337.4 = 3577.1$

$\eta = \dfrac{1170.2}{3577.1} = 0.327 \Rightarrow 32.7\%$

Turbine is only 85%, but adiabatic

$\Rightarrow -W_{turbine}^{ideal} = 3914.5 - 2741.8 = 1172.7$

$\quad -W_{turbine}^{act} = 0.85 \times 1172.7 = 996.8$

$\Rightarrow \hat{H}_4 = 3914.5 - 996.8 = 2917.7$ kJ/kg

So state $4 \Rightarrow P = 47.39$; $\hat{H} = 2917.7$

$T = 200°\text{C}$; $\hat{H} = 2877.7$; $\hat{S} = 8.1580$

$T = 250°\text{C}$; $\hat{H} = 2976.0$; $\hat{S} = 8.3556$

$\Rightarrow T = 220.3°\text{C}$; $\hat{S} = 8.2384$ kJ/kg K

$\eta = \dfrac{996.8 - 2.5}{3577.1} = 27.8\%$

	P	T	$\hat{H}$	$\hat{S}$
①	47.39 kPa	80	334.91	1.0753
②	2.5 MPa			1.0753
③	2.5 MPa	700°C	3462.1	7.8435
4	47.39 kPa	~190	2860.2	

If turbine is only 85% efficient

$W = 3462.1 - 2754.0 = 708.1$ in previous case

$W = 601.9 \Rightarrow H_4 = 3462.1 - 601.9 = 2860.2$

$\eta =\sim 0.85 \times 0.226 = 0.192$

$\hat{U}^L = 963.73$ kJ/kg ; $\hat{S}^L = 2.5639$ kJ/kg K ; $\hat{U}^L = 2603.3$ kJ/kg ; $\hat{S}^L = 6.2503$

		P kPa	T	$\hat{H}$	$\hat{S}$	$\hat{V}$
①	sat L	47.39 kPa	80	334.91	1.0753	0.001029
②		2.5 MPa			1.0753	
③	superheated vapor	2.5 MPa	700°C	3462.1	7.8435	
④	superheated vapor	47.39	~138°C	2754	7.8435	

$$Q_{in} = \hat{H}_3 - \hat{H}_2 = \hat{H}_3 - \hat{H}_1 = 3462.1 - 334.91$$

$$W = \hat{H}_4 - \hat{H}_3 = 2754 - 3462.1$$

$$\eta = \frac{W}{Q} = \frac{3462.1 - 2754}{3462.1 - 334.91} = 0.226$$

3.30 Energy balance around whole cycle

S.B.: $0 = \dot{Q}_H + \dot{Q}_L + \dot{Q}_M$; $-\dot{Q}_M = \dot{Q}_H + \dot{Q}_L$

$$0 = \frac{\dot{Q}_H}{T_H} + \frac{\dot{Q}_L}{T_L} + \frac{\dot{Q}_M}{T_M}$$

$$\frac{\dot{Q}_L}{T_L} = -\frac{\dot{Q}_H}{T_H} - \frac{\dot{Q}_M}{T_M} = -\left(\frac{\dot{Q}_H}{T_H} + \frac{\dot{Q}_M}{T_M}\right)$$

$$\dot{Q}_L = -T_L\left(\frac{\dot{Q}_H}{T_H} + \frac{\dot{Q}_M}{T_M}\right)$$

$$0 = \frac{\dot{Q}_H}{T_H} + \frac{\dot{Q}_L}{T_L} - \left(\frac{\dot{Q}_H}{T_M} + \frac{\dot{Q}_L}{T_M}\right)$$

$$0 = \dot{Q}_H\left(\frac{1}{T_H} - \frac{1}{T_L}\right) + \dot{Q}_L\left(\frac{1}{T_L} - \frac{1}{T_M}\right)$$

$$\dot{Q}_H\left(\frac{1}{T_H} - \frac{1}{T_M}\right) = -\dot{Q}_L\left(\frac{1}{T_L} - \frac{1}{T_M}\right)$$

$$\frac{\dot{Q}_L}{\dot{Q}_H} = -\frac{[(1/T_H) - (1/T_M)]}{[(1/T_L) - (1/T_M)]} = -\left(\frac{T_M - T_H}{T_M T_H}\right)\frac{T_M T_L}{T_M - T_L}$$

$$= -\left(\frac{T_M - T_H}{T_M - T_L}\right)\cdot\frac{T_L}{T_H} = \left(\frac{T_H - T_M}{T_M - T_L}\right)\cdot\frac{T_L}{T_H}$$

3.31 First write balance equations for the contents of the turbine. This is a steady-state, constant-volume, adiabatic system.

M.B. $0 = \dot{M}_1 + \dot{M}_2 \Rightarrow \dot{M}_2 = -\dot{M}_1$

E.B. $0 = \dot{M}_1\hat{H}_1 + \dot{M}_2\hat{H}_2 + \dot{W}_s \Rightarrow -\dot{W}_s = \dot{N}_1(\underline{H}_1 - \underline{H}_2)$

S.B. $0 = \dot{M}_1\hat{S}_1 + \dot{M}_2\hat{S}_2 + \cancel{\frac{\dot{Q}}{T}}^{\,0} + \dot{S}_{gen}$

Maximum work $\Rightarrow$ reversible process $\Rightarrow \dot{S}_{gen} = 0$ (see Sec. 3.2) $\Rightarrow \hat{S}_1 = \hat{S}_2$. Thus the inlet and exit turbine conditions are connected by a vertical line on the Mollier diagram.

(a) $\hat{H}_1 = 2880$ J/g $\xrightarrow[\substack{\text{connecting 540 K,}\\\text{36 bar and 1 bar}}]{\text{Vertical line}}$ $\hat{H}_2 = 2270$ J/g, $T_2 = 99.65°$C

$P_2 = 1$ bar $\quad \left(\substack{\text{Saturation } T\\ \text{for } P = 1 \text{ bar}}\right)$

$$-\frac{\dot{W}_s}{\dot{M}} = \hat{H}_1 - \hat{H}_2 = (2880 - 2270) \text{ J/g} = 610 \text{ J/g}$$

(b) Two stage turbine. Use balance equations above for each stage.

Stage 1

$T_1 = 540$ K $= 266.85°$C $\qquad \hat{H}^i = 2770$ J/g

$P_1 = 36$ bar $\qquad\qquad\qquad T^* = 118°$C

$\Downarrow \qquad\qquad\qquad\qquad\qquad \Uparrow$

$\hat{H}_1 = 2880$ J/g $\qquad\qquad\quad P^* = 18.5$ bar

$\hat{S}_1 = 6.28$ J/g K $\qquad \longrightarrow \quad \hat{S}^* = 6.28$ J/g K

After reheating in the reactor

$$\text{Stage 2}$$

$$P^* = 18.5 \text{ bar} \qquad\qquad \hat{H}_2 = 2440 \text{ J/g}$$

$$T^* = 266.85° \text{C} \qquad\qquad T_2 = 99.63° \text{C}$$

$$\Downarrow \qquad\qquad\qquad \Uparrow$$

$$\hat{H} = 2960 \text{ J/g} \qquad\qquad P_2 = 1 \text{ bar}$$

$$\hat{S} = 6.70 \text{ J/g} \quad \longrightarrow \quad \hat{S}_2 = 6.70$$

Note: There is no work done in reheating step (no shaft work, and no change of reheater boundaries). Only energy transfer step is heating; $\dot{Q}/\dot{M} = 2960 - 2770 = 190 \text{ J/g}$

$$\text{Total work out/g} \ = -\frac{\dot{W}_s}{\dot{M}} = (2880 - 2770) + (2960 - 2440) = 630 \text{ J/g}$$

$$(20 \text{ J/g additional work})$$

(c) Similar to part (b) above, except that intermediate pressure is 6.0 bar

$$\dot{Q}/\dot{M} = 445 \text{ J/g}$$

$$-\dot{W}_s/\dot{M} = 685 \text{ J/g} \qquad\qquad (75 \text{ J/g additional work})$$

3.32 System: contents of the tank at any time (open, adiabatic, constant volume system).

(a) Mass balance: $\dfrac{dN}{dt} = -\dot{N}$

ideal gas law $N = \dfrac{PV}{RT}$; $\dot{N} = \dfrac{P\dot{V}}{RT}$ where $\dot{V} = $ volumetric flow rate.

Thus, $\dfrac{d}{dt}\left(\dfrac{PV}{RT}\right) = -\dfrac{P\dot{V}}{RT} \Rightarrow V\dfrac{d}{dt}\left(\dfrac{P}{T}\right) = -\dfrac{P}{T}\dot{V}$ since V and $\dot{V}$ are both constant.

$\dfrac{d}{dt}\ln\left(\dfrac{P}{T}\right) = -\dfrac{\dot{V}}{V}$ or $\left.\dfrac{P}{T}\right|_{5\min} = \left.\dfrac{P}{T}\right|_0 \exp\left(-\dfrac{\dot{V}t}{V}\right) = 1.082 \times 10^{-3} \dfrac{\text{bar}}{\text{K}}$ or

$$P(5 \text{ min}) = 1.082 \times 10^{-3} T(5 \text{ min}) \qquad \{P = \text{bar}, \ T = \text{K}\} \qquad (1)$$

Energy balance: $\dfrac{d}{dt}(N\underline{U}) = -\dot{N}\underline{H} \Rightarrow \underline{U}\dfrac{dN}{dt} + N\dfrac{d\underline{U}}{dt} = \underline{H}\dfrac{dN}{dt}$

or $N\dfrac{d\underline{U}}{dt} = \dfrac{dN}{dt}(\underline{H} - \underline{U}) \Rightarrow RT\dfrac{dN}{dt} = NC_V\dfrac{dT}{dt}$

using $N = PV/RT$ yields $R\dfrac{dP}{dt} = \dfrac{P}{T}C_P\dfrac{dT}{dt}$ or $T_2 = T_1\left(\dfrac{P_2}{P_1}\right)^{R/C_P}$

[Note: could have gotten this result from the entropy balance also!]

$$\Rightarrow T(5 \text{ min}) = 340\left(\dfrac{P(5 \text{ min})}{1 \text{ bar}}\right)^{8.314/39} \qquad (2)$$

simultaneously solving equations (1) and (2) yields

$$P(5 \text{ min}) = 0.281 \text{ bar and } T(5 \text{ min}) = 259.3 \text{ K}$$

(b) Since pump is adiabatic and reversible, $\underline{S}_{in} = \underline{S}_{out}$ or $T_3 = T_2\left(\dfrac{P_3}{P_2}\right)^{R/C_P}$ since $P_3 = P_1$. This equation

implies that $T_3 = T_1 = 340$ K .

3.33 Number of moles of gas in tank initially $= N_0 = N(0)$

$$N(0) = \frac{P(0)V}{RT(0)} = \frac{15 \text{ bar} \times 0.2 \text{ m}^3 \times 10^5 \text{ J/m}^3 \text{ bar}}{8.314 \text{ J/mol K} \times (22 + 273.15)\text{K}} = 122.26 \text{ mol}$$

$$\frac{dN}{dt} = \dot{N} = -4.5 \text{ mol/min} \Rightarrow N(t) = 122.26 - 4.5t \text{ mol} \quad (t = \text{min})$$

(a) Entropy balance on an element of gas that remains in the tank (see Illustration 3.5-2) yields

$$\underline{S}(t) - \underline{S}(0) = 0 \Rightarrow \frac{T(t)}{T(0)} = \left(\frac{P(t)}{P(0)}\right)^{R/C_P} \Rightarrow T(t) = 295.15\left(\frac{P(t)}{15}\right)^{0.3779} \quad (1)$$

From the ideal gas equation of state

$$P(t)V = N(t)RT(t) \Rightarrow \frac{T(t)N(t)}{P(t)} = \frac{V}{R} = \frac{T(0)N(0)}{P(0)}$$

Thus

$$\frac{T(t)}{P(t)} = \frac{295.15 \text{ K}}{15 \text{ bar}} \times \frac{122.26}{122.26 - 4.5t} = \frac{19.68}{1 - 0.03681t} \quad (2)$$

Now using eqn. (1) in eqn. (2) to solve for $P(t)$ and $T(t)$ yields

$$P(t) = 15 \times (1 - 0.03681t)^{1.6075}$$
$$T(t) = 295.15 \times (1 - 0.03681t)^{0.6075}$$

But $T(t)$ is temperature in the tank. What about temperature of gas leaving the throttling valve? Gas going thru valve undergoes a Joule-Thomson expansion $\Rightarrow \underline{H}_{in} = \underline{H}_{out}$. Since gas is ideal, this implies $T_{in} = T_{out}$. Thus, $T(t)|_{out\,of\,valve} = 295.15 \times (1 - 0.03681t)^{0.6075}$

(b) If tank is isothermal, then, instead of eqn. (2), we have

$$\frac{P(t)}{N(t)} = \frac{RT}{V} = \frac{P(0)}{N(0)} \Rightarrow P(t) = 15(1 - 0.03681t)\text{bar}$$

and $T(t) = \text{constant} = 295.15$ K

Summary

	$T(K)$	$P(\text{bar})$
Adiabatic	$295.15(1 - 0.03681t)^{0.6075}$	$15(1 - 0.03681t)^{1.6075}$
Isothermal	295.15	$15(1 - 0.03681t)$

3.34   This is a tough problem!
Subscript 1 denotes properties in initally filled tank
Subscript 2 denotes properties in initially "evacuated" tank
We will use i and f (superscripts) to denote initial and final properties, and we will assume negligible mass hold-up in engine.

1) Mass balance on closed system consisting of both tanks

$$N_1^i + N_2^i = N_1^f + N_2^f \Rightarrow \frac{P_1^i V_1}{T_1^i} + \frac{P_2^i V_2}{T_2^i} = \frac{P_1^f V_1}{T_1^f} + \frac{P_2^f V_2}{T_2^f}$$

but

$$P_1^f = P_2^f = P^f \Rightarrow P^f \left(\frac{0.3}{T_1^f} + \frac{0.75}{T_2^f} \right) = \frac{14.0 \times 0.3}{973.15} + \frac{0.35 \times 0.75}{298.15}$$

$$= 5.196 \times 10^{-3} \frac{\text{bar m}^3}{\text{K}}$$

(1)

2) Entropy balance on gas contained in tank 1 initially and finally. This is a closed, adiabatic, reversible system

$$\frac{dS}{dt} = 0 \Rightarrow S_1^i = S_1^f \Rightarrow C_{\text{P}} \ln\left(\frac{T_1^f}{T_1^i} \right) = R \ln\left(\frac{P_1^f}{P_1^i} \right)$$

(2)

Thus

$$T_1^f = T_1^i \left(\frac{P_1^f}{P_1^i} \right)^{R/C_{\text{P}}} = 973.15 \left(\frac{P_1^f}{14.0} \right)^{2/7}$$

(3)

Equation (2) implies that T_1 and P_1 are related as follows

$$\frac{d \ln T_1}{dt_1} = \frac{R}{C_{\text{P}}} \frac{d \ln P_1}{dt}$$

(4)

3) Mass and energy balances on tank 1

$$\frac{dN_1}{dt} = \dot{N}_1 \equiv -\dot{N} \; ; \; \frac{d}{dt} = (N_1 \underline{U}_1) = -\dot{N} \underline{H}_1 = \underline{U}_1 \frac{dN_1}{dt} + N_1 \frac{d\underline{U}_1}{dt}$$

or $N_1 C_{\text{V}} \dfrac{dT_1}{dt} = \dfrac{dN_1}{dt}(\underline{H}_1 - \underline{U}_1) = RT_1 \dfrac{dN_1}{dt} = -RT_1 \dot{N}$

using eqn. (4) gives

$$N_1 \frac{C_{\text{V}}}{C_{\text{P}}} \frac{d \ln P_1}{dt} = -\dot{N} = \frac{dN_1}{dt}$$

(5)

4) balances on the engine: adiabatic, reversible (for maximum work) and since no hold-up of mass, $dN_1/dt = 0$
Subscript eng refers to gas leaving engine and going into tank 2.

$$0 = \left(\underline{H}_1 - \underline{H}_{\text{eng}} \right) \dot{N} + \dot{W}_s$$

$$0 = \left(\underline{S}_1 - \underline{S}_{\text{eng}} \right) \dot{N}$$

$$\Rightarrow \underline{S}_1 = \underline{S}_{\text{eng}};$$

Also $P_2 = P_{\text{eng}}$

$$\Rightarrow T_{\text{eng}} = T_1 \left(P_{\text{eng}} / P_1 \right)^{R/C_\text{P}} = T_1 \left(P_2 / P_1 \right)^{R/C_\text{P}} \tag{6}$$

(Note that $T_{\text{eng}} \ne T_2$)

and

$$-\dot{W}_s = \dot{N} C_\text{P} \left(T_1 - T_{\text{eng}} \right) \tag{7}$$

5) balances on tank 2 [Note, irreversible mixing occurs unless, fortuitously, $T_{\text{eng}} = T_2$ at all times (can this occur?). Thus, $S_{\text{gen}} > 0$, and entropy balance gives no useful information]

Mass balance: $dN_2 / dt = \dot{N}$

Energy balance: $\dfrac{d \left(N_2 \underline{U}_2 \right)}{dt} = \underline{U}_2 \dfrac{dN_2}{dt} + N_2 \dfrac{d \underline{U}_2}{dt} = \dot{N} \underline{H}_{\text{eng}} = \dfrac{dN_2}{dt} \underline{H}_{\text{eng}}$ But,

$$\left. \begin{array}{l} \underline{H} = C_\text{P} \left(T - T_0 \right) \\ \underline{U} = C_\text{V} \left(T - T_0 \right) - RT_0 = C_\text{V} T - C_\text{P} T_0 \end{array} \right\} \quad \text{where } T_0 = \text{ reference temperature}$$

$$\Rightarrow$$

$$\dfrac{dN_2}{dt} \left(\underline{H}_{\text{eng}} - \underline{U}_2 \right) = \dfrac{dN_2}{dt} \left\{ C_\text{P} T_{\text{eng}} - C_\text{P} T_0 - C_\text{V} T_2 + C_\text{P} T_0 \right\} = N_2 C_\text{V} \dfrac{dT_2}{dt}$$

or

$$\dot{N} \left\{ C_\text{P} T_{\text{eng}} - C_\text{V} T_2 \right\} = N_2 C_\text{V} \dfrac{dT_2}{dt} \tag{8}$$

and

$$\dot{N} = \dfrac{d}{dt} \left(N_2 \right) = \dfrac{d}{dt} \left(\dfrac{P_2 V_2}{R T_2} \right) = -\dfrac{P_2 V_2}{R T_2^2} \dfrac{dT_2}{dt} + \dfrac{V_2}{R T_2} \dfrac{dP_2}{dt}$$

$$\Rightarrow \dfrac{dT_2}{dt} = -\dfrac{R T_2^2 \dot{N}}{P_2 V_2} + \dfrac{T_2}{P_2} \dfrac{dP_2}{dt_2} \tag{9}$$

using eqns. (6) and (9) in eqn. (8)

$$\dot{N} \left\{ C_\text{P} T_1 \left(\dfrac{P_2}{P_1} \right)^{R/C_\text{P}} - C_\text{V} T_2 \right\} = -N_2 C_\text{V} \cdot \dfrac{R T_2^2}{P_2 V_2} \dot{N} + N_2 C_\text{V} \dfrac{T_2}{P_2} \dfrac{dP_2}{dt_2}$$

$$= -C_\text{V} T_2 \dot{N} + \dfrac{P_2 V_2}{R T_2} \cdot C_\text{V} \dfrac{T_2}{P_2} \dfrac{dP_2}{dt_2}$$

$$\dot{N} C_\text{P} T_1 \left(\dfrac{P_2}{P_1} \right)^{R/C_\text{P}} = \dfrac{C_\text{V} V_2}{R} \dfrac{dP_2}{dt}$$

and using eqn. (5)

$$-N\frac{C_V}{C_P}C_PT_1\left(\frac{P_2}{P_1}\right)^{R/C_P}\frac{d\ln P_1}{dt}=C_V\frac{V_2}{R}\frac{dP_2}{dt}$$

or, finally

$$-V_1\left(\frac{P_2}{P_1}\right)^{R/C_P}\frac{dP_1}{dt}=V_2\frac{dP_2}{dt}$$

$$V_2P_2^{-R/C_P}\frac{dP_2}{dt}=-V_1P_1^{-R/C_P}\frac{dP_1}{dt}$$

or

$$-V_2\int_{P_2^i}^{P_2^f}\frac{dP_2}{P_2^{R/C_P}}=V_1\int_{P_1^i}^{P_1^f}\frac{dP_1}{P_1^{R/C_P}}$$

$\Rightarrow$

$$2.5\left\{\left(P^f\right)^{C_V/C_P}-(0.35)^{C_V/C_P}\right\}=-\left\{\left(P^f\right)^{C_V/C_P}-(14.0)^{C_V/C_P}\right\}$$

$\Rightarrow P^f=3.053$ bar: using Eqn. (3), $T_1^f=629.8$ K .

Now using eqn. (1), $T_2^f=611.9$ K

Finally, to get the total work, we do an overall energy balance (system = two tanks; adiabatic, closed, constant volume).

$$N^f\underline{U}_1^f+N_2^f\underline{U}_2^f-N_1^i\underline{U}_1^i-N_2^i\underline{U}_2^i=W_s$$

$$W_s=\frac{C_V}{R}\left\{P^f\left(V_1+V_2\right)-P_1^iV_1-P_2^iV_2\right\}$$

$$=\frac{5}{2}\{3.053(0.3+0.75)-14\times0.3-0.35\times0.75\}$$

$$=-3.142\text{ bar m}^3=-3.142\times10^5\text{ J}=-314.2\text{ kJ}$$

3.35 (a) ~63% sat vapor

37% liquid produced

Work in stage 1 $473-290=183$ kJ/kg

Work in stage 2 $388-269=119$ kJ/kg

$\phantom{\text{Work in stage 2}}$ 302 kJ/kg

kJ/kg liquid N$_2$ $=\dfrac{302}{0.37}=816.2$ kJ/kg N$_2$ produced

$$\dot{M}_3=\dot{M}_{5'}+\dot M_6$$

$$\dot M_3\hat H_3=\dot M_5\hat H_5+\dot M_6\hat H_6$$

$$1.15=x\cdot278+(1-x)29$$

$$x(278-29)+29$$

$$x=\frac{153-29}{278-29}=\frac{124}{228}=0.498=\text{fraction vapor}$$

$\Rightarrow 0.502$ fraction of liquid

Enthalpy of stream before compressor

Stage 1 $425 - 272$

Stage 2 $\dfrac{272}{0.4693} = 579.6 \ \text{kJ/kg N}_2$

(as before)

$0.498\hat{H}(0.1 \ \text{MPa},125 \ \text{K}) + 0.502\hat{H}(0.1 \ \text{MPa},135 \ \text{K})$

$= 0.498 \times 278 + 0.502 \times 290 = 284.02 \ \text{kJ/kg}$

Stage 1 $463 - 284 = 179$

Stage 2 119

as before $179 + 119 = 298 \ \text{kJ/kg}$

$\dfrac{298}{0.502} = 593.6 \ \text{kJ/kg LN}_2$

3.36   Note: be careful about coordinate system. A mass flow in the negative × direct is negative!
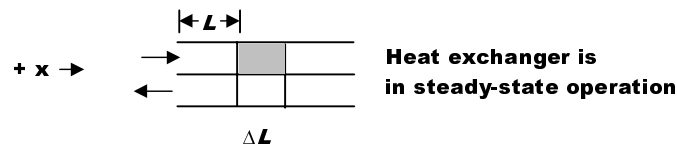
Case I: Concurrent flow
Mass balance on shaded volume

mass in		mass in		mass in		mass out
element at	$-$	element	$=$	at face	$-$	at face at
time $t + \Delta t$		at time t		at L in Δt		$L + \Delta L$ in Δt

$$\begin{array}{l} 0 \\ (\text{steady - state}) \end{array} = \left(\dot{M}_L - \dot{M}_{L+\Delta L}\right)\Delta t$$

$$\dot{M}_L + \dot{M}_{L+\Delta L} = \dot{M}$$

Energy balance on the shaded volume

energy in		energy in		energy flow in		energy flow out
element	$-$	element	$=$	by mass flow	$+$	by mass flow at
at $t + \Delta t$		at t		at L in Δt		$L + \Delta L$ in Δt

$\qquad$ energy flow in

$+$ $\quad$ by heat flow

$\qquad$ in time Δt

$$(\text{steady-state})$$

$$0 = \dot{M}_L \underline{H}_L \Delta t - \dot{M}_{L+\Delta L}\underline{H}_{L+\Delta L}\Delta t + \dot{Q}\Delta L \Delta t$$

$$\dot{M}(\underline{H}_{L+\Delta L} - \underline{H}_L) = \dot{M}C_{\mathrm{P}}(T_{L+\Delta L} - T_L) = \dot{Q}\Delta L$$

dividing by ΔL, taking limit as $\Delta L \to 0$, and using subscript 1 to denote fluid 1

$$\dot{M}_1 C_{\mathrm{P},1}\frac{dT_1}{dC} = \dot{Q} = \kappa(T_2 - T_1)$$

$\dot{Q}$ = heat flow rate per unit length of exchanger.
Similarly, for fluid 2 (other part of exchanger)

$$\dot{M}_2 C_{P,2} \frac{dT_2}{dL} = -\dot{Q} = -\kappa(T_2 - T_1)$$

($\dot{M}_1$ and $\dot{M}_2$ are both + for concurrent flow)
Adding the 2 equations

$$\dot{M}_1 C_{P,1} \frac{dT_1}{dL} = \dot{M}_2 C_{P,2} \frac{dT_2}{dL} = 0$$

From problem statement, $\dot{M}_1 = \dot{M}_2$ and $C_{P,1} = C_{P,2}$

$$\Rightarrow \frac{dT_1}{dL} + \frac{dT_2}{dL} = \frac{d}{dL}(T_1 + T_2) = 0 \text{ or } T_1 + T_2 = \text{constant} = C$$

and $T_1 = C - T_2$; $T_2 = C - T_1$
now going back to

$$\frac{dT_1}{dL} = \frac{\kappa}{\dot{M}C_P}(T_2 - T_1) = \frac{\kappa(C - 2T_1)}{\dot{M}C_P}$$

and integrating

$$\ln\left(\frac{C - 2T_1^f}{C - 2T_1^i}\right) = -\frac{2\kappa L}{\dot{M}C_P} = -\frac{L^*}{L_0} ; \ L_0 = \frac{\dot{M}C_P}{2\kappa}$$

$T_1^f = 15°C$, $T_1^i = 35°C$, $T_2^f = 5°C$, $T_2^i = -15°C$.
Also, $C = T_1^i + T_2^i = T_1^f + T_2^f = 20°C$
[i = initial conditions, conditions at $L = 0$; f = final conditions, conditions at L^* where L^* = length of exchanger]
Using this in equation above gives

$$\frac{L^*}{L_0} = \ln\left(\frac{20 - 70}{20 - 30}\right) = \ln 5 = 1.609$$

And, more generally, at any point in the exchanger

$$\frac{C - 2T_1(L)}{C - 2T_1^i} = \exp\left(-\frac{L}{L_0}\right) \Rightarrow T_1(L) = \frac{C}{2}\left(1 - \exp\left(-\frac{L}{L_0}\right)\right) + T_1^i \exp\left(-\frac{L}{L_0}\right)$$

$$T_1(L) = 10 + 25\exp\left(-\frac{L}{L_0}\right)°C$$

$$T_2(L) = C - T_1(L) = 10 - 25\exp\left(-\frac{L}{L_0}\right)°C$$

Now writing an entropy balance

$$0 = \dot{M}_L \hat{S}_L \Delta t - \dot{M}_{L+\Delta L} \hat{S}_{L+\Delta L} \Delta t = \frac{\dot{Q}}{T} \Delta L \Delta t$$

$$\Rightarrow \dot{M} \frac{d\hat{S}}{dL} = \frac{\dot{Q}}{T_1} = \frac{\kappa(T_2 - T_1)}{T_1} = \frac{-\kappa 50 \exp(-L/L_0)}{10 + 25 \exp(-L/L_0) + \underset{\substack{need\ absolute \\ T\ here}}{273.15}}$$

$$d\hat{S} = \frac{-50\kappa L_0}{\dot{M}} \frac{\exp(-L/L_0)}{283.15 + 25 \exp(-L/L_0)} d\left(\frac{L}{L_0}\right)$$

$$= -C_p \frac{25 \exp(-L/L_0)}{283.15 + 25 \exp(-L/L_0)} d\left(\frac{L}{L_0}\right)$$

$$\Rightarrow \hat{S}(L) = \hat{S}(L = 0) + C_p \ln\left\{ \frac{283.15 + 25 \exp(-L/L_0)}{308.15} \right\}$$

Case II Countercurrent flow

$$\dot{M}_2 = -\dot{M}_1$$

$$\dot{M}_1 C_P \frac{dT_1}{dL} = \kappa(T_2 - T_1) \qquad\qquad (1)$$

$$\dot{M}_2 C_P \frac{dT_2}{dL} = -\kappa(T_2 - T_1) \qquad\qquad (2)$$

$$\dot{M}_1 C_P \frac{dT_2}{dL} = \kappa(T_2 - T_1) \qquad\qquad (3)$$
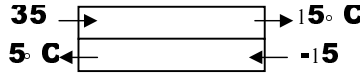
Eqn. (3) comes from eqn. (2) using $\dot{M}_2 = -\dot{M}_1$. Subtracting eqn. (1) from eqn. (3) gives

$$\frac{d}{dL}(T_1 - T_2) = 0 \Rightarrow T_1 - T_2 = \text{constant} = C = 30°\,C$$

$$T_2 = T_1 - 30°\,C$$

Thus

$$\dot{M}_1 C_P \frac{dT_1}{dL} = \kappa(T_2 - T_1) = -30\kappa$$

$$T_1 = -\frac{30\kappa L}{\dot{M} C_P} + T_1^i$$

$$T_2 = 5 - 15\frac{L}{L_0} = 35 - \frac{30\kappa L}{\dot{M} C_P} = 35 - 15\frac{L}{L_0}$$

where $L_0 = \dfrac{\dot{M} C_P}{2\kappa}$ and the entropy balance

$$\dot{M} \frac{d\hat{S}_1}{dL} = \frac{\dot{Q}}{T_1} = \frac{-\kappa 30}{T_1}$$

$$\frac{d\hat{S}_1}{dL} = \frac{-\kappa 30}{\dot{M}(35 - 30\kappa L/\dot{M} C_P + \underset{\substack{absolute \\ temperature \\ needed\ here}}{273.15})}$$

$$d\hat{S}_1 = \frac{-30\kappa L_0}{\dot{M}(308.15 - 30\kappa L/\dot{M}C_{\mathrm{P}})}d\left(\frac{L}{L_0}\right) = \frac{-15C_{\mathrm{P}}}{308.15 - 15\,L/L_0}d\left(\frac{L}{L_0}\right)$$

$$= -\frac{C_{\mathrm{P}}}{20.54 - x}dx$$

$$\Rightarrow \hat{S}(L) = \hat{S}(0) + C_{\mathrm{P}}\,\ln\left(1 - 0.048\,\frac{L}{L_0}\right)$$

Summary
Concurrent flow

$$T_1 = 10 + 25\exp\left(-\frac{L}{L_0}\right)$$

$$T_2 = 10 - 25\exp\left(-\frac{L}{L_0}\right)$$

$$\hat{S}(L) = \hat{S}(L=0) + C_{\mathrm{P}}\,\ln\left\{\frac{283.15 + 25\exp(-L/L_0)}{308.15}\right\}$$

Countercurrent flow

$$T_1 = 35 - 15\frac{L}{L_0}$$

$$T_2 = 5 - 15\frac{L}{L_0}$$

$$\hat{S}(L) = \hat{S}(0) + C_{\mathrm{P}}\,\ln\left(1 - 0.048\,\frac{L}{L_0}\right)$$

3.37 (a)
$$\frac{dU}{dt} = \dot{W}_S + \dot{Q} - P\frac{dV}{dt} = \dot{W}_S + \dot{Q} - P_0\frac{dV}{dt} - (P - P_0)\frac{dV}{dt}$$

and

$$\frac{dS}{dt} = \frac{\dot{Q}}{T_0} + \dot{S}_{gen}$$

Now let

$$\dot{W} = \dot{W}_S - P_0\frac{dV}{dt} - (P - P_0)\frac{dV}{dt}$$

and

$$\dot{W}_u = \dot{W} + P_0\frac{dV}{dt} = \dot{W}_S - (P - P_0)\frac{dV}{dt} \Rightarrow \frac{dU}{dt} = \dot{W}_u + \dot{Q} - P_0\frac{dV}{dt}$$

or

$$U_2 - U_1 = W_u + Q - P_0(V_2 - V_1)$$

$$S_2 - S_1 = \frac{Q}{T_0} + S_{gen} \Rightarrow Q = T_0 S_2 - T_0 S_1 - T_0 S_{gen}$$

and

$$U_2 - U_1 = W_u + T_0 S_2 - T_0 S_1 - T_0 S_{gen} - P_0(V_2 - V_1)$$
$$W_u = (U_2 + P_0 V_2 - T_0 S_2) - (U_1 + P_0 V_1 - T_0 S_1) + T_0 S_{gen}$$
$$\text{since } T_0 S_{gen} \geq 0$$
$$W_u^{max} = A_2 - A_1, \text{ where } A = U + P_0 V - T_0 S$$

(b)
$$0 = \dot{M}\underline{H}_1 - \dot{M}\underline{H}_2 + \dot{Q} + \dot{W}_S$$

$$0 = \dot{M}\underline{S}_1 - \dot{M}\underline{S}_2 + \frac{\dot{Q}}{T_0} + S_{gen}$$

Here $\dot{W}_S = \dot{W}_u$

$$\Rightarrow \dot{W}_u = \dot{M}\underline{H}_2 - \dot{M}\underline{H}_1 - \dot{Q} = \dot{M}\underline{H}_2 - \dot{M}\underline{H}_1 + \dot{M}T_0\underline{S}_1 - \dot{M}T_0\underline{S}_2 + T_0 S_{gen}$$
$$\Rightarrow \dot{W}_u = \dot{M}(\underline{H}_2 - T_0\underline{S}_2) - \dot{M}(\underline{H}_1 - T_0\underline{S}_1) + T_0 S_{gen}$$
Since $T_0 S_{gen} \geq 0$
$$\dot{W}_u^{max} = \dot{M}(\underline{B}_2 - \underline{B}_1) \text{ where } \underline{B} = \underline{H} - T_0\underline{S}$$

(c) Using the Steam Tables we find
    i)   at 30 bar $= 3$ MPa and 600°C
       $\hat{U} = 3285.0$ kJ/kg, $\hat{S} = 7.5085$ kJ/kg K, $\hat{V} = 0.13243$ m³/kg

$$\hat{A}_1 = \hat{U} + P_0\hat{V} - T_0\hat{S}$$

$$= 3285.0 + 1.013 \text{ bar} + 0.13243 \text{ m}^3/\text{kg} \times 10^2 \text{ kJ}/\text{bar}\cdot\text{m}^3 - 298.15 \times 7.5085$$

$$= 1059.76 \text{ kJ}/\text{kg}$$

ii) at 5 bar $= 0.5$ MPa and $300\,°C$

$\hat{U} = 2802.9 \text{ kJ}/\text{kg}$, $\hat{S} = 7.4599 \text{ kJ}/\text{kg K}$, $\hat{V} = 0.5226 \text{ m}^3/\text{kg}$

$$\hat{A}_2 = 2802.9 + 1.013 \times 0.5226 \times 10^2 - 298.15 \times 7.4599 = 631.67 \text{ kJ}/\text{kg}$$

$$\hat{W}_u = \hat{A}_2 - \hat{A}_1 = (631.67 - 1059.76) \text{ kJ}/\text{kg} = -428.09 \text{ kJ}/\text{kg}$$

This is the maximum useful work that can be obtained in the transformation with the environment at $25\,°C$ and 1.013 bar. It is now a problem of clever engineering design to develop a device which will extract this work from the steam in a nonflow process.

(d) Since the inlet and exit streams are at $25\,°C$ and $P = 1.013$ bar, any component which passes through the power plant unchanged (i.e., the organic matter, nitrogen and excess oxygen in the air, etc.) does not contribute to the change in availability, or produce any useful work. Therefore, for each kilogram of coal the net change is:

$$0.7 \text{ kg of carbon} = 58.33 \text{ mol of C}$$
$$+58.33 \text{ mol of O}_2$$
$$\text{to produce } 58.33 \text{ mol CO}_2$$

also

$0.15 \text{ kg of water} = 8.33 \text{ mol of H}_2\text{O}$ undergoes a phase change
from liquid to vapor

Therefore

$$\dot{M}\hat{B}_{\text{in}} = \sum_i \left(\dot{N}_i \underline{B}_i\right)_{\text{in}} = \underset{\text{(carbon)}}{58.33 \times 0} + \underset{\text{(oxygen)}}{58.33 \times 0} + 8.33 \times \underset{\text{(liquid water)}}{(-68.317 + 298.15 \times 0.039)}$$

$$= -1976 \text{ kJ}/\text{kg coal}$$

$$\dot{M}\hat{B}_{\text{out}} = \sum_i \left(\dot{N}_i \underline{B}_i\right)_{\text{out}} = 58.33 \times \underset{\text{(carbon dioxide)}}{(-94.052)} + 8.33 \times \underset{\text{(water vapor)}}{(-57.8 + 298.15 \times 0.0106)}$$

$$= -24858 \text{ kJ}/\text{kg coal}$$

$$W_u^{\text{max}} = -24858 - (1976) \text{ kJ}/\text{kg coal} = 22882 \text{ kJ}/\text{kg coal}$$

$$W_u^{\text{actual}} = -2.2 \text{ kW-hr}/\text{kg coal} = 7920 \text{ kJ}/\text{kg coal}$$

$$\text{Efficiency in \%} = \frac{7920 \times 100}{22882} = 34.6\%$$

Thus a coal-fired electrical power generation plants converts slightly more than 1/3 of the useful work obtainable from the coal it consumes. This suggests that it would be useful to look for another method of generating electrical power from coal . . . for example, using an electro-chemical fuel cell. Considering the amount of coal consumed each year in power generation, and the consequences (strip mining, acid rain, greenhouse effect, etc.) the potential economic savings and environmental impact of using only 1/3 as much coal is enormous.

3.38 Assumptions:
1) Turbine and pump operate reversibly and adiabatically
2) No pressure drop across condenser and boiler
3) Only heat transfer occurs at condenser and boiler
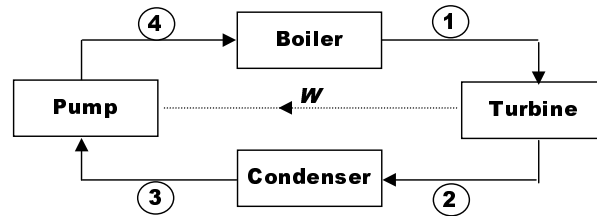
Location	Path	State	$T(°C)$	P (bar)	$\hat{H}$ kJ/kg	$\hat{S}$ kJ/kgK	$\hat{V}$ m^3 / kg
1		superheated vapor	700	20	3917.4	7.9487	
	$\Delta S = 0$						
2		superheated vapor	67	0.2	2623.2	7.9487	
	$P =$ constant						
3		sat'd liq	60.1	0.2	251.4	0.8320	0.00102
	$\Delta S = 0$						
4		comp liq	60.1	20	253.4	0.8320	
	$P =$ constant						
1			700	20	3917.4	7.9487	

[At each state the properties in boxes were known and used with the steam stables to find the remaining properties.] Now ready to answer questions.

(a) Net work output per kilogram

$$= -\left[\left(\hat{H}_1 - \hat{H}_2\right) + \left(\hat{H}_3 - \hat{H}_4\right)\right]$$
$$= -\left[(3917.4 - 2623.2) + (251.4 - 253.4)\right] = -1292.2 \text{ kJ/kg}$$

(b) Heat discarded by condenser

$$= \hat{H}_3 - \hat{H}_2 = 251.4 - 2623.2 = -2371.8 \text{ kJ/kg}$$

(c) Fraction of work used by pump (%)

$$= \frac{(251.4 - 253.4) \times 100}{-(3917.4 - 2623.2)} = 0.154\%$$

(d) Heat absorbed in boiler $= (3917.4 - 253.4) = 3664.0 \text{ kJ/kg}$

(e) Thermal efficiency (%)

$$= \frac{-\text{Net work out}}{\text{Heat in}} \times 100 = \frac{1292.2 \times 100}{3664.0} = 35.27\%$$

Carnot efficiency (1100°C and 15°C)

$$= \frac{T_1 - T_2}{T_1} = \frac{(1100 + 273.15) - (15 + 273.15)}{(1100 + 273.15)} \times 100 = 79.02\%$$

For comparison, Carnot efficiency (700°C and 60.1°C) which are the temperature levels of working fluid (steam) in the closed-loop power cycle

$$= \frac{(700 + 273.15) - (60.1 + 273.15)}{700 + 273.15} \times 100 = 65.76\%$$

which is almost twice as high as the actual efficiency.

3.39 Three subsystems: unknowns T_1^f, P_1^f, T_2^f, P_2^f, T_3^f, P_3^f (6 unknowns)

After process $P_1^f = P_2^f = P_3^f$ (2 equations)

Subsystem 1 has undergone a reversible adiabatic expansion

$$\Rightarrow \underline{S}_1^f = \underline{S}_1^i, \text{ or } T_1^f = T_1^i \left(\frac{P_1^f}{P_1^i} \right)^{R/C_P} \quad \text{(1 equation)} \qquad (\#1)$$

Subsystem 3 has undergone a reversible adiabatic compression

$$\Rightarrow \underline{S}_3^f = \underline{S}_3^i, \text{ or } T_3^f = T_3^i \left(\frac{P_3^f}{P_3^i} \right)^{R/C_P} = T_3^i \left(\frac{P^f}{P_3^i} \right)^{R/C_P} \quad \text{(1 equation)} \qquad (\#2)$$

Mass balance subsystems $1 + 2$

$$N_1^f + N_2^f = N_1^i + N_2^i \Rightarrow \frac{P_1^f V_1}{T_1^f} + \frac{P_2^f V_2}{T_2^f} = \frac{P_1^i V_1}{T_1^i} + \frac{P_2^i V_2^i}{T_2^i}$$

or

$$P^f \left(\frac{0.5}{T_1^f} + \frac{V_2^f}{T_2^f} \right) = \frac{10 \times 0.5}{293.15} + \frac{1 \times 0.25}{293.15} = 0.017909 \quad \text{(1 equation)} \qquad (\#3)$$

Energy balance on subsystems $1 + 2 + 3$

$$N_1^f \underline{U}_1^f + N_2^f \underline{U}_2^f + N_3^f \underline{U}_3^f = N_1^i \underline{U}_1^i + N_2^i \underline{U}_2^i + N_3^i \underline{U}_3^i$$

$$\frac{P_1^f V_1}{R T_1^f} C_V T_1^f + \frac{P_2^f V_2}{R T_2^f} C_V T_2^f + \frac{P_3^f V_3}{R T_3^f} C_V T_3^f = \frac{P_1^i V_1}{R T_1^i} C_V T_1^i + \frac{P_2^i V_2}{R T_2^i} C_V T_2^i + \frac{P_3^i V_3}{R T_3^i} C_V T_3^i$$

$$P^f \left(V_1 + V_2^f + V_3^f \right) = P_1^i V_1 + P_2^i V_2 + P_3^i V_3$$

but $V_1 + V_2^f + V_3^f = V_1 + V_2^i + V_3^i = (0.5 + 0.25 + 0.25) = 1 \text{ m}^3$

$$P^f = \frac{10 \times 0.5 + 1 \times 0.25 + 1 \times 0.25}{1} = 5.5 \text{ bar}$$

using this result   in eqn. (1) $\rightarrow T_1^f = 252.45 \text{ K}$

                       in eqn. (2) $\rightarrow T_3^f = 448.93 \text{ K}$

$$V_3^f = V_3^i \frac{P_3^i}{P_3^f} \cdot \frac{T_3^f}{T_3^i} = 0.25 \times \frac{1}{5.5} \times \frac{448.93}{293.15} = 0.06961 \text{ m}^3$$

$$V_2^f = 0.25 \times 2 - 0.06961 = 0.4304 \text{ m}^3$$

Now using Eqn. (#3)

$$P_f \left(\frac{0.5}{T_1^f} + \frac{V_2^f}{T_2^f} \right) = 5.5 \left(\frac{0.5}{252.45} + \frac{0.4304}{T_2^f} \right) = 0.017909 \Rightarrow T_2^f = 337.41 \text{ K}$$

Thus the state of the system is as follows

	Initial	Final
T_1	293.15 K	252.45 K
P_1	10 bar	5.5 bar
T_2	293.15 K	337.41 K
P_2	1 bar	5.5 bar
V_2	0.25 m³	0.4304 m³
T_3	293.15 K	448.93 K
P_3	1	5.5 bar
V_3	0.25 m³	0.0696 m³

Work done on subsystem 3

    Energy balance

$$N_3^f \underline{U}_3^f - N_3^i \underline{U}_3^i = W = -\int P dV$$

$$\frac{P_3^f V_3^f}{RT_3^f} C_V T_3^f - \frac{P_3^i V_3^i}{RT_3^i} C_V T_3^i = P_3^f V_3^f \frac{C_V}{R} - P_3^i V_3^i \frac{C_V}{R} = W$$

$$W = \frac{C_P - R}{R} \left(P_3^f V_3^f - P_3^i V_3^i \right) = 3(5.5 \times 0.0696 - 1 \times 0.25)$$

$$= 0.3984 \text{ bar} \cdot \text{m}^3 = 39.84 \text{ kJ}$$

3.40 For the mass and energy balances, consider the composite system of can + tire as the system. Also gas is ideal for this system $Q = 0$ and $W = 0$

mass balance: $N_1^f + N_2^f = N_1^i + N_2^i \Rightarrow \dfrac{P_1^f V_1}{T_1^f} + \dfrac{P_2^f V_2}{T_2^f} = \dfrac{P_1^i V_1}{T_1^i} + \dfrac{P_2^i V_2}{T_2^i}$ (1)

energy balance

$$N_1^f \underline{U}_1^f + N_2^f \underline{U}_2^f = N_1^i \underline{U}_1^i + N_2 \underline{U}_2^i \Rightarrow P_1^f V_1 + P_2^f V_2 = P_1^i V_1 + P_2^i V_2 \qquad (2)$$

(see derivation of eqn. (c) of Illustration 2.5-5)
Also $P_1^f = P_2^f = 2.6 \text{ bar}(\leftarrow 3)$; using eqn. (3) in eqn. (2) yields

$$P_1^i = \frac{P_1^f V_1 + P_2^f V_2 - P_2^i V_2}{V_1} = \frac{2.6 \times \left(4.06 \times 10^{-2}\right) - 1 \times 4 \times 10^{-2}}{6 \times 10^{-4}} = 109.27 \text{ bar}$$

To use eqn. (1) to get final temperatures, need another independent equation relating T_1^f and T_2^f. Could do an energy balance around tank 1, as in derivation of eqn. (f) of Illustration 2.5-5. A more direct way is to do an entropy balance around a small fluid element, as in Illustration 3.5-2 and immediately obtain Eqn. (e) of that illustration

$$\left(\frac{T_1^f}{T_1^i}\right)^{C_P/R} = \left(\frac{P_1^f}{P_1^i}\right)$$

Thus

$$T_1^f = T_1^i\left(\frac{P_1^f}{P_1^i}\right)^{R/C_P} = 295\left(\frac{2.6}{109.27}\right)^{8.314/30} = 104.69 \text{ K} \quad (\text{very cold!})$$

Using this result in eqn. (1) gives $T_2^f = 303.26$ K.

3.41 (a) System: Gas in the tank — system boundary is just before exit to the tank. System is open, adiabatic, and of constant volume.

M.B.: $\dfrac{dN}{dt} = \dot{N}$

S.B.: $\dfrac{d(N\underline{S})}{dt} = \dot{N}\underline{S}$

$\Rightarrow \underline{S}\dfrac{dN}{dt} + N\dfrac{d\underline{S}}{dt} = \dot{N}\underline{S} = \dfrac{dN}{dt}\underline{S} \Rightarrow N\dfrac{d\underline{S}}{dt} = 0$ or $\underline{S}$ = constant (since $N \neq 0$)

Note: Gas just leaving system has the same thermodynamic properties as gas in the system by the "well-mixed" assumption.

For the ideal gas this implies

$$T_2 = T_1\left(\frac{P_2}{P_1}\right)^{R/C_P}$$

(b) $T_2 = (22 + 273.15)\left(\dfrac{1 \text{ bar}}{17.5 \text{ bar}}\right)^{8.314/30} = 133.52$ K

(c) System: Gas in the tank + engine (open, constant-volume, adiabatic)

M.B.: $N_f - N_i = \Delta N$

ΔN = amount of mass (moles) that left the system

E.B.: $N_f\underline{U}_f - N_i\underline{U}_i = \Delta N\underline{H}_{out} + W_S$

Note: $\underline{H}_{out}$ = constant, since gas leaving engine is of constant properties.

Thus

$$+W_S = N_f\underline{U}_f - N_i\underline{U}_i - \Delta N\underline{H}_{out}$$
$$= N_f\underline{U}_f - N_i\underline{U}_i - N_f\underline{H}_{out} + N_i\underline{H}_{out}$$
$$= N_fC_V - N_iC_VT_i - N_fC_PT_{out} + N_iC_PT_{out}; \quad \text{but } T_{out} = T_i$$
$$= N_f\left[C_VT_f - C_PT_i\right] + N_iRT_i$$

$$\downarrow \text{ reference temperature}$$

$$\left. \begin{array}{l} \underline{H} = C_P(T - T_0) \\ \underline{U} = C_V(T - T_0) - RT_0 \end{array} \right\} \text{ see Eqn. (2.4 - 8)}$$

Now $PV = NRT \Rightarrow N = \dfrac{PV}{RT}$

$$N_i = \frac{17.5\text{ bar} \times 0.5\text{ m}^3}{295.15\text{ K} \times 8.314 \times 10^{-2}\text{ bar} \cdot \text{m}^3/\text{kmol K}} = 0.3566\text{ kmol}$$

$$N_f = \frac{1\text{ bar} \times 0.5\text{ m}^3}{133.52\text{ K} \times 8.314 \times 10^{-2}} = 0.04504\text{ kmol}$$

$$W_s = 0.04504[(30 - 8.314) \times 133.52 - 30 \times 295.15] + 0.3566 \times 8.314 \times 295.15$$
$$= 606.6\text{ kJ}$$

Since $W_S > 0$, work must be put into the engine if the outlet temperature is to be maintained at $22\,^\circ\text{C}$. (Alternatively, heat could be added and work extracted.)

We should check to see if the process considered above is indeed possible. Can do this by using the entropy balance and ascertaining whether $S_{\text{gen}} \geq 0$.

Entropy balance

$$N_f \underline{S}_f - N_i \underline{S}_i = (N_f - N_i)\underline{S}_{\text{out}} + S_{\text{gen}}$$

$$\Rightarrow N_f C_P \ln\frac{T_f}{T_{\text{out}}} - N_f R \ln\frac{P_f}{P_{\text{out}}} - N_i C_P \ln\frac{T_i}{T_{\text{out}}} + N_i R \ln\frac{P_i}{P_{\text{out}}} = S_{\text{gen}}$$

But $T_{\text{out}} = T_i = 295.15\,\text{K}$, and $P_{\text{out}} = P_f = 1\text{ bar}$ so

$$N_f C_P \ln\frac{T_f}{T_i} + N_i R \ln\frac{P_i}{P_f} = S_{\text{gen}}$$

or

$$S_{\text{gen}} = 0.04505 \times 30 \ln\frac{133.52}{295.15} + 0.3566 \times 8.314 \ln\frac{17.5}{1} = 7.414\ \text{kJ/K}$$

Thus, $S_{\text{gen}} > 0$, and the process is possible!

(d) Similar process, but now isothermal: system = gas in tank and engine.

M.B.: $N_f - N_i = \Delta N$

E.B.: $N_f \underline{U}_f - N_i \underline{U}_i = \Delta N \underline{H}_{\text{out}} + Q + W_s = (N_f - N_i)\underline{H}_{\text{out}} + Q + W_s$

S.B.: $N_f \underline{S}_f - N_i \underline{S}_i = \Delta N \underline{S}_{\text{out}} + \dfrac{Q}{T} + S_{\text{gen}} = (N_f - N_i)\underline{S}_{\text{out}} + \dfrac{Q}{T} + S_{\text{gen}}$

Set $S_{\text{gen}} = 0$, since we want maximum work (see Sec. 3.2). Thus

$$Q = T\left(N_f \underline{S}_f - N_i \underline{S}_i\right) - \left(N_f - N_i\right)T\underline{S}_{out}$$

$$= TN_f\left(\underline{S}_f - \underline{S}_{out}\right) - TN_i\left(\underline{S}_i - \underline{S}_{out}\right)$$

$$= -N_f TR\ln\frac{P_f}{P_{out}} + N_i RT\ln\frac{P_i}{P_{out}}$$

But $P_f = P_{out} = 1$ bar and

$$Q = 0.3566 \times 8.314 \times 295.15\ln\left(\frac{17.5}{1}\right) = 2504.6 \text{ kJ}$$

$$W_s = N_f\underline{U}_f - N_i\underline{U}_i - N_f\underline{H}_{out} + N_i\underline{H}_{out} - Q$$

$$= -N_f RT + N_i RT - Q = \left(N_i - N_f\right)RT - Q$$

but $N_f = \dfrac{PV}{RT} = \dfrac{1 \times 0.5}{295.15 \times 8.314 \times 10^{-2}} = 2.038 \times 10^{-2}$ kmol and

$W_s = (0.3566 - 0.0204) \times 8.314 \times 295.15 - 2504.6 = -1679.6$ kJ . In this case we obtain work!

3.42   a) For each stage of the compressor, assuming steady-state operation and reversible adiabatic operation we have from the mass, energy and entropy balances, respectively

$0 = \dot{M}_{in} + \dot{M}_{out}$ 　　　　　or　　$\dot{M}_{out} = -\dot{M}_{in} = -\dot{M}$

$0 = \dot{M}_{in}\hat{H}_{in} + \dot{M}_{out}\hat{H}_{out} + \dot{W}$　　or　　$\dot{W} = \dot{M}(\hat{H}_{out} - \hat{H}_{in})$

and

$0 = \dot{M}_{in}\hat{S}_{in} + \dot{M}_{out}\hat{S}_{out}$ 　　　or　　$\hat{S}_{out} = \hat{S}_{in}$

So through each compressor (but not intercooler) stage, one follows a line on constant entropy in Fig. 2.4-2 Therefore, for first compressor stage we have

$\hat{H}_{in}(T = 200 \text{ K}, P = 1 \text{ bar}) = 767$ kJ / kg and $\hat{S}_{in}(T = 200 \text{ K}, P = 1 \text{ bar}) = 6.5$ kJ / kg K

$\hat{H}_{out}(\hat{S} = 6.5$ kJ / kg K, $P = 5$ bar$) = 963$ kJ / kg and $T_{out} = 295$ K

Therefore the first stage work per kg. of methane flowing through the compressor is

$\dot{W}$ (first stage) $= 963 - 767$ kJ / kg $= 196$ kJ / kg

After cooling, the temperature of the methane stream is 200 K, so that for the second compressor stage we have

$\hat{H}_{in}(T = 200 \text{ K}, P = 5 \text{ bar}) = 760$ kJ / kg and $\hat{S}_{in}(T = 200 \text{ K}, P = 5 \text{ bar}) = 5.65$ kJ / kg K

$\hat{H}_{out}(\hat{S} = 5.65$ kJ / kg K, $P = 25$ bar$) = 960$ kJ / kg and $T_{out} = 300$ K

Therefore the second stage work per kg. of methane flowing through the compressor is

$\dot{W}$ (sec ond stage) $= 960 - 760$ kJ / kg $= 200$ kJ / kg

Similarly, after intercooling, the third stage compressor work is found from

$\hat{H}_{in}(T = 200 \text{ K}, P = 25 \text{ bar}) = 718$ kJ / kg and $\hat{S}_{in}(T = 200 \text{ K}, P = 25 \text{ bar}) = 4.65$ kJ / kg K

$\hat{H}_{out}(\hat{S} = 4.65$ kJ / kg K, $P = 100$ bar$) = 855$ kJ / kg and $T_{out} = 288$ K

Therefore the third stage work per kg. of methane flowing through the compressor is

$\dot{W}$ (third stage) $= 855 - 718$ kJ / kg $= 137$ kJ / kg

Consequently the total compressor work through all three stages is
$\dot{W} = 196 + 200 + 137 = 533$ kJ / kg

b) The liquefaction process is a Joule-Thomson expansion, and therefore occurs at constant enthalpy. The enthalpy of the methane leaving the cooler at 100 bar and 200 K is 423 kJ/kg. At 1 bar the enthalpy of the saturate vapor is 582 kJ/kg, and that of the liquid is 71 kJ/kg. Therefore from the energy balance on the throttling valve and flash drum we have

$\hat{H}_{in} = \hat{H}_{out}$ or

$\hat{H}(200 \text{ K, } 100 \text{ bar}) = (1-x)\hat{H}(\text{sat'd. vapor, 1 bar}) + x\hat{H}(\text{sat'd. liquid, 1 bar})$

$423 \dfrac{\text{kJ}}{\text{kg}} = (1-x)\cdot 71\dfrac{\text{kJ}}{\text{kg}} + x\cdot 582 \dfrac{\text{kJ}}{\text{kg}}$

where $x = 0.689$ is the fraction of vapor leaving the flash drum, and $(1-x) = 0.311$ is the fraction of the methane that has been liquefied. Therefore, for each kilogram of methane that enters the simple liquefaction unit, 689 grams of methane are lost as vapor, and only 311 grams of LNG are produced. Further, since 533 kJ of work are required in the compressor to produce 311 grams of LNG, approximately 1713 kJ of compressor work are required for each kg. of LNG produced.

c) As in the illustration, we choose the system for writing balance equations to be the subsystem consisting of the heat exchanger, throttle valve and flash drum (though other choices could be made). The mass and energy balances for this subsystem (since there are no heat losses to the outside or any work flows) are

$\dot{M}_3 = \dot{M}_{5'} + \dot{M}_6$ or taking $\dot{M}_3 = 1$ and letting x be the fraction of vapor

$1 = (1-x) + x$

$\dot{M}_3\hat{H}_3 = \dot{M}_5\hat{H}_{5'} + \dot{M}_6\hat{H}_6$

$1\cdot \hat{H}(T = 200 \text{ K, } P = 100 \text{ bar}) = x\cdot \hat{H}(T = 200 \text{ K, } P = 1 \text{ bar}) + (1-x)\cdot \hat{H}(\text{sat'd.liquid, } P = 1 \text{ bar})$

$423 \dfrac{\text{kJ}}{\text{kg}} = x\cdot 718 \dfrac{\text{kJ}}{\text{kg}} + (1-x)\cdot 71 \dfrac{\text{kJ}}{\text{kg}}$

The solution to this equation is $x = 0.544$ as the fraction of vapor which is recycled, and 0.456 as the fraction of liquid.
The mass and energy balances for the mixing of the streams immediately before the compressor are
$\dot{M}_{5'} + \dot{M}_1 = \dot{M}_{1'}$; then basing the calculation of 1 kg of flow into the compressor
$\dot{M}_{1'} = 1,\ \dot{M}_{5'} = 0.544$ and $\dot{M}_1 = 0.456$
However, since both the recycle vapor and the inlet vapor are at 200 K and 1 bar, the gas leaving the mixing tee must also be at these conditions, so that the inlet conditions to the first compressor are the same as in the simple liquefaction process, and $\hat{H}_{1'} = 718\dfrac{\text{kJ}}{\text{kg}}$. Also, all other compressor stages operate as in the simple liquefaction process.

Therefore, the total compressor work per kg of methane passed through the compressor is
$\dot{W} = 196 + 200 + 137 = 533$ kJ / kg of methane through the compressor. However, each kg. of methane through the compressor results in only 0.456 kg. of LNG (the remainder of the methane is recycled). Consequently the compressor work required per kg. of LNG produced is (533 kJ/kg)/0.456 kg = 1168 kJ/kg of LNG produced. This is to be compared to 1713 kJ/kg of LNG produced in the simple liquefaction process.
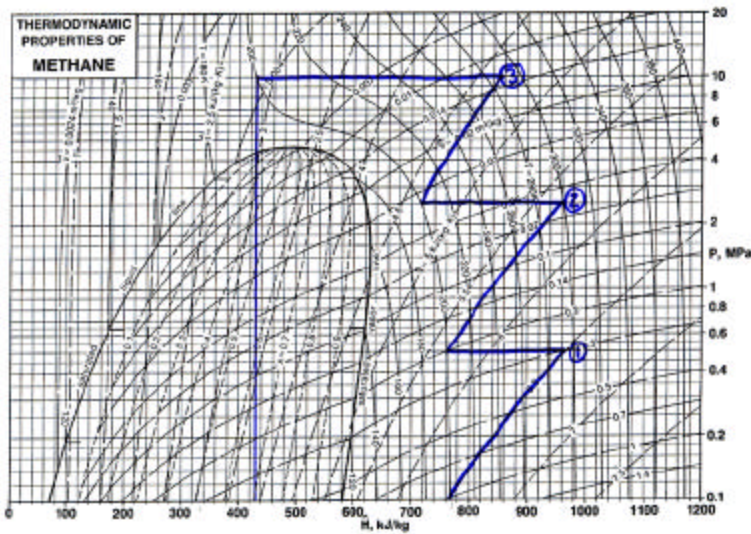
3.43 (also available as a Mathcad worksheet)

Problem 3.43 with MATHCAD

$bar := 101300 \cdot Pa$ $mol := 1$ $RE := 8.314 \cdot \dfrac{joule}{mol \cdot K}$ $RG := 0.00008314 \cdot \dfrac{bar \cdot m^3}{mol \cdot K}$

Heat capacity $Cp := 2.5 \cdot RE$

Initial Conditions (Vt=total volume, m^3): $Ti := 298 \cdot K$ $Pi := 400 \cdot bar$ $Vt := 0.045 \cdot m^3$

Find initial molar volume and number of moles
Start with initial guess for volume, m^3/mol
$$Vi := \frac{RG \cdot Ti}{Pi} \qquad Vi = 6.194 \cdot 10^{-5} \; \cdot m^3$$

Initial molar volume and number of moles
$$Vi = 6.194 \cdot 10^{-5} \; \cdot m^3 \qquad N := \frac{Vt}{Vi} \qquad N = 726.518 \cdot mol$$

Final pressure is 1.013 bar, and final temperature is unknown; will be found by equating the initial and final entropies. Guess final temperature is 200 K

$Pf := 1.013 \cdot bar$ $T := 50 \cdot K$ $Vf := \dfrac{RG \cdot T}{Pf}$

Solve for final temperature using S(final) - S(initial) = 0   Given $0 = \left(Cp \cdot \ln\left(\dfrac{T}{Ti}\right) - RG \cdot \ln\left(\dfrac{Pf}{Pi}\right) \right)$ $Tf := FIND(T)$

Final temperature $Tf = 26.432 \; \cdot K$

$$W := \frac{3}{2} \cdot RE \cdot (Tf - Ti) \cdot N \qquad W = -2.461 \cdot 10^6 \; \cdot joule$$

$$TNTeq := -\left(\frac{W}{4600000 \cdot \dfrac{joule}{kg}} \right) \qquad TNTeq = 0.535 \cdot kg$$

3.44 (also available as a Mathcad worksheet)

3.44 N2 $R := 8.314$ $RR := 8.314 \cdot 10^{-5}$

Note that in the 1st and 2nd printings, carbon dioxide was used as the fluid. This gave unreasonable answers when this problem was revisited with the Peng-Robinson eqn. of state, as both the initial and final states were found to be in the liquid state. Therefore from the 3rd printing on, the fluid has been changed to nitrogen.

Heat capacity constants for nitrogen

$Cp_0 := 28.883$ $Cp_1 := -0.157 \cdot 10^{-2}$ $Cp_2 := 0.808 \cdot 10^{-5}$ $Cp_3 := -2.871 \cdot 10^{-9}$

$Ti := 298.15$ $Tf := 100$

Given

$$\int_{Ti}^{Tf} \frac{\left(Cp_0 + Cp_1 \cdot T + Cp_2 \cdot T^2 + Cp_3 \cdot T^3\right)}{T} dT = R \cdot \ln\left(\frac{1.013}{140}\right)$$

$Tf := find(Tf)$ $Tf = 72.054$

Number of moles = N = PV/RT $N := \dfrac{\left[140 \cdot 3.1416 \cdot (.01)^2 \cdot .06\right]}{RR \cdot 298.15}$ $N = 0.106$ moles

$$W := N \cdot \int_{Ti}^{Tf} \left(Cp_0 + Cp_1 \cdot T + Cp_2 \cdot T^2 + Cp_3 \cdot T^3\right) dT$$

$W = -695.114$ joules   4600 J = 1 gram TNT

Grams of TNT = $G := \dfrac{-W}{4600}$ $G = 0.151$ grams of TNT

3.44CO2 $R := 8.314$ $RR := 8.314 \cdot 10^{-5}$

Note that in the 1st and 2nd printings, carbon dioxide was used as the fluid. This gave unreasonable answers when this problem was revisited with the Peng-Robinson eqn. of state, as both the initial and final states were found to be in the liquid state. Therefore from the 3rd printing on, the fluid has been changed to nitrogen.

Heat capacity constants

$Cp0 := 22.243$ $Cp1 := 5.977 \cdot 10^{-2}$ $Cp2 := -3.499 \cdot 10^{-5}$ $Cp3 := 7.464 \cdot 10^{-9}$

$Ti := 298.15$ $Tf := 200$

Given

$$\int_{Ti}^{Tf} \frac{\left(Cp0 + Cp1 \cdot T + Cp2 \cdot T^2 + Cp3 \cdot T^3\right)}{T} dT = R \cdot \ln\left(\frac{1.013}{140}\right)$$

Tf := find(Tf)   Tf = 79.836

Number of moles = N = PV/RT $N := \dfrac{\left[140 \cdot 3.1416 \cdot (.01)^2 \cdot .06 \right]}{RR \cdot 298.15}$ N = 0.106   moles

To calculate work done (energy released), we need the internal energy change. Therefore
Cv = Cp - R

$$W := N \cdot \int_{Ti}^{Tf} \left(Cp0 - 8.314 + Cp1 \cdot T + Cp2 \cdot T^2 + Cp3 \cdot T^3 \right) dT$$

W = ⁻555.558   joules   4600 J = 1 gram TNT

Grams of TNT = $G := \dfrac{-W}{4600}$ G = 0.121   grams of TNT

3.45   25 bar = 2.5 MPa; 600°C
$\hat{H} = 3686.3$ kJ/kg ; $\hat{S} = 7.5960$ kJ/kg K

1 bar   100°C $\hat{S} = 7.3614$
          150          $\hat{S} = 7.6314$
$\Delta = 0.27$ 1311
$\Rightarrow T = 143.44° C$
$\hat{H} = 2776.4 - 13.1 = 2763.3$ kJ/kg
$W = -3686.3 + 2763.3 = -923$ kJ/kg
                    -16614 kJ/mol
          (ideal gas $= -16830$ kJ/mol)
Actual work 784.55
$$\frac{dU}{dt} = 0 = \dot{M}_1 \left(\hat{H}_1 - \hat{H}_2 \right) + \dot{Q} - P \frac{dV}{dt} + \dot{W}_s$$

$$\hat{H}_2 = \hat{H}_1 + \frac{\dot{W}_s}{\dot{M}_1} = 3686.3 - 784.55 = 2901.75$$

Final state $P = 1$ bar ; $\hat{H} = 2901.75$
$\left. \begin{array}{l} \hat{H}(1 \text{ bar, } 200°C) = 2875.3 \\ \hat{H}(1 \text{ bar, } 250°C) = 2974.9 \end{array} \right\} 99.6$ $\dfrac{\Delta T}{\Delta \hat{H}} = \dfrac{50}{99.6}$

$2901.75 - \hat{H}(1 \text{ bar, } 200°C) = 26.45$

$T = 200 + \dfrac{50}{99.6} 26.45 = 213.28$

$\hat{S}(1 \text{ bar, } 250) = 8.0333$

$\hat{S}(1 \text{ bar, } 200) = 7.8343$

$\hat{S}(1 \text{ bar, } 213.28) = 7.8872$

$$\frac{dS}{dt} = 0 = \dot{M}\left(\hat{S}_1 - \hat{S}_2\right) + \dot{S}_{gen};$$

$$\frac{\dot{S}_{gen}}{\dot{M}} = -\hat{S}_2 - \hat{S}_1 = 7.8872 - 7.5960 = 0.2912 \text{ kJ/kg K}$$

$$5.2416 \text{ kJ/kg K}$$

$$(\text{ideal gas} = 5.468)$$

PR: $T = 600°\text{C}$; $P = 25 \text{ bar}$

$\underline{H} = 2.16064 \times 10^4$

$\underline{S} = 14.74377$

Now $P = 1 \text{ bar}$, $\underline{S} = 14.74377$.   Guess $T = 213°\text{C}$.

T	$\underline{S}$	$\underline{H}$
213	19.67116	7271.95
150	14.74399	5034.86

$$\frac{\dot{W}}{\dot{M}} = 5034.86 - 21606.4 = -16571.54 \text{ J/mol}$$

Actual work $\Rightarrow \underline{H}_f = 7520.59$

T	$\underline{S}$	$\underline{H}$
213	19.67116	7271.95
230	20.90787	7883.64
220	20.18472	7523.41
219.9	20.17742	7519.80
219.92	20.17888	7520.53

$$S = 20.17888 - 14.74377 = 5.43511$$

3.46   From simple statics the change in atmospheric pressure dP accompanying a change in height dh is
$$dP = -\mathbf{r}gdh$$

where $\mathbf{r}$ is the local mass density and g is the gravitational constant. Assuming a packet of air undergoes an altitude change relatively rapidly (compared to heat transfer), the entropy change for this process is

$$d\underline{S} = \frac{C_P}{T}dT - \frac{R}{P}dP = 0 \text{ since both } \dot{Q} \text{ and } \dot{S}_{gen} \text{ equal zero.}$$

Combining the two equations above we have

$$\frac{C_P}{T}dT = \frac{R}{P}dP = -\frac{R}{P}\mathbf{r}gdh = -\frac{R}{P}\frac{N}{V}Mgdh = -\frac{M}{T}gdh$$

or $\dfrac{dT}{dh} = -\dfrac{Mg}{C_P}$

For dry air $\dfrac{dT}{dh} \cong -9.7\dfrac{\text{K}}{\text{km}}$. Note that $\dfrac{dT}{dh}$ is referred to as the adiabatic lapse rate.

Also, its value will be less than that above as the humidity increases.

In fact, if the humidity is 100%, so water will condense as the pressure decreases, the adiabatic lapse rate will be almost zero.

4

4.1   Using the Mollier diagram

$$\boldsymbol{m} = \left(\frac{\partial T}{\partial P}\right)_H = \left(\frac{\Delta T}{\Delta P}\right)_H = \frac{(510 - 490)^\circ\,\mathrm{C}}{\left(1.241 \times 10^7 - 7.929 \times 10^6\right)\mathrm{Pa}}$$

$$= 4.463 \times 10^{-6}\,^\circ\mathrm{C/Pa} = 4.463\,^\circ\mathrm{C/MPa}$$

$$\boldsymbol{k}_S = \left(\frac{\partial T}{\partial P}\right)_S \approx \left(\frac{\Delta T}{\Delta P}\right)_S = \frac{(510 - 490)^\circ\,\mathrm{C}}{\left(1.069 \times 10^7 - 9.515 \times 10^6\right)\mathrm{Pa}}$$

$$= 1.702 \times 10^{-5}\,^\circ\mathrm{C/Pa} = 17.02\,^\circ\mathrm{C/MPa}$$

$$\frac{(\partial H/\partial S)_T}{(\partial H/\partial S)_P} = \frac{\partial(H,T)}{\partial(S,T)} \times \frac{\partial(S,P)}{\partial(H,P)} = \frac{\partial(H,T)}{\partial(H,P)} \times \frac{\partial(S,P)}{\partial(S,T)}$$

$$= \frac{\partial(T,H)}{\partial(P,H)} \times \frac{\partial(P,S)}{\partial(T,S)} = \frac{\boldsymbol{m}}{\boldsymbol{k}_S} = 0.262 \;\; \text{(unitless)}$$

4.2   (a)   Start from eqn. 4.4-27

$$\underline{H}(T,P) - \underline{H}^{\mathrm{IG}}(T,P) = RT(Z-1) + \int_{\underline{V}=\infty}^{\underline{V}} \left[T\left(\frac{dP}{dT}\right)_{\underline{V}} - P \right] d\underline{V}$$

$$P = \frac{RT}{\underline{V}-b} - \frac{a(T)}{\underline{V}^2 + 2b\underline{V} - b^2} \; ; \; \left(\frac{\partial P}{\partial T}\right)_{\underline{V}} = \frac{R}{\underline{V}-b} - \frac{da/dt}{\underline{V}^2 + 2b\underline{V} - b^2} \;\; \text{so}$$

$$\underline{H}(T,P) - \underline{H}^{\mathrm{IG}}(T,P)$$

$$= RT(Z-1) + \int_{\underline{V}=\infty}^{\underline{V}} \left[T\left\{ \frac{R}{\underline{V}-b} - \frac{da/dt}{\underline{V}^2 + 2b\underline{V} - b^2} \right\} - \frac{RT}{\underline{V}-b} + \frac{a(T)}{\underline{V}^2 + 2b\underline{V} - b^2} \right] d\underline{V}$$

$$= RT(Z-1) + \left(a + T\frac{da}{dT} \right) \int_{\underline{V}=\infty}^{\underline{V}} \frac{d\underline{V}}{\underline{V}^2 + 2b\underline{V} - b^2}$$

From integral tables we have

$$\int \frac{dx}{a'x^2 + b'x + c'} = \frac{1}{\sqrt{b'^2 - 4a'c'}} \ln\left| \frac{2a'x + b' - \sqrt{b'^2 - 4a'c'}}{2a'x + b' + \sqrt{b'^2 - 4a'c'}} \right| \;\; \text{for } 4a'c' - b'^2 < 0$$

In our case $a' = 1$, $b' = 2b$, $c = -b^2$; so $4a'c' - b'^2 = 4 \cdot 1 \cdot \left(-b^2\right) - (2b)^2 = -8b^2$ and $\sqrt{(b')^2 - 4a'c'} = \sqrt{8b^2} = 2\sqrt{2}b$.

$$\underline{H}(T,P) - \underline{H}^{IG}(T,P)$$

$$= RT(Z-1) + \frac{(a - Tda/dT)}{2\sqrt{2}b}\left[\ln\frac{2\underline{V}+2b-2\sqrt{2}b}{2\underline{V}+2b+2\sqrt{2}b}\Big|_{\underline{V}} - \ln\frac{2\underline{V}+2b-2\sqrt{2}b}{2\underline{V}+2b+2\sqrt{2}b}\Big|_{\underline{V}=\infty}\right]$$

$$= RT(Z-1) + \frac{(a - Tda/dT)}{2\sqrt{2}b}\ln\frac{\underline{V}+\left(1-\sqrt{2}\right)b}{\underline{V}+\left(1+\sqrt{2}\right)b}$$

or finally

$$\underline{H}(T,P) - \underline{H}^{IG}(T,P) = RT(Z-1) + \frac{(Tda/dT - a)}{2\sqrt{2}b}\ln\left[\frac{Z+\left(1+\sqrt{2}\right)B}{Z+\left(1-\sqrt{2}\right)B}\right]$$

(b) This part is similar except that we start from eqn. (4.4-28)

$$\underline{S}(T,P) - \underline{S}^{IG}(T,P) = R\ln Z + \int_{\underline{V}=\infty}^{\underline{V}}\left[\left(\frac{dP}{dT}\right)_{\underline{V}} - \frac{R}{\underline{V}}\right]d\underline{v}$$

$$= R\ln Z + \int_{\underline{V}=\infty}^{\underline{V}}\left[\frac{R}{\underline{V}-b} - \frac{da/dT}{\underline{V}^2+2b\underline{V}-b^2} - \frac{R}{\underline{V}}\right]d\underline{V}$$

$$= R\ln Z + R\ln\frac{\underline{V}-b}{\underline{V}}\Big|_{\underline{V}=\infty}^{\underline{V}} + \frac{da/dT}{2\sqrt{2}b}\ln\frac{\underline{V}+\left(1+\sqrt{2}\right)b}{\underline{V}+\left(1-\sqrt{2}\right)b}\Big|_{\underline{V}=\infty}^{\underline{V}}$$

$$= R\ln(Z-B) + \frac{da/dT}{2\sqrt{2}b}\ln\left(\frac{Z+\left(1+\sqrt{2}\right)B}{Z+\left(1-\sqrt{2}\right)B}\right)$$

4.3 Start with eqn. (4.2-21): $d\underline{U} = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P\right]d\underline{V}$. Thus $\left(\frac{\partial \underline{U}}{\partial T}\right)_{\underline{V}} = C_V$;

$$\left(\frac{\partial \underline{U}}{\partial T}\right)_{P} = C_V + \left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P\right]\left(\frac{\partial \underline{V}}{\partial T}\right)_{P} \text{ and}$$

$$\left(\frac{\partial \underline{U}}{\partial T}\right)_{P} - \left(\frac{\partial \underline{U}}{\partial T}\right)_{\underline{V}} = \left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P\right]\left(\frac{\partial \underline{V}}{\partial T}\right)_{P}.$$

(a) Ideal gas $P\underline{V} = RT$

$$T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P = 0 \Rightarrow \left(\frac{\partial \underline{U}}{\partial T}\right)_{P} = \left(\frac{\partial \underline{U}}{\partial T}\right)_{\underline{V}}$$

(b) van der Waals gas

$$P = \frac{RT}{\underline{V}-b} - \frac{a}{\underline{V}^2}; \left(\frac{\partial P}{\partial T}\right)_{\underline{V}} = \frac{R}{\underline{V}-b}; \Rightarrow \left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P\right] = \frac{a}{\underline{V}^2}$$

Also: $dP = \frac{RdT}{\underline{V}-b} - \frac{RT}{(\underline{V}-b)^2}d\underline{V} + \frac{2a}{\underline{V}^3}d\underline{V}$

$$\Rightarrow \left(\frac{\partial \underline{V}}{\partial T}\right)_P = \frac{R/(\underline{V}-b)}{RT/(\underline{V}-b)^2 - 2a/\underline{V}^3} = \left[\frac{T}{(\underline{V}-b)} - \frac{2a(\underline{V}-b)}{R\underline{V}^3}\right]^{-1}$$

$$\Rightarrow \left(\frac{\partial \underline{u}}{\partial T}\right)_P - \left(\frac{\partial \underline{u}}{\partial T}\right)_{\underline{V}} = \frac{a}{\left[\underline{V}^2 T/(\underline{V}-b)\right] - \left[2a(\underline{V}-b)/R\underline{V}\right]}$$

$$= \frac{aR\underline{V}(\underline{V}-b)}{RT\underline{V}^3 - 2a(\underline{V}-b)^2}$$

(c) The Virial Equation of State

$$\frac{P\underline{V}}{RT} = 1 + \frac{B}{\underline{V}} + \frac{C}{\underline{V}^2} + \cdots = 1 + \sum_{i=1}^{\infty} \frac{B_i}{\underline{V}^i}$$

or $P = \dfrac{RT}{\underline{V}} + \sum_{i=1} \dfrac{B_i RT}{\underline{V}^{i+1}}$

$$\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} = \frac{R}{\underline{V}} + \sum_{i=1} \frac{B_i R}{\underline{V}^{i+1}} + \sum_{i=1} \frac{RT}{\underline{V}^{i+1}} \left(\frac{dB_i}{dT}\right) \leftarrow$$

Note: This is a total derivative, since B_i is a function of only temperature

$$\Rightarrow T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P = \sum_{i=1} \frac{RT}{\underline{V}^{i+1}} \frac{dB_i}{d\ln T}$$

Also need $(\partial \underline{V}/\partial T)_P$, but this is harder to evaluate alternatively. Since

$$\left(\frac{\partial \underline{V}}{\partial T}\right)_P \left(\frac{\partial P}{\partial \underline{V}}\right)_T \left(\frac{\partial T}{\partial P}\right)_{\underline{V}} = -1 \Rightarrow \left(\frac{\partial \underline{V}}{\partial T}\right)_P = -\frac{(\partial P/\partial T)_{\underline{V}}}{(\partial P/\partial \underline{V})_T}$$

$\left(\dfrac{\partial P}{\partial T}\right)_{\underline{V}}$ is given above.

$$\left(\frac{\partial P}{\partial \underline{V}}\right)_T = -\frac{RT}{\underline{V}^2} - \sum_{i=1} \frac{(i+1)B_i RT}{\underline{V}^{i+2}}$$

$$\Rightarrow \left(\frac{\partial \underline{V}}{\partial T}\right)_P = \frac{\underline{V}\left(RT/\underline{V} + \sum_{i=1}\left[B_i RT/\underline{V}^{i+1}\right] + \sum\left(RT/\underline{V}^{i+1}\right)(dB_i/d\ln T)\right)}{T\left(RT/\underline{V} + \sum_{i=1}\left[(i+1)B_i RT/\underline{V}^{i+1}\right]\right)}$$

Using $\dfrac{RT}{\underline{V}} = P - \sum_{i=1} \dfrac{B_i RT}{\underline{V}^{i+1}}$, we get

$$\left(\frac{\partial \underline{V}}{\partial T}\right)_P = \frac{\underline{V}\left[P + \sum\left(RT/\underline{V}^{i+1}\right)(dB_i/d\ln T)\right]}{T\left[P + \sum(iB_i RT)/\underline{V}^{i+1}\right]}$$

and

$$\left(\frac{\partial U}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V = \sum \frac{R}{\underline{V}^i}\frac{dB_i}{d\ln T}\left[\frac{P + \sum\left(RT/\underline{V}^{i+1}\right)(dB_i/d\ln T)}{P + \sum i B_i RT/\underline{V}^{i+1}}\right]$$

4.4 (a) Start from

$$\mu = -\frac{1}{C_P}\left[\underline{V} - T\left(\frac{\partial \underline{V}}{\partial T}\right)_P\right] \Rightarrow C_P = -\frac{1}{\mu}\left[\underline{V} - T\left(\frac{\partial \underline{V}}{\partial T}\right)_P\right]$$

but $\left[\underline{V} - T\left(\dfrac{\partial \underline{V}}{\partial T}\right)_P\right] = -T^2\left(\dfrac{\partial(\underline{V}/T)}{\partial T}\right)_P$ and $C_P = \dfrac{T^2}{\mu}\left(\dfrac{\partial(\underline{V}/T)}{\partial T}\right)_P$.

(b) $\left(\dfrac{\partial(\underline{V}/T)}{\partial T}\right)_P = \dfrac{\mu C_P}{T^2}$; integrate $\left(\dfrac{\underline{V}}{T}\right)_{T_2,P} - \left(\dfrac{\underline{V}}{T}\right)_{T_1,P} = \displaystyle\int_{T_1,P}^{T_2,P} \dfrac{\mu C_P}{T^2}dT$.

Thus $\underline{V}(T_2,P) = \underline{V}(T_1,P)\dfrac{T_2}{T_1} + T_2\displaystyle\int_{T_1,P}^{T_2,P}\dfrac{\mu C_P}{T^2}dT$.

4.5 $P = \dfrac{RT}{\underline{V}-b} - \dfrac{a}{\underline{V}^2}$

$$\left(\frac{\partial P}{\partial \underline{V}}\right)_T = -\frac{RT}{(\underline{V}-b)^2} + \frac{2a}{\underline{V}^3} \tag{1}$$

$$\left(\frac{\partial^2 P}{\partial \underline{V}^2}\right)_T = \frac{2RT}{(\underline{V}-b)^3} - \frac{6a}{\underline{V}^4} \tag{2}$$

at the critical point $P \to P_C$, $T \to T_C$ and $\underline{V} \to V_C$

$$\left(\frac{\partial P}{\partial \underline{V}}\right)_T = 0 \Rightarrow \frac{RT_C}{(\underline{V}_C-b)^2} = \frac{2a}{\underline{V}_C^3} \tag{1'}$$

$$\left(\frac{\partial^2 P}{\partial \underline{V}^2}\right)_T = 0 \Rightarrow \frac{2RT_C}{(\underline{V}_C-b)^3} = \frac{6a}{\underline{V}_C^4} \tag{2'}$$

Dividing (1') by (2') $\Rightarrow \dfrac{1}{2}(\underline{V}_C - b) = \dfrac{1}{3}\underline{V}_C \Rightarrow b = \dfrac{V}{3}$ from (1')

$$a = \frac{\underline{V}_C^3 RT_C}{2(\underline{V}_C-b)^2} = \frac{(3b)^3 RT_C}{2(3b-b)^2} = \frac{27bRT_C}{8} = \frac{9V_C RT_C}{8}$$

Also $\dfrac{P\underline{V}}{RT} = \dfrac{\underline{V}}{\underline{V}-b} - \dfrac{a}{RT\underline{V}}$; and $P_C = \dfrac{8a}{27b(2b)} - \dfrac{a}{9b^2} = \dfrac{a}{27b^2}$

$$\Rightarrow Z_C = \frac{P_C\underline{V}_C}{RT_C} = \frac{\underline{V}_C}{\underline{V}_C-b} - \frac{a}{RT_C V_C} = \frac{\underline{V}_C}{(2/3)\underline{V}_C} - \frac{(9/8)\underline{V}_C RT_C}{\underline{V}_C RT_C}$$

$$= \frac{3}{2} - \frac{9}{8} = \frac{3}{8} = 0.375$$

4.6 $d\underline{S} = \dfrac{C_P}{T}dT - \left(\dfrac{\partial \underline{V}}{\partial T}\right)_P dP$ [eqn. (4.2-20)]

For the ideal gas $d\underline{S}^{IG} = \dfrac{C_P^*}{T}dT - \dfrac{R}{P}dP$. Thus, at constant temperature

$d\left(\underline{S} - \underline{S}^{IG}\right) = \left[\dfrac{R}{P} - \left(\dfrac{\partial \underline{V}}{\partial T}\right)_P\right]dP$ and

$$\left[\underline{S}(T,P) - \underline{S}^{IG}(T,P)\right] - \left[\underline{S}(T,P=0) - \underline{S}^{IG}(T,P=0)\right] = \int_{P=0}^{P}\left\{\dfrac{R}{P} - \left(\dfrac{\partial \underline{V}}{\partial T}\right)_P\right\}dP$$

However, $\underline{S}(T,P=0) - \underline{S}^{IG}(T,P=0) = 0$, since all fluids are ideal at $P=0$. Also $P\underline{V} = Z(T_r, P_r)RT$. Thus

$$\left(\dfrac{\partial \underline{V}}{\partial T}\right)_P = \dfrac{1}{P}\left\{RZ(T_r, P_r) + RT\left(\dfrac{\partial Z(T_r, P_r)}{\partial T}\right)_P\right\}$$

and

$$\dfrac{R}{P} - \left(\dfrac{\partial \underline{V}}{\partial T}\right)_P = -\dfrac{R}{P}\{Z(T_r, P_r) - 1\} - \dfrac{RT}{P}\left(\dfrac{\partial Z}{\partial T}\right)_P$$

$$\Rightarrow \underline{S}(T,P) - \underline{S}^{IG}(T,P) = -R\int_{T,P=0}^{T,P}\left[\dfrac{Z-1}{P} + \dfrac{T}{P}\left(\dfrac{\partial Z}{\partial T}\right)_P\right]dP$$

$$= -R\int_{T_r,P_r=0}^{T_r,P_r}\left[\dfrac{Z(T_r,P_r)-1}{P_r} + \dfrac{T_r}{P_r}\left(\dfrac{\partial Z}{\partial T_r}\right)_{P_r}\right]dP_r$$

4.7 (a) Ideal gas

$$P\underline{V} = NRT$$

$$N = \dfrac{(50\ \text{bar})(100\ \text{m}^3)}{(273.15 + 150)\text{K} \times 8.314 \times 10^{-2}\ \text{bar} \cdot \text{m}^3/\text{kmol K}} = 142.1\ \text{kmol}$$

Energy balance, closed nonflow system

$$\Delta U = Q - \int P dV = Q + W.$$

However, for ideal gas $\Delta U = 0$ since T is constant (isothermal). Thus

$$W = -Q = -\int P dV = -\int \dfrac{NRT}{V}dV = -NRT\ln\dfrac{V_2}{V_1} = -NRT\ln\dfrac{P_1}{P_2}$$

$$= -142.1\ \text{kmol} \times 8.314\ \text{J/mol K} \times (273.15 + 150) \times \ln\left(\dfrac{50}{300}\right)$$

$$= 895.9 \times 10^3\ \text{kJ} = 895.9\ \text{MJ}$$

$$Q = -895.9\ \text{MJ}$$

Also, by Ideal Gas Law at fixed T and N

$$P_1 V_1 = P_2 V_2 \Rightarrow V_2 = V_1 \frac{P_1}{P_2} = 100 \text{ m}^3 \times \frac{50}{300} = 16.67 \text{ m}^3$$

(b) Corresponding states

	T_r	P_r	Z	$\dfrac{\underline{H}^{IG} - \underline{H}}{T_C}$	$\underline{S}^{IG} - \underline{S}$
initial state	$\dfrac{150 + 273.15}{304.2} = 1.391$	$\dfrac{50}{73.76} = 0.679$	0.94	0.7	0.4
final state	1.391	$\dfrac{300}{73.76} = 4.067$	0.765	4.5	2.4
				$\dfrac{\text{cal}}{\text{mol K}}$	$\dfrac{\text{cal}}{\text{mol K}}$

Number of moles of gas $= N = \dfrac{PV}{ZRT} = \dfrac{142.1}{0.94} = 151.2 \text{ kmol}$ $\left(142.1 = \dfrac{PV}{RT} \text{ from above}\right)$

Final volume $= V_f = \dfrac{ZNRT}{P_f}$

$$= \frac{0.765 \times 151.2 \times 8.314 \times 10^{-2} \times (273.15 + 150)}{300} = 13.56 \text{ m}^3$$

Energy balance on gas: $\Delta U = Q + W$

Entropy balance on gas processes in gas are reversible: $\Delta S = \dfrac{Q}{T} + S_{\text{gen}} \Rightarrow S_{\text{gen}} = 0$. Therefore

$\Delta S = \dfrac{Q}{T}$ or $Q = T\Delta S$

$$\Delta S = S_f - S_i = N\left(\underline{S}_f - \underline{S}_i\right) = N\left\{\left(\underline{S}_f - \underline{S}_f^{IG}\right) + \left(\underline{S}_f^{IG} - \underline{S}_i^{IG}\right) - \left(\underline{S}_i - \underline{S}_i^{IG}\right)\right\}$$

$$= N\left\{-2.4 \times 4.184 - 8.314 \ln\frac{P_f}{P_i} - (-0.4 \times 4.184)\right\}$$

$$= N\left\{-8.368 - 8.314 \ln\frac{300}{50}\right\} = -23.26 N \text{ J/K}$$

$Q = T\Delta S = (273.15 + 150) \times 151.2 \text{ kmol} \times (-23.26) = -1488.5 \text{ MJ}$

$W = \Delta U - Q = N\left[\underline{U}_f - \underline{U}_i\right] - Q = N\left[\underline{H}_f - \underline{H}_i\right] - N\left[P_f \underline{V}_f - P_i \underline{V}_i\right] - Q$

$$= N\left[T_C \frac{\left(\underline{H}_f - \underline{H}_f^{IG}\right)}{T_C} + \underset{\underset{\text{Since process}}{0}}{\left(\underline{H}_f^{IG} - \underline{H}_i^{IG}\right)} - T_C \frac{\left(\underline{H}_i - \underline{H}_i^{IG}\right)}{T_C} - Z_f RT_f + Z_i RT_i\right] - Q$$

is isothermal.

$$= 151.2 \text{ kmol}\left[\begin{array}{l} 304.2(-4.5 - (-0.7)) \times 4.184 - 8.314 \\ \times(273.15 + 150) \times (0.765 - 0.94) \end{array}\right] + 1488.5 \text{ MJ}$$

$$= 151.2 \times 10^3\left[-4836.5 + 615.7\right]\text{J} + 1488.5 \text{ MJ} = -638.2 + 1488.5 \text{ MJ}$$

$$= 850.3 \text{ MJ}$$

(c) Peng-Robinson E.O.S.
Using the program PR1 with $T = 273.15$, $P = 1 \text{ bar}$ as the reference state, we obtain
$T = 150°C$, $P = 50 \text{ bar}$
$Z = 0.9202$; $\underline{V} = 0.6475 \times 10^{-3} \text{ m}^3/\text{mol}$; $\underline{H} = 4702.48 \text{ J/mol}$; $\underline{S} = -17.57 \text{ J/mol K}$.
$T = 150°C$, $P = 300 \text{ bar}$

$Z = 0.7842$; $\underline{V} = 0.9197 \times 10^{-4}$ m^3/mol; $\underline{H} = -60.09$ J/mol; $\underline{S} = -41.24$ J/mol.

$$N = \frac{V}{\underline{V}} = \frac{100 \text{ m}^3}{0.6475 \times 10^{-3} \text{ m}^3/\text{mol}} = 154.44 \text{ kmol}$$

$$Q = TN\Delta\underline{S} = (273.15 + 150) \times 154.44 \times (-41.24 - (-17.57)) = -1546.9 \text{ MJ}$$

$$W = \Delta U - Q = (H - PV)_f - (H - PV)_i - Q$$

$$= N\left[(\underline{H} - P\underline{V})_f - (\underline{H} - P\underline{V})_i\right] - Q$$

$$= 154.44 \begin{bmatrix} -60.09 - 300 \times 0.9197 \times 10^{-4} \\ \times 10^5 \text{ J/bar} \cdot \text{m}^3 - 4702.48 \\ +50 \times 0.6475 \times 10^{-3} \times 10^5 \end{bmatrix} \times 10^3 + 1546.9 \times 10^6$$

$$= 885.25 \text{ MJ}$$

{Note that N, Q and W are close to values obtained from corresponding states.}

4.8

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{\partial(T, \underline{S})}{\partial(P, \underline{S})} = \frac{\partial(T, \underline{S})}{\partial(P, T)} \cdot \frac{\partial(P, T)}{\partial(P, \underline{S})} = -\frac{\partial(\underline{S}, T)/\partial(P, T)}{\partial(\underline{S}, P)/\partial(T, P)}$$

$$= \frac{-(\partial \underline{S}/\partial P)_T}{(\partial \underline{S}/\partial T)_P} = \frac{(\partial \underline{V}/\partial T)_P}{C_P/T} = \frac{\underline{V}\alpha T}{C_P}$$

and

$$\frac{k_S}{k_T} = \frac{(1/\underline{V})(\partial\underline{V}/\partial P)_S}{(1/\underline{V})(\partial\underline{V}/\partial P)_T} = \frac{\partial(\underline{V}, \underline{S})/\partial(P, \underline{S})}{\partial(\underline{V}, T)/\partial(P, T)} = \frac{\partial(\underline{V}, \underline{S})}{\partial(\underline{V}, T)} \cdot \frac{\partial(P, T)}{\partial(P, \underline{S})}$$

$$= \frac{\partial(\underline{S}, \underline{V})}{\partial(T, \underline{V})} \cdot \frac{\partial(T, P)}{\partial(\underline{S}, P)} = \left(\frac{\partial \underline{S}}{\partial T}\right)_{\underline{V}} \cdot \left(\frac{\partial T}{\partial \underline{S}}\right)_P = \frac{C_V}{T} \cdot \frac{T}{C_P} = \frac{C_V}{C_P}$$

4.9 (a) $\left(\dfrac{\partial \underline{H}}{\partial \underline{V}}\right)_T = \dfrac{\partial(\underline{H}, T)}{\partial(\underline{V}, T)} = \dfrac{\partial(\underline{H}, T)}{\partial(P, T)} \cdot \dfrac{\partial(P, T)}{\partial(\underline{V}, T)} = \left(\dfrac{\partial \underline{H}}{\partial P}\right)_T \left(\dfrac{\partial P}{\partial \underline{V}}\right)_T$

Since $\left(\dfrac{\partial P}{\partial \underline{V}}\right)_T \neq 0$ (except at the critical point)

$$\left(\frac{\partial \underline{H}}{\partial \underline{V}}\right)_T = 0 \text{ if } \left(\frac{\partial \underline{H}}{\partial P}\right)_T = 0$$

(b) $\left(\dfrac{\partial \underline{S}}{\partial \underline{V}}\right)_P = \dfrac{\partial(\underline{S}, P)}{\partial(\underline{V}, P)} = \dfrac{\partial(\underline{S}, P)}{\partial(T, P)} \cdot \dfrac{\partial(T, P)}{\partial(\underline{V}, P)} = \left(\dfrac{\partial \underline{S}}{\partial T}\right)_P \cdot \left(\dfrac{\partial T}{\partial \underline{V}}\right)_P$

$$= \frac{C_P}{T} \cdot \frac{1}{\underline{V}} \cdot \underline{V}\left(\frac{dT}{d\underline{V}}\right)_P = \frac{C_P/T\underline{V}}{(1/\underline{V})(\partial\underline{V}/\partial T)_P} = \frac{C_P}{T\underline{V}\alpha} \Rightarrow \left(\frac{\partial \underline{S}}{\partial \underline{V}}\right)_P \sim \alpha^{-1}$$

4.10 (a) We start by using the method of Jacobians to reduce the derivatives

$$\left(\frac{\partial T}{\partial \underline{V}}\right)_H = \frac{\partial(T,\underline{H})}{\partial(\underline{V},\underline{H})} = \frac{\partial(T,\underline{H})}{\partial(T,P)} \cdot \frac{\partial(T,P)}{\partial(T,\underline{V})} \cdot \frac{\partial(T,\underline{V})}{\partial(\underline{V},\underline{H})}$$

$$= -\frac{\partial(\underline{H},T)}{\partial(P,T)} \frac{\partial(P,T)/\partial(\underline{V},T)}{\partial(\underline{H},\underline{V})/\partial(T,\underline{V})} = -\left(\frac{\partial \underline{H}}{\partial P}\right)_T \frac{(\partial P/\partial \underline{V})_T}{(\partial \underline{H}/\partial T)_{\underline{V}}}$$

$$= -\frac{(\partial \underline{H}/\partial \underline{V})_T}{(d\underline{H}/\partial T)_{\underline{V}}}$$

Now from Table 4.1 we have that

$$\left(\frac{\partial \underline{H}}{\partial P}\right)_T = \underline{V} - T\left(\frac{\partial \underline{V}}{\partial T}\right)_P \quad \text{and} \quad \left(\frac{\partial \underline{H}}{\partial T}\right)_{\underline{V}} = C_P + \left[\underline{V} - T\left(\frac{\partial \underline{V}}{\partial T}\right)_P\right]\left(\frac{\partial P}{\partial T}\right)_{\underline{V}}$$

alternatively, since $\underline{H} = \underline{U} + P\underline{V}$

$$\left(\frac{\partial \underline{H}}{\partial T}\right)_{\underline{V}} = \left(\frac{\partial \underline{U}}{\partial T}\right)_{\underline{V}} + \left(\frac{\partial(P\underline{V})}{\partial T}\right)_{\underline{V}} = C_V + \underline{V}\left(\frac{dP}{dT}\right)_{\underline{V}}$$

Thus

$$\left(\frac{\partial T}{\partial \underline{V}}\right)_H = \frac{-(\partial P/\partial \underline{V})_T\left[\underline{V} - T(\partial \underline{V}/\partial T)_P\right]}{C_V + \underline{V}(\partial P/\partial T)_{\underline{V}}} = \frac{-\left[\underline{V}(\partial P/\partial \underline{V})_T + T(\partial P/\partial T)_{\underline{V}}\right]}{C_V + \underline{V}(\partial P/\partial T)_{\underline{V}}}$$

Note: I have used $\left(\frac{\partial P}{\partial \underline{V}}\right)_T\left(\frac{\partial \underline{V}}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_{\underline{V}}$.

$$\left(\frac{\partial T}{\partial \underline{V}}\right)_{\underline{S}} = \frac{\partial(T,S)}{\partial(\underline{V},S)} = \frac{\partial(T,\underline{S})}{\partial(\underline{V},T)} \cdot \frac{\partial(\underline{V},T)}{\partial(\underline{V},\underline{S})} = -\frac{\partial(\underline{S},T)}{\partial(\underline{V},T)} \cdot \frac{\partial(T,\underline{V})}{\partial(\underline{S},\underline{V})}$$

$$= \left(\frac{\partial \underline{S}}{\partial \underline{V}}\right)_T\left(\frac{\partial T}{\partial \underline{S}}\right)_{\underline{V}} = -\frac{T}{C_V}\left(\frac{\partial P}{\partial T}\right)_{\underline{V}}$$

(b) For the van der Waals fluid

$$\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} = \frac{R}{\underline{V} - b}, \quad \left(\frac{\partial P}{\partial \underline{V}}\right)_T = \frac{-RT}{(\underline{V} - b)^2} + \frac{2a}{\underline{V}^3}$$

Thus

$$\left(\frac{\partial T}{\partial \underline{V}}\right)_H = \frac{-\left\{\left[-RT\underline{V}/(\underline{V} - b)^2 + 2a/\underline{V}^2\right] + RT/(\underline{V} - b)\right\}}{C_V + \left[\underline{V}R/\underline{V} - b\right]}$$

after simplification we obtain

$$\left(\frac{\partial T}{\partial \underline{V}}\right)_H = \frac{-\left[2a(\underline{V} - b)^2 - RT\underline{V}^2 b\right]}{C_C(\underline{V} - b)^2\underline{V}^2 + R(\underline{V} - b)\underline{V}^3}$$

and

$$\left(\frac{\P T}{\P \underline{V}}\right)_{\underline{S}} = -\frac{RT}{C_V(\underline{V}-b)}$$

4.11 There are a number of ways to solve this problem. The method I use is a little unusual, but the simplest that I know of. At the critical point all three roots of $\underline{V}$ are equal, and equal to $\underline{V}_C$.

Mathematically this can be expressed as $(\underline{V}-\underline{V}_C)^3 = 0$ which, on expansion, becomes

$$\underline{V}^3 - 3\underline{V}_C\underline{V}^2 + 3\underline{V}_C^2\underline{V} - \underline{V}_C^3 = 0 \tag{1}$$

compare this with

$$P = \frac{RT}{\underline{V}-b} - \frac{a}{\underline{V}(\underline{V}+b)+b(\underline{V}-b)} = \frac{RT}{\underline{V}-b} - \frac{a}{\underline{V}^2+2b\underline{V}-b^2}$$

which multiplying through by the denominators can be written as

$$\underline{V}^3 + \underline{V}^2\left(b - \frac{RT}{P}\right) + \left(-3b^2 - \frac{2bRT}{P} + \frac{a}{P}\right)\underline{V} + \left(b^3 + \frac{RTb^2}{P} - \frac{ab}{P}\right) = 0 \tag{2}$$

Comparing the coefficients of $\underline{V}$ in Eqns. (1) and (2) gives T_C, P_C

$$\underline{V}^2: \quad b - \frac{RT_C}{P_C} = -3\underline{V}_C \tag{3}$$

$$\underline{V}: \quad -3b^2 - \frac{2bRT_C}{P_C} + \frac{a}{P_C} = 3\underline{V}_C^2 \tag{4}$$

$$\underline{V}^0: \quad b^3 + \frac{RT_C}{P_C}b^2 - \frac{ab}{P_C} = -\underline{V}_C^3 \tag{5}$$

From Eqn. (3)

$$\frac{P_C b}{RT_C} - 1 = \frac{-3P_C\underline{V}_C}{RT_C} = -3Z_C \quad \text{or} \quad \frac{P_C b}{RT_C} = 1 - 3Z_C \tag{6}$$

For convenience, let $y = 1 - 3Z_C$ or $Z_C = \frac{1-y}{3}$. Then

$$\frac{P_C b}{RT_C} = y$$

From Eqn. (4)

$$-3\left(\frac{P_C b^2}{RT_C}\right) - 2\left(\frac{P_C b}{RT_C}\right) + \frac{aP_C}{(RT_C)^2} = 3Z_C^2$$

$$\Rightarrow -3y^2 + 2y + \frac{aP_C}{(RT_C)^2} = \frac{3(1-y)^2}{9}$$

or expanding and rearranging

$$\frac{aP_C}{(RT_C)^2} = \frac{1}{3}\left(10y^2 + 4y + 1\right) \tag{7}$$

Finally from eqn. (5)

$$\left(\frac{P_C b}{RT_C}\right)^3 + \left(\frac{bP_C}{RT_C}\right)^2 - \left(\frac{P_C b}{RT_C}\right)\left(\frac{aP_C}{(RT_C)^2}\right) = -Z_C^3$$

$$y^3 + y^2 - y \cdot \frac{1}{3}\left(10y^2 + 4y + 1\right) = -\frac{1}{27}(1-y)^3$$

or

$$64y^3 + 6y^2 + 12y - 1 = 0 \tag{8}$$

This equation has the solution $y = 0.077796074$

$$\Rightarrow b = 0.077796074\,\frac{RT_C}{P_C} \quad \text{(from Eqn. (6))}$$

$$a = 0.457235529\,\frac{(RT_C)^2}{P_C} \quad \text{(from Eqn. (7))}$$

Also $Z_C = \dfrac{1-y}{3} = 0.307401309$.

Note that we have equated a and b to T_C and P_C only at the critical point. Therefore these functions could have other values away from the critical point. However, as we have equated functions of $\underline{V}$, we have assumed a and b would only be functions of T. Therefore, to be completely general we could have

$$a = 0.457235529\,\frac{(RT_C)^2}{P_C}\,\boldsymbol{a}\!\left(\frac{T}{T_C}\right)$$

$$b = 0.077796074\,\frac{RT_C}{P_C}\,\boldsymbol{b}\!\left(\frac{T}{T_C}\right)$$

with $\boldsymbol{a}\!\left(\dfrac{T}{T_C}\right) \to 1$ as $\dfrac{T}{T_C} \to 1$ and $\boldsymbol{b}\!\left(\dfrac{T}{T_C}\right) \to 1$ as $\dfrac{T}{T_C} \to 1$.

In fact, Peng and Robinson (and others) have set $\boldsymbol{b} = 1$ at all temperatures and adjusted $\boldsymbol{a}$ as a function of temperature to give the correct vapor pressure (see chapter 5).

4.12 (also available as a Mathcad worksheet)

M.B. $\quad \dfrac{dN}{dt} = \dot N_1 + \dot N_2 = 0 \Rightarrow \dot N_2 = -\dot N_1$

$\dot N_1 \rightarrow \boxed{} \rightarrow \dot N_2$

$\uparrow \dot Q$

E.B. $\quad \dfrac{dU}{dt} = \dot N_1 \underline H_1 + \dot N_2 \underline H_2 + \dot Q = 0 \Rightarrow \dfrac{\dot Q}{\dot N_1} = \underline H_2 - \underline H_1$

Also, now using the program PR1 with $T = 273.15$, $P = 1$ bar reference state we obtain

$$
\begin{array}{cc}
T = 100°\text{C} & T = 150°\text{C} \\
P = 30 \text{ bar} & P = 20 \text{ bar} \\
Z = 0.9032 & Z = 0.9583 \\
\underline V = 0.9340\times10^{-3}\ \text{m}^3/\text{mol} & \underline V = 0.1686\times10^{-2}\ \text{m}^3/\text{mol} \\
\underline H = 3609.72\ \text{J}/\text{mol} & \underline H = 6796.06\ \text{J}/\text{mol} \\
\underline S = -15.84\ \text{J}/\text{mol K} & \underline S = -4.68\ \text{J}/\text{mol}
\end{array}
$$

$$\frac{\dot Q}{\dot N} = 6796.06 - 3609.72 = 3186.34\ \text{J}/\text{mol}$$

4.13 (also available as a Mathcad worksheet)

Since process is adiabatic and reversible $\Delta \underline S = 0$ or $\underline S_i = \underline S_f$, i.e., $\underline S(310\text{ K, }14\text{ bar}) = \underline S(T = ?,\ 345\text{ bar})$. Using the program PR1 with the $T = 273.15$ K and $P = 1$ bar reference state we obtain $T = 310$ K, $P = 14$ bar, $Z = 0.9733$, $\underline V = 0.1792\times10^{-2}\ \text{m}^3/\text{mol}$, $\underline H = 10908.3$ J/mol and $\underline S = 15.75$ J/mol K .

By trial and error (knowing P and $\underline S$, guessing T) we obtain $T = 341.91$ K, $P = 345$ bar, $Z = 0.9717$, $\underline V = 0.8007\times10^{-4}\ \text{m}^3/\text{mol}$, $\underline H = 18860.9$ J/mol, $\underline S = 15.75$ J/mol K $\Rightarrow T_f = 341.91$ K.

System = contents of compressor

M.B.: $\dfrac{dN}{dt} = 0 = \dot N_1 + \dot N_2 \Rightarrow \dot N_2 = -\dot N_1$

E.B.: $\dfrac{dU}{dt} = 0 = \dot N_1 \underline H_1 + \dot N_2 \underline H_2 + \overset{\overset{\text{adiabatic}}{0}}{\cancel{\dot Q}} + \dot W_s - P\ \overset{\overset{\substack{\text{volume of}\\\text{compressor}\\\text{constant}}}{0}}{\cancel{\dfrac{dV}{dt}}}$

$\dot W_S = -\dot N_1 \underline H_1 + \dot N_2 \underline H_2$ or $\dfrac{\dot W_S}{\dot N} = \underline H_2 - \underline H_1 = 18860.9 - 10908.3 = 7952.6$ J/mol

4.14 (a) $\left(P + \dfrac{a}{\underline V^2}\right)(\underline V - b) = RT \Rightarrow \dfrac{P\underline V}{RT} = \dfrac{\underline V}{\underline V - b} - \dfrac{a}{RT\underline V}$

i) $\displaystyle \lim_{\substack{P\to 0\\ \underline V\to\infty}} \frac{P\underline V}{RT} = \lim_{\underline V\to\infty}\left(\frac{\underline V}{\underline V - b} - \frac{a}{RT\underline V}\right) = 1$

ii) $B = \displaystyle \lim_{\substack{P\to 0\\ \underline V\to\infty}} \underline V\left(\frac{P\underline V}{RT} - 1\right) = \lim_{\underline V\to\infty} \underline V\left\{\frac{\underline V}{\underline V - b} - \frac{a}{RT\underline V} - 1\right\}$

$= \displaystyle \lim_{\underline V\to\infty} \underline V\left\{\frac{\underline V - (\underline V - b)}{(\underline V - b)} - \frac{a}{RT\underline V}\right\} = \lim_{\underline V\to\infty}\left\{\frac{b\underline V}{(\underline V - b)} - \frac{a}{RT}\right\} = b - \frac{a}{RT}$

iii) $\quad C = \lim_{\substack{P \to 0 \\ V \to \infty}} V^2 \left(\dfrac{PV}{RT} - 1 - \dfrac{B}{V} \right) = \lim_{V \to \infty} V \left\{ \dfrac{bV - b(V - b)}{V - b} \right\} = \lim_{V \to \infty} \dfrac{b^2 V}{V - b} = b^2$

$\Rightarrow C = b^2$

(b) At the Boyle temperature: $\quad \lim_{P \to 0} V \left(\dfrac{PV}{RT} - 1 \right) = 0 \Rightarrow B = 0$

$0 = b - \dfrac{a}{RT_B}$, $\quad T_B = \dfrac{a}{R_b}$ but $a = \dfrac{9V_c RT_c}{8}$, $\quad b = \dfrac{V_c}{3}$ (Eqns. 4.6-3a)

$T_B = \dfrac{9/8 V_c RT_c}{RV_c/3} = \dfrac{27}{8} T_c = 3.375 T_c$

4.15 (a) From table: $\quad T_B \sim 320\ \text{K}$, i.e., $B(T_B) = B(320\ \text{K}) = 0$

The inversion temperature is the temperature at which

$$\left(\frac{\partial T}{\partial P} \right)_H = 0 = -\frac{1}{C_P} \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right]$$

$$\left(\frac{\partial T}{\partial P} \right)_P = \frac{\partial}{\partial T} \bigg|_P \left[\frac{RT}{P} + B \right] = \frac{R}{P} + \frac{dB}{dT}$$

$$V - T \left(\frac{\partial V}{\partial T} \right)_P = \frac{RT}{P} + B - \frac{RT}{P} - T \frac{dB}{dT} = B - T \frac{dB}{dT}$$

Thus, T^{inv} is the temperature at which $B - T \dfrac{dB}{dt} = 0$.

Plot up B vs. T, obtain dB/dT either graphically, or numerically from the tabular data. I find $T^{inv} \sim 600\ \text{K}$. Also, dB/dT decreases with increasing temperature (i.e., $dB/dT \sim 4.56\ \text{cm}^3/\text{mol K}$ at 87.5 K and 0.027 $\text{cm}^3/\text{mol K}$ at 650 K. Presumably it is negative at even higher temperature!)

(b) Generally

$$\mu = \left(\frac{\partial T}{\partial P} \right)_H = -\frac{1}{C_P} \left\{ V - T \left(\frac{\partial V}{\partial T} \right)_P \right\} = -\frac{1}{C_P} \left\{ B - T \frac{dB}{dT} \right\}$$

Using the data in the table it is easy to show that for $T < T^{inv}$, $B - T \dfrac{dB}{dT} < 0 \Rightarrow \mu > 0$, while for $T > T^{inv}$, $B - T \dfrac{dB}{dT} > 0 \Rightarrow \mu < 0$.

(c) Since Fig. 2.4-3 for nitrogen is an H-P plot is easiest to proceed as follows

$$\left(\frac{\partial T}{\partial P} \right)_H = \frac{-1}{(\partial H/\partial T)_P (\partial P/\partial H)_T} = \frac{-(\partial H/\partial P)_T}{(\partial H/\partial T)_P}$$

Since $(\partial H/\partial T)_P = C_P$ is > 0 and less than ∞ [Except at a phase transition—see Chap. 5 and Problem **5.1**—however, μ has no meaning in the two-phase region], if $(dT/dP)_H$ is to be zero, then $(d H/dP)_T$ must equal zero. That is, an inversion point occurs when isotherms are parallel to lines of constant H (vertical line). This occurs at low pressures (ideal gas region) and at high

pressures (nonideal gas region). See, for example, $T = -200°\text{C}$ isotherm near 30 MPa (which is off the figure).

To identify the inversion temperatures of nitrogen we can use Fig. 2.4-2b, a temperature-entropy diagram. From part a of this problem we note that at T^{inv}

$$\underline{V} = T^{\text{inv}} \left(\frac{\partial \underline{V}}{\partial T} \right)_P \Rightarrow P = -T^{\text{inv}} \left(\frac{\partial P}{\partial T} \right)_P$$

Thus at each inversion temperatures T^{inv} we can find a density (or pressure) for which this equation is satisfied. Unfortunately, it is difficult to read the figure.

4.16 18 kg ; $\hat{V} = \dfrac{0.03 \text{ m}^3}{18 \text{ kg}} = 1.667 \times 10^{-3} \text{ m}^3/\text{kg}$. Using Fig. 2.4-2 we find $P \approx 91$ bar

Using the program PR1, with $T = 423.15 \text{ K}$ and $\hat{V} = 1.667 \times 10^{-3} \text{ m}^3/\text{kg}$, we find, by trial-and-error that $P = 108.0$ bar .

4.17 Using the program PR1 we find at 300 °C and 35 bar; $Z = 0.6853$; $\underline{V} = 0.9330 \times 10^{-3} \text{ m}^3/\text{mol}$; $\underline{H} = 21{,}033 \text{ J}/\text{mol} = 21.033 \text{ kJ}/\text{mol}$ and $\underline{S} = 7.06 \text{ J}/\text{mol K}$.

To use the principle of corresponding states we will assume the state of $T = 16°\text{C}$ and $P = 0.1$ bar is an ideal gas state (i.e., don't need corrections for nonideality at this condition). At 300°C and 35 bar we have

$$T_r = \frac{300 + 273.15}{283.2 + 273.15} = 1.0302$$

$$P_r = \frac{35}{45.6} = 0.76754$$

We find $Z = 0.71$; $\left(\underline{H}^{\text{IG}} - \underline{H} \right)/T_C = 8.37 \text{ J}/\text{mol}$; $\underline{S}^{\text{IG}} - \underline{S} = 7.113 \text{ J}/\text{mol K}$.

From Appendix II

$$C_P^* = 22.243 + 0.05977T - 3.499 \times 10^{-5} T^2 + 7.464 \times 10^{-9} T^3$$

$$\Delta \underline{H}^{\text{IG}} = \int_{289.15}^{573.15} C_P^* dT = 11910 \text{ J}/\text{mol}$$

$$\Delta \underline{S}^{\text{IG}} = \int_{289.15}^{573.15} \frac{C_P^*}{T} dT - R \ln\left(\frac{35 \text{ bar}}{0.1 \text{ bar}} \right) = -20386 \text{ J}/\text{mol K}$$

Thus

$$\underline{H}(T = 300° \text{C, } 35 \text{ bar})$$

$$= \underline{H}(16° \text{C, } 0.1 \text{ bar}) + \Delta \underline{H}^{\text{IG}} + T_C \left(\frac{H - H^{\text{IG}}}{T_C} \right)_{300°\text{C, } 35 \text{ bar}}$$

$$= 0 + 11910 - (283.2 + 273.15)(8.37) = 7253 \text{ J}/\text{mol}$$

$$\underline{S}(T = 300° \text{C, } 35 \text{ bar}) = 0 - 20.386 - 7.113 = 27.499 \text{ J}/\text{mol K}$$

Finally $P\underline{V} = ZRT$; $\underline{V} = \dfrac{0.71 \times 8.314 \times 10^{-5} \times 573.15}{35} = 0.9666 \times 10^{-3} \text{ m}^3/\text{mol}$.

4.18 Equation of state $P(\underline{V} - b) = RT$

(a) $\left(\dfrac{\partial P}{\partial T} \right)_{\underline{V}} = \dfrac{R}{\underline{V} - b} = \dfrac{P}{T}$; $\left(\dfrac{\partial \underline{V}}{\partial T} \right)_P = \dfrac{R}{P} = \dfrac{\underline{V} - b}{T}$; and $\left(\dfrac{\partial P}{\partial \underline{V}} \right)_T = -\dfrac{P}{\underline{V} - b}$

Thus

$$C_P = C_V + T \left(\frac{\partial \underline{V}}{\partial T} \right)_P \left(\frac{\partial P}{\partial T} \right)_{\underline{V}} = C_V + T \frac{R}{P} \cdot \frac{P}{T} = C_V + R$$

for $C_P(P,T) = C_P^*(T)$, we must have that

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 \underline{V}}{\partial T^2}\right)_P = 0$$

$$\left(\frac{\partial^2 \underline{V}}{\partial T^2}\right)_P = \frac{\partial}{\partial T}\bigg|_P\left(\frac{\partial \underline{V}}{\partial T}\right)_P = \frac{\partial}{\partial T}\bigg|_P \frac{R}{P} = 0 \Rightarrow C_P(T,P) = C_P^*(T)$$

Similarly, for $C_V(\underline{V},T) = C_V^*(T)$, we must have that $\left(\frac{\partial C_V}{\partial \underline{V}}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0$.

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_{\underline{V}} = \frac{\partial}{\partial T}\bigg|_{\underline{V}}\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} = \frac{\partial}{\partial T}\bigg|_{\underline{V}} \frac{R}{\underline{V}-b} = 0 \Rightarrow C_V(T,V) = C_V^*(T)$$

(b) First case is clearly a Joule-Thomson expansion $\Rightarrow H = $ constant

$$\left(\frac{\partial T}{\partial P}\right)_{\underline{H}} = -\frac{1}{C_P}\left[\underline{V} - T\left(\frac{\partial \underline{V}}{\partial T}\right)_P\right] = -\frac{1}{C_P}\left[\frac{RT}{P} + b - \frac{RT}{P}\right] = -\frac{b}{C_P}$$

Since C_P is independent of P, integration can be done easily

$$\int_{T_1}^{T_2} C_P(T)dT = -b(P_2 - P_1)$$

to proceed, we need to know how C_p depends on T. If C_p is independent of T we have

$$T_2 = T_1 - \frac{b}{C_P}(P_2 - P_1) \tag{1}$$

Eqn. (1) also holds if C_P is a function of T, but then it is the average heat capacity over the temperature interval which appears in Eqn. (1).

The second expansion is at constant entropy (key words are reversible and adiabatic)

$$\left(\frac{\partial T}{\partial P}\right)_{\underline{S}} = -\frac{(\partial \underline{S}/\partial P)_T}{(\partial \underline{S}/\partial T)_P} = +\frac{(\partial V/\partial T)_P}{C_P/T} = \frac{T}{C_P}\frac{R}{P} \Rightarrow \int_{T_1}^{T_2} C_P \frac{dT}{T} = R\int_{P_1}^{P_2}\frac{dP}{P}$$

If C_P is independent of T, then

$$T_2 = T_1\left(\frac{P_2}{P_1}\right)^{R/C_P}; \tag{2}$$

more complicated expression arises if $C_P = C_P(T)$.

4.19 (also available as a Mathcad worksheet)
General:
mass balance: $N_1^i = N_1^f + N_2^f$ $\qquad\qquad$ (1)
energy balance: $N_1^i \underline{U}_1^i = N_1^f \underline{U}_1^f + N_2^f \underline{U}_2^f$ $\qquad\qquad$ (2)

state variable constraints: $T_1^f = T_2^f = T^f$; $P_1^f = P_2^f = P^f$; $V_1 = V_2 \Rightarrow \underline{U}_1^f = \underline{U}_2^f$

(a) Ideal gas solution

Eqns. of state: $PV = NRT$; $\underline{U} = C_V T - C_P T_R$

From M.B. get: $\dfrac{P_1^i}{T_1^i} = \dfrac{2P^f}{T_f^f}$

From E.B. get: $T_1^i = T^f \Rightarrow T_1^i = T^f = 20°C$; $P^f = \dfrac{1}{2}P_1^i = 250 \text{ bar}$.

(b) Corresponding states solution

$$PV = ZNRT \text{ or } P\underline{V} = ZRT$$

$$\underline{U}(T) = \underline{U}^{IG}(T) + \left(\underline{U} - \underline{U}^{IG}(T)\right) = \underline{U}^{IG}(T) + \left(\underline{H} - \underline{H}^{IG}\right)_T - P\underline{V} + (P\underline{V})^{IG}$$

$$= \underline{U}^{IG}(T) + \left(\underline{H} - \underline{H}^{IG}\right) + (1 - Z)(P\underline{V})^{IG}$$

$$= \underline{U}^{IG}(T) + \left(\underline{H} - \underline{H}^{IG}\right) + (1 - Z)RT$$

From the mass balance

$$\frac{P_1^i}{Z^i T_1^i} = \frac{500 \times 10^7}{(20 + 273.15) \times 1.22} = 1.398 \times 10^5 = 2 \times \frac{P^f}{Z^f T^f}; \text{ or } \frac{P^f}{Z^f T^f} = 6.990 \times 10^4$$

where we have used

$$Z^i = Z\left(T_r = \frac{20 + 273.15}{190.7} = 1.538, P_r = \frac{5 \times 10^7}{4.64 \times 10^6} = 10.77\right) = 1.22$$

From energy balance

$$N_1^i \underline{U}_1^i = N_1^f \underline{U}_1^f + N_2^f \underline{U}_2^f = \left(N_1^f + N_2^f\right)\underline{U}^f = \left(N_1^f + N_2^f\right)\underline{U}^i \Rightarrow \underline{U}^f = \underline{U}^i$$

where we have used the fact that $\underline{U}_1^f = \underline{U}_2^f$. Since $T_1^f = T_2^f$ and $P_1^f = P_2^f$. But

$$\underline{U}_1^f - \underline{U}_1^i = 0 = \underline{U}^{IG}(T^f) - \underline{U}^{IG}(T^i) + \left(\underline{H} - \underline{H}^{IG}\right)_{T^f, P^f} - \left(\underline{H} - \underline{H}^{IG}\right)_{T^i, P^i}$$

$$+ (1 - Z)RT\big|_{T^f, P^f} - (1 - Z)RT\big|_{T^i, P^i}$$

and

$$\underline{U}^{IG}(T^f) - \underline{U}^{IG}(T^i) = C_V(T^f - T^i) = 27.25 \text{ J/mol K}(T^f - 293.15 \text{ K})$$

$$\left(\underline{H} - \underline{H}^{IG}\right)_{T^i, P^i} = -18.0 \times 190.7 = -3432.6 \text{ J/mol}$$

$$(1 - Z)RT\big|_{T^i, P^i} = -0.22 \times 8.314 \times 293.15 = -536.2 \text{ J/mol}$$

$$\Rightarrow 0 = 27.25 T_f + 293.15\{-27.25 + 0.22 \times 8.314\} + 18.0 \times 190.7 + \left(\underline{H} - \underline{H}^{IG}\right)_{T^f, P^f}$$

$$+ (1 - Z)RT\big|_{T^f, P^f}$$

$$27.25 T_f + \left(\underline{H} - \underline{H}^{IG}\right)_{T^f, P^f} + (1 - Z)RT\big|_{T^f, P^f} = 4{,}021 \qquad (1)$$

To be solved along with

$$\frac{P^f}{T^f Z^f} = 6.99 \times 10^4 \qquad (2)$$

I found the solution by making a guess for T^f, using eqn. (2) and Fig. 4.6-3 to find P^f, by trial and error. Then, guessed T^f and computed P^f were tested in eqn. (1). Solution found: $T^f \sim 237$ K $= -36.15^\circ$C ; $P^f \sim 1.011 \times 10^7$ Pa $= 101.1$ bar .

(c) The van der Waals gas

We know that: $\underline{U}^i = \underline{U}^f$ and $\underline{V}^i = \frac{1}{2}\underline{V}^f$. To evaluate the final temperature we start from

$$dT = \left(\frac{\partial T}{\partial \underline{V}}\right)_U d\underline{V} + \left(\frac{\partial T}{\partial \underline{U}}\right)_V d\underline{U} \Rightarrow T^f - T^i\Big|_{\substack{\text{along} \\ \text{path of} \\ \text{const.} \underline{U}}} = \int_{\underline{V}^i}^{\underline{V}^f} \left(\frac{\partial T}{\partial \underline{V}}\right)_U d\underline{V}$$

but

$$\left(\frac{\partial T}{\partial \underline{V}}\right)_U = -\frac{(\partial \underline{U}/\partial \underline{V})_T}{(\partial \underline{U}/\partial T)_V} = -\frac{T(\partial P/\partial T)_V + P}{C_V} = -\frac{a}{C_V \underline{V}^2}$$

Now, by Eqn. (4.2-36)

$$\left(\frac{\partial C_V}{\partial \underline{V}}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V \quad \text{for vdW eos } P = \frac{RT}{\underline{V} - b} - \frac{a}{\underline{V}^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{\underline{V} - b} \; ; \; \left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0 \Rightarrow C_V \text{ is independent of volume} \Rightarrow C_V = C_V^*$$

but $C_V^* = C_P^* - R = 35.565 - 8.314 = 27.25$ J/mol K

$$\Rightarrow T^f - T^i = -\int_{\underline{V}^i}^{\underline{V}^f} \frac{a}{C_V \underline{V}^2} dV = -\frac{a}{C_V} \int_{\underline{V}^i}^{\underline{V}^f} \frac{dV}{\underline{V}^2} = +\frac{a}{C_V}\left(\frac{1}{\underline{V}^f} - \frac{1}{\underline{V}^i}\right)$$

$$= -\frac{a}{2C_V \underline{V}^i} \quad \text{since } \underline{V}^i = \frac{1}{2}\underline{V}^f .$$

Thus the first step is to find $\underline{V}^i$.

$$\left(P_i + \frac{a}{\left(\underline{V}^i\right)^2}\right)\left(\underline{V}^i - b\right) = RT$$

$$\Rightarrow \underline{V}^i = 6.678 \times 10^{-5} \text{ m}^3/\text{mol}; \ \underline{V}^f = 1.336 \times 10^{-4} \text{ m}^3/\text{mol}.$$

$$T^f - T^i = \frac{-0.2283 \text{ Pa} \cdot \text{m}^6/\text{mol}^2}{2 \times (27.25 \text{ J/mol K}) \times \left(6.678 \times 10^{-5} \text{ m}^3/\text{mol}\right)} = -62.73 \text{ K}$$

$$\Rightarrow T^f = 293.15 - 62.73 = 230.42 \text{ K} = -42.73^\circ\text{C}$$

$$P_f = \frac{RT^f}{\left(\underline{V}^f - b\right)} - \frac{a}{\left(V^f\right)^2} = \frac{8.314 \times 230.42}{1.336 \times 10^{-4} - 4.269 \times 10^{-5}} - \frac{0.2283}{\left(1.336 \times 10^{-4}\right)^2}$$

$$P_f = 8.286 \times 10^6 \text{ Pa} = 82.86 \text{ bar}$$

(d) Here we will use the program PR1. Using the 273.15 K and 1 bar reference state we find that at the initial conditions $Z = 1.1005$, $\underline{V}^i = 0.5365 \times 10^{-4} \text{ m}^3/\text{mol}$, $\underline{H}^i = -3281.85 \text{ J/mol}$ and $\underline{S}^i = -59.12 \text{ J/mol K}$. Therefore

$$\underline{U}^i = \underline{H}^i - P^i\underline{V}^i = -3281.85 - 500 \times 0.5365 \times 10^{-4} \times 10^5 = -5964.35 \text{ J/mol}$$

Now since $\underline{U}^f = \underline{U}^i = -5964.35 \text{ J/mol}$ and
$\underline{V}^f = 2\underline{V}^i = 1.073 \times 10^{-4} \text{ m}^3/\text{mol}$.
We must, by trial-and-error, find the temperature and pressure of the state having these properties. I find the following as the solution $T_f = 230.9 \text{ K}$; $P \sim 99 \text{ bar}$ (for which $\underline{V} = 0.1075 \text{ m}^3/\text{mol}$ and $\underline{U} = -5968.4 \text{ J/mol}$). To summarize, we have the following answers for the different parts of the problem:

	P^f	T^f
Ideal gas	250 bar	293.15 K
Corresponding states	101.1 bar	237 K
van der Waals	82.86 bar	230.42 K
Peng-Robinson	99 bar	230.9 K

Once again, the ideal gas solution is seriously in error.

4.20 Mass balance (system = both tanks): $N_1^i = N_1^f + N_2^f$

energy balance (system = both tanks): $N_1^i\underline{U}_1^i = N_1^f\underline{U}_1^f + N_2^f\underline{U}_2^f$

entropy balance (system = portion of initial contents of tank 1, also in there finally): $\underline{S}_1^i = \underline{S}_1^f$

Also, $P_1^f = P_2^f = P^f$; $N_1^i = \dfrac{V_1}{\underline{V}_1^i}$; $N_1^f = \dfrac{V_1}{\underline{V}_1^f}$ and $N_2^f = \dfrac{V_2}{\underline{V}_2^f}$

(a) Ideal gas solution: obtain $\dfrac{P_1^i}{T_1^i} = \dfrac{P_1^f}{T_1^f} + \dfrac{P_2^f}{T_2^f}$ from mass balance and

$$P_1^i = P_1^f + P_2^f = 2P^f \Rightarrow P^f = 250 \text{ bar} = 2.5 \times 10^7 \text{ Pa from energy balance}$$

$$T_1^f = T_1^i \left(\frac{P_1^f}{P_1^i} \right)^{R/C_P} \Rightarrow T_1^f = (20 + 273.15) \left(\frac{1}{2} \right)^{8.314/35.565} = 249.3 \text{ K}$$

$$= -23.9° \text{ C from entropy balance}$$

and

$$\frac{1}{T_2^f} = \frac{2}{T_1^i} - \frac{1}{T_1^f} \Rightarrow T_2^f = 355.9 \text{ K} = 82.7° \text{ C}$$

Also

$$\frac{N_1^f}{N_1^i} = \frac{P_1^f V_1}{RT_1^f} \cdot \frac{RT_1^i}{P_1^i V_1} = \frac{2.5 \times 10^7}{249.3} \cdot \frac{293.15}{5.00 \times 10^7} = 0.588$$

and

$$\frac{N_2^f}{N_1^i} = 1 - \left(\frac{N_1^f}{N_1^i} \right) = 0.412$$

(b) Corresponding States Solution:

Initial conditions $\quad T_r = \dfrac{293.15}{190.7} = 1.538 \; ; \qquad P_r = \dfrac{5 \times 10^7}{4.64 \times 10^6} = 10.77 \; ; \qquad \Rightarrow Z = 1.22 \; ;$

$$\frac{\underline{H}^{\text{IG}} - \underline{H}}{T_C} = 18.0 \text{ J/mol K} \; ; \; \underline{S}^{\text{IG}} - \underline{S} = 9.6 \text{ J/mol K}.$$

Mass balance:

$$\frac{P_1^i}{Z_1^i T_1^i} = P^f \left\{ \frac{1}{Z_1^f T_1^f} + \frac{1}{Z_2^f T_2^f} \right\} = \frac{5.0 \times 10^7}{1.22 \times 293.15} = 1.398 \times 10^5 \qquad (1)$$

Entropy balance:

$$\underline{S}_1^f - \underline{S}_1^i = 0 = \left(\underline{S}_1 - \underline{S}_1^{\text{IG}} \right)^f + \left(\underline{S}_1^{\text{IG},f} - \underline{S}_1^{\text{IG},i} \right) - \left(\underline{S}_1 - \underline{S}_1^{\text{IG}} \right)^i$$

or

$$\left(\underline{S}_1 - \underline{S}_1^{\text{IG}} \right)^f + C_P \ln \frac{T_1^f}{293.15} - R \ln \frac{P^f}{5.0 \times 10^7} = -9.6 \qquad (2)$$

Energy balance:

$$N_1^i \underline{U}_1^i = N_1^f \underline{U}_1^f + N_2^f \underline{U}_2^f \text{ but } N_1^i = N_1^f + N_2^f \Rightarrow N_1^f \left(\underline{U}_1^f - \underline{U}_1^i \right) + N_2^f \left(\underline{U}_2^f - \underline{U}_2^i \right) = 0$$

or

$$\frac{P_1^f V_1}{Z_1^f RT_1^f}\left\{\left(\underline{H}_1^f - P_1^f \underline{V}_1^f\right) - \left(\underline{H}_1^i - P_1^i \underline{V}_1^i\right)\right\} + \frac{P_2^f V_2}{Z_2^f RT_2^f}\left\{\left(\underline{H}_2^f - P_2^f \underline{V}_2^f\right) - \left(\underline{H}_1^i - P_1^i \underline{V}_1^i\right)\right\} = 0$$

$$\frac{1}{Z_1^f T_1^f}\left\{\left(\underline{H}_1^f - \underline{H}_1^{f,\,IG}\right) + \left(\underline{H}_1^{f,\,IG} - \underline{H}_1^{i,\,IG}\right) - \left(\underline{H}_1^i - \underline{H}_1^{i,\,IG}\right) - Z_1^f RT_1^f + Z_1^i RT_1^i\right\}$$

$$+\frac{1}{Z_2^f T_2^f}\left\{\left(\underline{H}_2^f - \underline{H}_2^{f,\,IG}\right) + \left(\underline{H}_2^{f,\,IG} - \underline{H}_1^{i,\,IG}\right) - \left(\underline{H}_1^i - \underline{H}_1^{i,\,IG}\right) - Z_2^f RT_2^f + Z_1^i RT_1^i\right\} = 0$$

Substituting in the known values gives

$$\frac{1}{Z_1^f T_1^f}\left\{\left(\underline{H}_1^f - \underline{H}_1^{f,\,IG}\right) + 35.565\left(T_1^f - 293.15\right) - 8.314 Z_1^f T_1^f + 6{,}406.5\right\}$$

$$+\frac{1}{Z_2^f T_2^f}\left\{\left(\underline{H}_2^f - \underline{H}_2^{f,\,IG}\right) + 35.565\left(T_2^f - 293.15\right) - 8.314 Z_2^f T_2^f + 6{,}406.5\right\} = 0 \ (3)$$

Eqns. (1-3) now must be solved. One possible procedure is
i)   Guess P^f
ii)   Use Eqn. (2) to find T_1^f
iii) Use Eqn. (1) to find T_2^f
iv)   Use Eqn. (3), together with T_1^f and T_2^f to see if guessed P^f is correct. If not, go back to step i.
After *many* iterations, I found the following solution $P^f = 97.87$ bar ; $T_1^f = 221.6$ K ; $T_2^f = 259.4$ K ; $N_1^f/N_1^i = 0.645$; $N_2^f/N_1^i = 0.355$.

(c) Peng-Robinson equation of state
Here we use the equations

$$N_1^i = N_1^f + N_2^f \tag{4}$$

$$N_1^i \underline{U}_1^i = N_1^f \underline{U}_1^f + N_2^f \underline{U}_2^f \ \text{with} \ \underline{U} = \underline{H} - P\underline{V} \tag{5}$$

$$\underline{S}_1^i = \underline{S}^f \tag{6}$$

$$P_1^f = P_2^f = P^f$$

and $N_1^i = V_1/\underline{V}_1^i$; $N_1^f = V_1/\underline{V}_1^f$; $N_2^f = V_2/\underline{V}_2^f = V_1/\underline{V}_2^f$ since $V_1 = V_2$ (value of V_1 cancels out of problem, so any convenient value may be used). Procedure I used to solve problem was as follows. From PR1 we know $\underline{V}_1^i (\Rightarrow N_1^i)$ and $\underline{S}_1^i$ given initial conditions. Then

1. Guess value of T_1^f, find $P_1^f = P^f$ that satisfies $\underline{S}_1^f = \underline{S}_1^i$
2. Use T_1^f, P^f and $\underline{V}_1^f$ to get N_1^f ; then $N_2^f = N_1^i - N_1^f$ so $\underline{V}_2^f$ is known.
3. From P^f and $\underline{V}_2^f$ find (trial-and-error with PR1) T_2^f
4. See if eqn. (5) energy balance is satisfied; if not go back to step 1. After a number of iterations I find $P_f = 103.6$ bar ; $T_1^f = 222.3$ K ; $T_2^f = 255.5$ K ; $N_1^f/N_1^i = 0.619$; $N_2^f/N_1^i = 0.381$.

Summary

	ideal gas (part a)	Corresponding states (part b)	P-R E.O.S. (part c)
P^f	250 bar	97.87	103.6
T_1^f	249.3 K	221.6 K	222.3 K
T_2^f	355.9 K	259.4 K	255.5 K
N_1^f / N_1^i	0.588	0.645	0.619
N_2^f / N_1^i	0.412	0.355	0.381

Clearly, the ideal gas assumption is seriously in error!

4.21 System = contents of compressor. This is a steady-state, open constant volume system.

mass balance: $\dfrac{dN}{dt} = 0 = \dot{N}_1 + \dot{N}_2$

energy balance: $\dfrac{dU}{dt} = 0 = \dot{N}_1\underline{H}_1 + \dot{N}_2\underline{H}_2 + \dot{Q} + \dot{W}_s - P\,\dfrac{dV}{dt}^{\,0}$

$\Rightarrow 0 = \dot{N}_1(\underline{H}_1 - \underline{H}_2) + \dot{Q} + \dot{W}_s$

entropy balance: $\dfrac{dS}{dt} = 0 = \dot{N}_1\underline{S}_1 + \dot{N}_2\underline{S}_2 + \dfrac{\dot{Q}}{T} + \dot{S}_{gen}^{\,0} = \dot{N}_1(\underline{S}_1 - \underline{S}_2) + \dfrac{\dot{Q}}{T}$

Thus,

$$\dot{Q} = -T\dot{N}_1(\underline{S}_1 - \underline{S}_2)$$

$$\frac{\dot{Q}}{\dot{N}_1} = Q = T(\underline{S}_2 - \underline{S}_1)$$

and

$$\frac{\dot{W}_s + \dot{Q}}{\dot{N}_1} = W + Q = \underline{H}_2 - \underline{H}_1$$

(a) Corresponding states solution

$$Q = T(\underline{S}_2 - \underline{S}_1) = T\left\{ \left(\underline{S}_2 - \underline{S}_2^{IG}\right) + \left(\underline{S}_2^{IG} - \underline{S}_1^{IG}\right) - \left(\underline{S}_1 - \underline{S}_1^{IG}\right) \right\}$$

$$= T\left\{ \left(\underline{S}_2 - \underline{S}_2^{IG}\right) - \left(\underline{S}_1 - \underline{S}_1^{IG}\right) - R\ln\frac{P_2}{P_1} \right\}$$

Now $T_r = \dfrac{373.15}{405.6} = 0.92$; $P_{r,1} = \dfrac{1}{112.8} \sim 0.009$; $P_{r,2} = \dfrac{50}{112.8} = 0.443$. Thus

$$Q = -RT\ln\frac{50}{1} + T\left\{ \left(\underline{S}_2 - \underline{S}_2^{IG}\right)_{\substack{P_{r,2}=0.444 \\ T_r=0.92}} - \left(\underline{S}_1 - \underline{S}_1^{IG}\right)_{\substack{P_{r,1}=0.009 \\ T_r=0.92}} \right\}$$

$$= -8.314 \times 373.15 \times \ln 50 + 373.15(-5.23 - 0) = -14{,}088.1 \text{ J/mol}$$

and

$$W + Q = \underline{H}_2 - \underline{H}_1 = (\underline{H}_2 - \underline{H}_2^{IG}) + (\underbrace{\underline{H}_2^{IG} - \underline{H}_1^{IG}}_{\substack{0\text{ since} \\ T=\text{constant}}}) - (\underline{H}_1 - \underline{H}_1^{IG})$$

Thus

$$W + Q = T_C \left\{ \frac{\left(\underline{H}_2 - \underline{H}_2^{IG} \right)}{T_C} - \frac{\left(\underline{H}_1 - \underline{H}_1^{IG} \right)}{T_C} \right\} = 405.6 \times (-6.28 + 0)$$

$$= -2547.2 \ \text{J/mol}$$

$$W = -Q - 2547.2 = 11{,}540.9 \ \text{J/mol}$$

(b) Clausius gas

$$P(\underline{V} - b) = RT \ ; \ \underline{V} = \frac{RT}{P} + b \ ; \ \left(\frac{\partial \underline{V}}{\partial T} \right)_P = \frac{R}{P}$$

Thus

$$\Delta \underline{S} = \int_{P_1}^{P_2} \left(\frac{\partial \underline{S}}{\partial P} \right)_T dP = -\int_{P_1}^{P_2} \left(\frac{\partial \underline{V}}{\partial T} \right)_P dP = -R \int_{P_1}^{P_2} \frac{1}{P} dP = -R \ln \frac{P_2}{P_1}$$

$$Q = T\Delta S = -RT \ln \left(\frac{50}{1} \right) = -12{,}136.5 \ \text{J/mol}$$

$$\Delta \underline{H} = \int_{P_1}^{P_2} \left(\frac{\partial \underline{H}}{\partial P} \right)_T dP = \int_{P_1}^{P_2} \left[\underline{V} - T \left(\frac{\partial \underline{V}}{\partial T} \right)_P \right] dP = \int_{P_1}^{P_2} \left[\frac{RT}{P} + b - \frac{RT}{P} \right] dP$$

$$= \int_{P_1}^{P_2} b \, dP = b(P_2 - P_1) = 182.8 \ \text{J/mol}$$

So $W + Q = 182.8$ J/mol and

$$W = -Q + 182.8 = 12{,}136.5 + 182.8 = 12{,}319.3 \ \text{J/mol}$$

(c) Peng-Robinson equation of state
Using the program PR1 we find (for $T = 273.15$ and $P = 1$ bar ideal gas reference state) that

	100°C, 1 bar		100°C, 50 bar
$\underline{V}$	0.3089×10^{-1}	m³/mol	0.4598×10^{-3}
$\underline{H}$	3619.67	J/mol	1139.65
$\underline{S}$	11.32	J/mol K	−25.94

Note, from PR1, the vapor pressure of NH_3 at 100°C is 62.58 bar. Therefore, use vapor solution to P-R equation.
Then $Q = T(\underline{S}_2 - \underline{S}_1) = -13{,}903.6$ J/mol

$$W + Q = \underline{H}_2 - \underline{H}_1 = 1139.65 - 3619.67 = -2480.0 \ \text{J/mol}$$

and $W = -Q - 2480.0 = 11{,}423.6$ J/mol .

4.22 (also available as a Mathcad)

Considering the gas that is in the tank finally as the system, this is a closed system undergoing a reversible, adiabatic expansion. Therefore $\underline{S}_i = \underline{S}_f$.

(a) $d\underline{S} = \dfrac{C_P}{T}dT - \left(\dfrac{\partial \underline{V}}{\partial T}\right)_P dP$ but with $P(\underline{V}-b) = RT$ or $\underline{V} = \dfrac{RT}{P}+b$. Then $\left(\dfrac{\partial \underline{V}}{\partial T}\right)_P = \dfrac{R}{P}$; also

$\left(\dfrac{\partial C_P}{\partial P}\right)_T = -T\left(\dfrac{\partial^2 \underline{V}}{\partial T^2}\right)_P = -T\dfrac{\partial}{\partial T}\Big|_P \dfrac{R}{P} = 0 \Rightarrow C_P$ is independent of pressure. Therefore

$C_P = C_P^*$. Thus

$$0 = \Delta \underline{S} = \int_{T_i}^{T_f} \frac{C_P^*}{T}dT - R\int_{P_i}^{P_f}\frac{1}{P}dP$$

(1)

This has the solution $P_f = 13.10 \text{ bar}$. Now to find the initial and final molar volumes we use

$$\underline{V} = \frac{RT}{P}+b$$

$$\underline{V}_i = 0.000709 \text{ m}^3/\text{mol}$$
$$\underline{V}_f = 0.00197 \text{ m}^3/\text{mol}$$

So that $\dfrac{N_f}{N_i} = \dfrac{\underline{V}_i}{\underline{V}_f} = 0.3595$ (or 35.95%)

(b) Corresponding states

$$0 = \underline{S}_f - \underline{S}_i = \left(\underline{S}_f - \underline{S}_f^{IG}\right) + \left(\underline{S}_f^{IG} - \underline{S}_i^{IG}\right) - \left(\underline{S}_i - \underline{S}_i^{IG}\right)$$

Initial state

$$\begin{aligned}T_r &= \frac{400}{304.2} = 1.3149 \\ P_r &= \frac{50}{73.76} = 0.67787\end{aligned} \Rightarrow \begin{aligned}\underline{S}^{IG} - \underline{S} &= 0.49 \\ Z &= 0.906\end{aligned}$$

$$\left(\underline{S}_f^{IG} - \underline{S}_i^{IG}\right) = -12.4009 - 8.314\,\ln\frac{P_f}{50}$$

(As given by eqn. (1) above. Why?)
Guess for final state (use P from part a), then iterate. Final solution is $P_f = 11.52$ bar for which

$P_r = 0.156$, $\underline{S}^{IG} - \underline{S} \cong 0.29$ and $Z_f = 0.939$.

$$\frac{N_f}{N_i} = \frac{\left(P_f/Z_f RT_f\right)}{\left(P_i/Z_i RT_i\right)} = \frac{P_f}{Z_f T_f}\cdot\frac{Z_i T_i}{P_i} = \frac{11.52}{50}\times\frac{400}{300}\times\frac{0.906}{0.939} = 0.2964 \text{ (or 29.64\%)}$$

(c) Peng-Robinson equation of state
Use program PR1 with given heat capacity constants to find a pressure at 300 K which has the same entropy as the state $T = 400 \text{ K}$, $P = 50 \text{ bar}$. By trial-and-error we find that $P = 13.37 \text{ bar}$ (somewhat higher than the previous cases). Also, $\underline{V}_i = 0.5982\times10^{-3} \text{ m}^3/\text{mol}$ and

$$\underline{V}_f = 0.175 \times 10^{-2} \ \text{m}^3/\text{mol} \Rightarrow \frac{N_f}{N_i} = \frac{\underline{V}_i}{\underline{V}_f} = 0.3416 \ (\text{or } 34.16\%)$$

4.23 There are two obvious ways to proceed.

1) retain T and P as the independent variables since we have a program, PR1 that calculates $\underline{V}(T,P)$, $\underline{H}(T,P)$ and $\underline{S}(T,P)$. We can then use

$$\underline{U}(T,P) = \underline{H}(T,P) - P\underline{V} = \underline{H}(T,P) - ZRT \ (\text{where } Z = Z(T,P)) \qquad (1)$$

$$\underline{G}(T,P) = \underline{H}(T,P) - T\underline{S}(T,P) \qquad (2)$$

and

$$\underline{A}(T,P) = \underline{G} - P\underline{V} = \underline{U} - T\underline{S} = \underline{H} - P\underline{V} - T\underline{S} = \underline{H} - ZRT - T\underline{S} \qquad (3)$$

Now we will write

$$\underline{H}(T,P) = \underline{H}^{IG}(T) + RT(Z-1) + \frac{T(da/dT) - a}{2\sqrt{2}b}X \qquad (4)$$

and

$$\underline{S}(T,P) = \underline{S}^{IG}(T,P) + R\ln(Z-B) + \frac{T(da/dT)}{2\sqrt{2}b}X \qquad (5)$$

where for convenience, I have used

$$X = \ln\left[\frac{Z + (1+\sqrt{2})B}{Z + (1-\sqrt{2})B}\right]$$

Then we find

$$\underline{U}(T,P) = \underline{U}^{IG}(T) + \frac{T(da/dT) - a}{2\sqrt{2}b}X \ \text{where } \underline{U}^{IG} = \underline{H}^{IG} - RT \qquad (6)$$

$$\underline{G}(T,P) = \underline{G}^{IG}(T,P) + RT[(Z-1) - \ln(Z-B)] - \frac{a}{2\sqrt{2}b}X \qquad (7)$$

and

$$\underline{A}(T,P) = \underline{A}^{IG}(T,P) - RT\ln(Z-B) - \frac{a}{2\sqrt{2}b}X \qquad (8)$$

Thus we can either use eqns. (1 to 3) and previously calculated values Z, $\underline{H}$ and $\underline{S}$, or modify PR1 to use Eqns. (6-8) instead of Eqns. (4 and 5).

2) The second alternative is to take T and $\underline{V}$ as the independent variables and start from

$$d\underline{U} = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P\right]d\underline{V} \ \text{and} \ d\underline{S} = \frac{C_V}{T}dT + \left(\frac{\partial P}{\partial T}\right)_{\underline{V}}d\underline{V}$$

to get

$$\underline{S} - \underline{S}^{IG} = \int_{T, \underline{V}=\infty}^{T, \underline{V}} \left[\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - \frac{R}{\underline{V}}\right]d\underline{V}$$

and

$$\underline{U} - \underline{U}^{IG} = \int_{T, \underline{V}=\infty}^{T, \underline{V}} \left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P\right]d\underline{V}$$

Then put in the Peng-Robinson equation of state and from build up a procedure to calculate $\underline{S}$, $\underline{H}$, $\underline{U}$, P, $\underline{A}$ and $\underline{G}$ with T and $\underline{V}$ as the independent variables. We will not follow this alternative further.

4.24 We will do these calculations using

$$\underline{G} = \underline{H} - T\underline{S} \quad \text{and} \quad \underline{A} = \underline{G} - P\underline{V} = \underline{H} - P\underline{V} - TS$$

As an example, consider the $T = 0°\text{C}$ isotherm $P = 1$ bar , $\underline{H} = -742.14$ J/mol

$$\underline{G} = -742.14 - 273.15 \times (-2.59) = -34.68 \text{ J/mol}, \quad \begin{array}{l} S = -2.59 \text{ J/mol K} \\ \underline{V} = 22.6800 \text{ m}^3/\text{kmol} \end{array}$$

$$\underline{A} = -34.68 - 1 \text{ bar} \times 0.02268 \text{ m}^3/\text{mol} \times 10^5 \text{ J} = -2302.7 \text{ J/mol}$$

$P = 5$ bar $\underline{H} = -786.05$ J/mol
$\underline{S} = -16.09$ J/mol K $\Rightarrow$ $\underline{G} = 3608.9$ J/mol
$\underline{V} = 0.004513$ m³/mol $\underline{A} = 1352.4$ J/mol

$P = 10$ bar $\underline{H} = -840.75$ J/mol
$\underline{S} = -21.99$ J/mol K $\Rightarrow$ $\underline{G} = 5165.8$ J/mol
$\underline{V} = 0.002242$ m³/mol $\underline{A} = 2923.8$ J/mol

$P = 20$ bar $\underline{H} = -949.56$ J/mol
$\underline{S} = -28.06$ J/mol K $\Rightarrow$ $\underline{G} = 6715.0$ J/mol
$\underline{V} = 0.001107$ m³/mol $\underline{A} = 4501.0$ J/mol

$P = 40$ bar $\underline{H} = -1163.97$ J/mol
$\underline{S} = -34.40$ J/mol K $\Rightarrow$ $\underline{G} = 8232.4$ J/mol
$\underline{V} = 0.0005409$ m³/mol $\underline{A} = 6068.8$ J/mol

$P = 60$ bar $\underline{H} = -1372.64$ J/mol
$\underline{S} = -38.34$ J/mol K $\Rightarrow$ $\underline{G} = 9099.9$ J/mol
$\underline{V} = 0.0003532$ m³/mol $\underline{A} = 6978.9$ J/mol

$P = 80$ bar $\underline{H} = -1573.76$ J/mol
$\underline{S} = -41.29$ J/mol K $\Rightarrow$ $\underline{G} = 9704.6$ J/mol
$\underline{V} = 0.0002602$ m³/mol $\underline{A} = 7623.0$ J/mol

$P = 100$ bar $\underline{H} = -1765.61$ J/mol
$\underline{S} = -43.69$ J/mol K $\Rightarrow$ $\underline{G} = 10,168.3$ J/mol
$\underline{V} = 0.0002052$ m³/mol $\underline{A} = 8116.3$ J/mol

Similarly, $\underline{G}$ and $\underline{A}$ at other points could be computed, though this will not be done here.
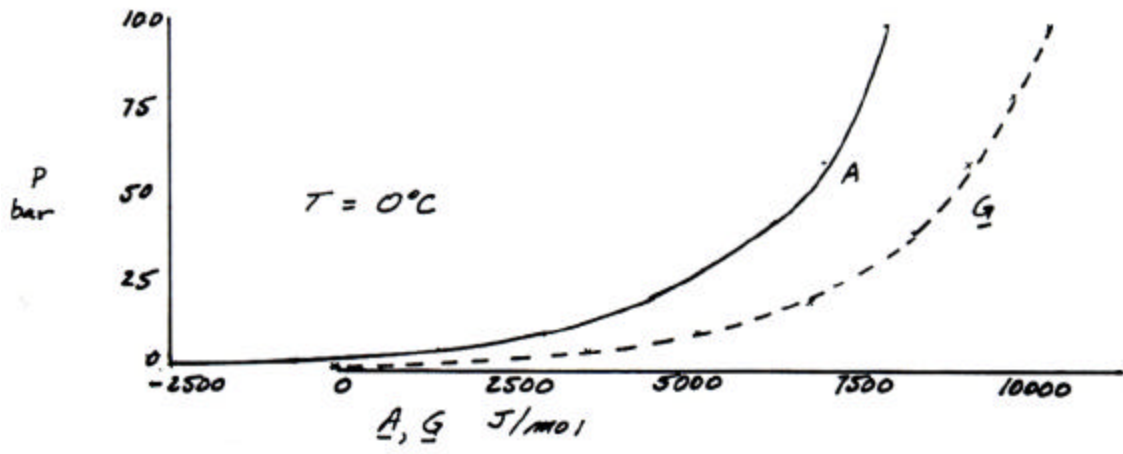
4.25 (a) $$\rho = \frac{1}{\underline{V}}$$

$$\partial \rho = \partial\left(\frac{1}{\underline{V}}\right) = -\underline{V}^{-2}\partial\underline{V} \Rightarrow \left(\frac{\partial P}{\partial \rho}\right)_S = -\underline{V}^2\left(\frac{\partial P}{\partial \underline{V}}\right)_S = +\frac{\underline{V}^2(\partial \underline{S}/\partial \underline{V})_P}{(\partial \underline{S}/\partial P)_{\underline{V}}}$$

by eqn. (4.1-6a)

Now

$$d\underline{S} = \frac{C_V}{T}dT + \left(\frac{\partial P}{\partial T}\right)_{\underline{V}} d\underline{V} \Rightarrow \left(\frac{\partial \underline{S}}{\partial P}\right)_{\underline{V}} = \frac{C_V}{T}\left(\frac{\partial T}{\partial P}\right)_{\underline{V}}$$

$$d\underline{S} = \frac{C_P}{T}dT + \left(\frac{\partial \underline{V}}{\partial T}\right)_P dP \Rightarrow \left(\frac{\partial \underline{S}}{\partial \underline{V}}\right)_P = \frac{C_P}{T}\left(\frac{\partial T}{\partial \underline{V}}\right)_P$$

$$\Rightarrow \left(\frac{\partial P}{\partial \rho}\right)_S = \underline{V}^2\frac{C_P}{T}\left(\frac{\partial T}{\partial \underline{V}}\right)_P \cdot \frac{T}{C_V}\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} = \underline{V}^2\gamma\left(\frac{\partial T}{\partial \underline{V}}\right)_P\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} = -\gamma\underline{V}^2\left(\frac{\partial P}{\partial \underline{V}}\right)_T$$

(by eqn. (4.1-6a))

Thus $v_S = \sqrt{-\gamma\underline{V}^2\left(\frac{\partial P}{\partial \underline{V}}\right)_T} = \sqrt{\gamma\underline{V}^2\left(\frac{\partial T}{\partial \underline{V}}\right)_P\left(\frac{\partial P}{\partial T}\right)_{\underline{V}}}$.

(b) $\gamma = \dfrac{C_P}{C_V}$ for the ideal gas $C_P = C_V + R \Rightarrow \gamma = \dfrac{C_V + R}{C_V} = 1 + \dfrac{R}{C_V}$

For the Clausius Gas

$$\gamma = \frac{C_P}{C_V} = \frac{C_V + T(\partial \underline{V}/\partial T)_P(\partial P/\partial T)_{\underline{V}}}{C_V} = 1 + \frac{T}{C_V}\left(\frac{\partial \underline{V}}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_{\underline{V}}$$

with $P(\underline{V} - b) = RT$

$$\left(\frac{\partial \underline{V}}{\partial T}\right)_P = \frac{R}{P} = \frac{\underline{V}-b}{T} \quad \text{and} \quad \left(\frac{\partial P}{\partial T}\right)_{\underline{V}} = \frac{R}{\underline{V}-b}$$

Thus

$$\gamma = 1 + \frac{T}{C_V} \cdot \frac{\underline{V}-b}{T} \cdot \frac{R}{\underline{V}-b} = 1 + \frac{R}{C_V}$$

To show that $C_v \neq C_v(\underline{V})$ we start from eqn. (4.2-35)

$$\left(\frac{\partial C_V}{\partial \underline{V}}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_{\underline{V}} \quad \text{but} \quad \left(\frac{\partial P}{\partial T}\right)_{\underline{V}} = \frac{R}{\underline{V}}; \quad \left(\frac{\partial^2 P}{\partial T^2}\right)_{\underline{V}} = 0 \quad \text{for ideal gas}$$

$$\text{and} \quad \left(\frac{\partial P}{\partial T}\right)_{\underline{V}} = \frac{R}{\underline{V}-b}; \quad \left(\frac{\partial^2 P}{\partial T^2}\right)_{\underline{V}} = 0 \quad \text{for Clausius gas]}$$

$$\Rightarrow \left(\frac{\partial C_V}{\partial \underline{V}}\right)_T = 0 \quad \text{for the ideal and Clausius Gases}$$

(c) $\quad v_S(\text{ideal gas}) = \sqrt{\gamma \underline{V}^2 \frac{T}{\underline{V}} \frac{P}{T}} = \sqrt{\gamma P\underline{V}} = \sqrt{\gamma RT}$

$$v_S(\text{Clausius gas}) = \sqrt{\gamma \underline{V}^2 \frac{T}{\underline{V}-b} \frac{R}{\underline{V}-b}} = \frac{\underline{V}}{\underline{V}-b}\sqrt{\gamma RT}$$

$$= \frac{\underline{V}}{\underline{V}-b}v_S(\text{ideal gas})\Big|_{\text{at same } T \text{ and } \underline{V}}$$

4.26 Preliminaries

Pressure = outward force per unit area exerted by gas

Force = tensile force exerted on fiber — at mechanical equilibrium fiber exerts an equal and opposite inward force

$\Rightarrow$ In all thermodynamic relations replace P by $-F/A$ and V by LA, and they will be applicable to fiber.

In particular, in place of $S = S(T,V)$ and $dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$. We will use $S = S(T, L)$

and $dS = \left(\frac{\partial S}{\partial T}\right)_L dT + \left(\frac{\partial S}{\partial L}\right)_T dL$. Also

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \Rightarrow \left(\frac{\partial S}{\partial T}\right)_L = \frac{C_L}{T}$$

$$\left(\frac{\partial S}{\partial T}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \Rightarrow \left(\frac{\partial S}{\partial L}\right)_T = -\left(\frac{\partial F}{\partial T}\right)_L$$

$$dS = \frac{1}{T}dU + \frac{P}{T}dV \Rightarrow dS = \frac{1}{T}dU = \frac{F}{T}dL$$

(a) From the above $dS = \left(\dfrac{\partial S}{\partial T}\right)_L dT + \left(\dfrac{\partial S}{\partial L}\right)_T dL = \dfrac{C_L}{T} dT + \left(\dfrac{\partial S}{\partial L}\right)_T dL$ and the analog of the

Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \Rightarrow \frac{1}{A}\left(\frac{\partial S}{\partial L}\right)_T = -\frac{1}{A}\left(\frac{\partial F}{\partial T}\right)_L$$

we get

$$dS = \frac{C_L}{T} dT - \left(\frac{\partial F}{\partial T}\right)_L dL = \frac{C_L}{T} dT - \gamma (L - L_0) dL$$

(b) $dU = TdS - PdV \Rightarrow dU = TdS + FdL$
$= C_L dT - \gamma T(L - L_0) dL + \gamma T(L - L_0) dL = C_L dT$
(Note: This is analog of ideal gas expression $U = U(T)$ or $dU = C_v dT$)

(c) $dS = \dfrac{C_L}{T} dT - \gamma (L - L_0) dL$

$$\Rightarrow S(L,T) - S(L_0, T_0) = \int_{L_0, T_0}^{L, T} \left\{ \frac{C_L}{T} dT - \gamma (L - L_0) dL \right\}$$

Choosing the path $(L_0, T_0) \rightarrow (L_0, T) \rightarrow (L, T)$ yields

$$S(L,T) - S(L_0, T_0) = \int_{T_0, L_0}^{T, L_0} \frac{\alpha + \beta T}{T} dT - \gamma \int_{T, L_0}^{T, L} (L - L_0) dL$$

$$= \alpha \ln \frac{T}{T_0} + \beta (T - T_0) - \frac{\gamma}{2}(L - L_0)^2$$

(d) A reversible (slow), adiabatic expansion $\Rightarrow S\left(L_f, T_f\right) - S(L_i, T_i) = 0$

$$0 = \left\{ S\left(L_f, T_f\right) - S(L_0, T_0) \right\} - \left\{ S(L_i, T_i) - S(L_0, T_0) \right\}$$

$$= \alpha \ln\left(\frac{T_f}{T_i}\right) + \beta(T_f - T_i) - \frac{\gamma}{2}\left[(L_f - L_0)^2 - (L_i - L_0)^2 \right]$$

Need to solve this transcendental equation to find T_f.

(e) $dU = C_L dT \Rightarrow \left(\dfrac{\partial U}{\partial L}\right)_T = 0 \Rightarrow F_U = 0$

$$F_S = -T\left(\frac{\partial S}{\partial L}\right)_T = -T\{-\gamma(L - L_0)\} = \gamma T(L - L_0) = -T\left(\frac{\partial F}{\partial T}\right)_L$$

4.27 (a) $dU = TdS - PdV + \underline{G}dN \Rightarrow \left(\dfrac{\partial U}{\partial S}\right)_{V,N} = T \ ; \ \left(\dfrac{\partial U}{\partial V}\right)_{S,N} = -P \ ; \ \text{and} \ \left(\dfrac{\partial U}{\partial N}\right)_{S,V} = \underline{G}$

Now equating mixed second derivatives

$$\left.\frac{\partial}{\partial V}\right|_{S,N}\left(\frac{\partial U}{\partial S}\right)_{V,N} = \left.\frac{\partial}{\partial S}\right|_{V,N}\left(\frac{\partial U}{\partial V}\right)_{S,N} \Rightarrow \left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N} \qquad (1)$$

$$\left.\frac{\partial}{\partial N}\right|_{S,V}\left(\frac{\partial U}{\partial S}\right)_{V,N} = \left.\frac{\partial}{\partial S}\right|_{V,N}\left(\frac{\partial U}{\partial N}\right)_{S,V} \Rightarrow \left(\frac{\partial T}{\partial N}\right)_{S,V} = -\left(\frac{\partial \underline{G}}{\partial S}\right)_{V,N} \qquad (2)$$

and

$$\left.\frac{\partial}{\partial N}\right|_{S,V}\left(\frac{\partial U}{\partial V}\right)_{S,N} = \left.\frac{\partial}{\partial V}\right|_{S,N}\left(\frac{\partial U}{\partial N}\right)_{S,V} \Rightarrow -\left(\frac{\partial P}{\partial N}\right)_{S,V} = \left(\frac{\partial \underline{G}}{\partial V}\right)_{S,N} \qquad (3)$$

(b), (c), and (d) are derived in similar fashion.

4.28 (also available as a Mathcad worksheet)

(a) The procedure that will be used is to first identify the temperature at which $\mu = 0$, and then show that $\mu < 0$ at larger temperatures, and $\mu > 0$ at lower temperatures. The starting point is, from Sec. 4.2

$$\mu = \left(\frac{\partial T}{\partial P}\right)_{\underline{H}} = -\frac{\underline{V}}{C_{\mathrm{P}}}(1 - T\alpha)$$

where, from Illustration 4.2-4, for the van der Waals gas,

$$\alpha^{-1} = \frac{T\underline{V}}{\underline{V}-b} - \frac{2a}{R\underline{V}^2}(\underline{V}-b) \ \text{ and } \ \mu = -\frac{\underline{V}}{C_{\mathrm{P}}}\left\{1 - \frac{1}{(\underline{V}/\underline{V}-b) - \left[2a(\underline{V}-b)/RT\underline{V}^2\right]}\right\}$$

Simplifying yields

$$\begin{aligned}
\mu &= -\frac{\underline{V}}{C_{\mathrm{P}}}\frac{(b/\underline{V}-b) - \left[2a(\underline{V}-b)/RT\underline{V}^2\right]}{(\underline{V}/\underline{V}-b) - \left[2a(\underline{V}-b)/RT\underline{V}^2\right]} \\
&= -\frac{\underline{V}}{C_{\mathrm{P}}}\frac{\left[RTb/(\underline{V}-b)\right] - \left[2a(\underline{V}-b)/\underline{V}^2\right]}{\left[RT\underline{V}/(\underline{V}-b)\right] - \left[2a(\underline{V}-b)/\underline{V}^2\right]}
\end{aligned} \qquad (1)$$

Now for μ to be zero, either the numerator must be zero, or the denominator infinity. Only the former is possible. Thus,

$$T^{\mathrm{inv}} = \frac{2a(\underline{V}-b)}{R\underline{V}^2} \cdot \frac{(\underline{V}-b)}{b} = \frac{2a(\underline{V}-b)^2}{R\underline{V}^2 b} \quad \text{the desired expression}$$

to determine the sign of the Joule-Thomson coefficient in the vicinty of the inversion temperature, we will replace T in eqn. (1) by $T^{\mathrm{inv}} + \delta$, where ϵ may be either positive or negative. The result is

$$m = -\frac{V}{C_P} \frac{[Rb/(V-b)]d}{[RV/(V-b)]d + [2a(V-b)^2/bV^2]}$$

It is easily shown that the denominator is always positive. Thus, m is proportional to $-d \Rightarrow$ if $T > T^{inv}$, so that $d > 0$, $m < 0$. Alternatively, if $T < T^{inv}$, $d < 0$ and $m > 0$.

(b) Using $a = \frac{9}{8} V_C R T_C$ and $b = \frac{V_C}{3}$

$$T^{inv} = 2 \cdot \frac{9}{8} V_C R T_C \frac{(V - V_C/3)^2}{(R V^2 V_C/3)} = \frac{27}{4} T_C \left(\frac{V_C}{3}\right)^2 \frac{(3V_r - 1)^2}{V^2}$$

$$\Rightarrow \frac{T^{inv}}{T_C} = \frac{9}{4} \left(\frac{V_C}{3}\right)^2 \frac{(3V_r - 1)^2}{V_r^2 V_C^2} \cdot 3 = \frac{3(3V_r - 1)^2}{4 V_r^2} = T_r^{inv}$$

(2)

(c) Expression above gives $T_r^{inv} = T_r^{inv}(V_r)$; what we want is T_r^{inv} as a function of P_r. Thus look at

$$\left(P_r + \frac{3}{V_r^2}\right)(3V_r - 1) = 8T_r \Rightarrow P_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}$$

(3)

Choose V_r as independent variable; use Eqn. (2) to get T_r^{inv}, and use Eqn. (3) to get P_r. Results are tabulated and plotted below.

V_r	T_r^{inv}	T^{inv} (K)	P_r	P (bar)	T^{inv} (°C)
0.5	0.75	94.65	0	0	−178.55
0.625	1.455	183.62	5.622	190.8	−89.6
0.75	2.048	262.5	7.977	270.7	−10.7
1.0	3.0	378.6	9.0	305.5	105.4
1.25	3.63	458.1	8.64	293.2	184.9
1.50	4.083	515.3	8.0	271.5	242.1
1.75	4.422	558.1	7.344	249.3	284.9
2.0	4.688	591.6	6.751	229.1	318.4
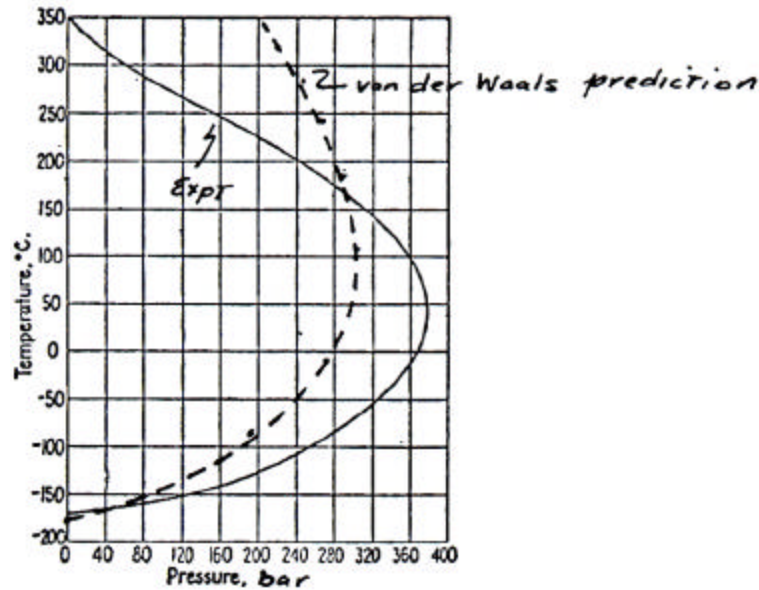
4.29 (also available as a Mathcad worksheet)

4.29   Take the gas to be nitrogen

Enter constants $R := 8.314 \cdot \dfrac{Pa \cdot m^3}{mole \cdot K}$ $Ti := 273.15 \cdot K$

System is the gas to be compressed. System is closed and isothermal (constant temperature).

Energy balance is   U(final) - U(initial) = Q + W = Q - PdV

Initial conditions are 0 C and 1 bar, final conditions are 0 C and 100 bar

a) Ideal gas

$P1(V,T) := \dfrac{R \cdot T}{V}$ $T \cdot \left(\dfrac{d}{dT} P1(V,T) \right) - P1(V,T) \to 0$

Consequently, as we already knew, the internal energy of an ideal gas is not a function of pressure or volume, only temperature.

$Vi := \dfrac{R \cdot Ti}{100000 \cdot Pa}$ $Vi = 0.0227 \cdot m^3 \cdot mole^{-1}$

Initial and final volumes

$Vf := \dfrac{R \cdot Ti}{10000000 \cdot Pa}$ $Vf = 2.271 \cdot 10^{-4} \cdot m^3 \cdot mole^{-1}$

$W := -\displaystyle\int_{Vi}^{Vf} P1(V,Ti)\, dV$ $W = 1.0458 \cdot 10^4 \cdot mole^{-1} \cdot joule$

U(final)-U(initial)=0, so Q = -W

$Q := -W$ $Q = -1.0458 \cdot 10^4 \cdot mole^{-1} \cdot joule$

b) Virial equation of state

$B := -10.3 \cdot 10^{-6} \cdot \dfrac{m^3}{mole}$ $C := 1.517 \cdot 10^{-9} \cdot \dfrac{m^6}{mole^2}$

$$P2(V,T) := \frac{R \cdot T}{V} \cdot \left(1 + \frac{B}{V} + \frac{C}{V^2}\right)$$

Consequently, the internal energy of this gas is also not a function of pressure or volume, only temperature. However, if the virial coefficient were a function of temperature (which is the actual case) then the internal energy of this gas would be a function of temperature.

$$T \cdot \left(\frac{d}{dT} P2(V,T)\right) - P2(V,T) \to 0$$

Guesses for Initial and final volumes

$$Vi := \frac{R \cdot Ti}{10000 \cdot Pa} \qquad Vf := \frac{R \cdot Ti}{1000000 \cdot Pa}$$

Given

$$100000 \cdot Pa = P2(Vi, Ti) \qquad Vi := find(Vi) \qquad Vi = 0.0227 \cdot m^3 \cdot mole^{-1}$$

Given

$$10000000 \cdot Pa = P2(Vf, Ti) \qquad Vf := find(Vf) \qquad Vf = 2.2353 \cdot 10^{-4} \cdot m^3 \cdot mole^{-1}$$

$$W := -\int_{Vi}^{Vf} P2(V, Ti) \, dV \qquad W = 1.0424 \cdot 10^4 \cdot mole^{-1} \cdot joule$$

U(final)-U(initial)=0, so Q = -W

$$Q := -W \qquad Q = -1.0424 \cdot 10^4 \cdot mole^{-1} \cdot joule$$

c) The van der Waals gas

$$a := 0.1368 \cdot \frac{Pa \cdot m^6}{mole^2} \qquad b := 3.864 \cdot 10^{-5} \cdot \frac{m^3}{mole}$$

$$P3(V,T) := \frac{R \cdot T}{V - b} - \frac{a}{V^2}$$

$$T \cdot \left(\frac{d}{dT} P3(V,T)\right) - P3(V,T) \to .1368 \cdot Pa \cdot \frac{m^6}{\left(mole^2 \cdot V^2\right)} \qquad = a/V^2 \qquad$$ In this case the internal energy is a function of volume (or pressure)

Guesses for Initial and final volumes

$$Vi := \frac{R \cdot Ti}{10000 \cdot Pa} \qquad Vf := \frac{R \cdot Ti}{1000000 \cdot Pa}$$

Given

$$100000 \cdot Pa = P3(Vi, Ti) \qquad Vi := find(Vi) \qquad Vi = 0.0227 \cdot m^3 \cdot mole^{-1}$$

Given

$$10000000 \cdot Pa = P3(Vf, Ti) \qquad Vf := find(Vf) \qquad Vf = 2.132 \cdot 10^{-4} \cdot m^3 \cdot mole^{-1}$$

$$W := -\int_{Vi}^{Vf} P3(V, Ti) \, dV \qquad W = 1.0414 \cdot 10^4 \cdot mole^{-1} \cdot joule$$

$$\Delta U := \int_{Vi}^{Vf} \frac{a}{V^2} \, dV \qquad \Delta U = -635.618 \cdot mole^{-1} \cdot joule$$

$$Q := \Delta U - W \qquad Q = -1.0424 \cdot 10^4 \cdot mole^{-1} \cdot joule$$

d) The Peng-Robinson fluid

$w := 0.04$

$b := 0.07780 \cdot R \cdot \dfrac{126.2 \cdot K}{33.94 \cdot 10^5 \cdot Pa}$

$b = 2.4051 \bullet 10^{-5} \quad \bullet m^3 \bullet mole^{-1}$

$ac := 0.45724 \cdot \dfrac{\left[R^2 \cdot (126.2 \cdot K)^2 \right]}{\left(33.94 \cdot 10^5 \cdot Pa \right)}$

$alf := \left[1 + (0.37464 + 1.54226 \cdot w - 0.26992 \cdot w \cdot w) \cdot \left[1 - \left(\dfrac{273.15}{124.6} \right)^{0.5} \right] \right]^2$

$alf = 0.6249$

$a := ac \cdot alf$

$a = 0.0927 \quad \bullet m^6 \bullet mole^{-2} \quad \bullet Pa$

$P4(V, T) := \dfrac{R \cdot T}{V - b} - \dfrac{a}{V \cdot (V + b) + b \cdot (V - b)}$

$T \cdot \left(\dfrac{d}{dT} P4(V, T) \right) - P4(V, T) \ \text{float}, 4 \ \rightarrow .09268 \cdot Pa \cdot \dfrac{m^6}{\left[mole^2 \cdot \left[V \cdot \left(V + 2.405 \cdot 10^{-5} \cdot \dfrac{m^3}{mole} \right) + 2.405 \cdot 10^{-5} \cdot \dfrac{m^3}{mole} \cdot \left(V - 2.405 \cdot 10^{-5} \cdot \dfrac{m^3}{mole} \right) \right] \right]}$

Which shows that the internal energy is a
function of volume (or pressure)

Guesses for Initial and final volumes $\qquad Vi := \dfrac{R \cdot Ti}{10000 \cdot Pa} \qquad Vf := \dfrac{R \cdot Ti}{1000000 \cdot Pa}$

Given $\qquad 100000 \cdot Pa = P4(Vi, Ti) \qquad Vi := find(Vi) \qquad Vi = 0.0227 \quad \bullet m^3 \bullet mole^{-1}$

Given $\qquad 10000000 \cdot Pa = P4(Vf, Ti) \qquad Vf := find(Vf) \qquad Vf = 2.2006 \bullet 10^{-4} \quad \bullet m^3 \bullet mole^{-1}$

$W := -\displaystyle\int_{Vi}^{Vf} P4(V, Ti) \, dV \qquad W = 1.041 \bullet 10^4 \quad \bullet mole^{-1} \bullet joule$

$T := 273.15 \cdot K$

$\Delta U := \displaystyle\int_{Vi}^{Vf} \left[T \cdot \left(\dfrac{d}{dT} P4(V, T) \right) - P4(V, T) \right] dV \qquad \Delta U = -378.0606 \quad \bullet mole^{-1} \bullet joule$

$Q := \Delta U - W \qquad Q = -1.0788 \bullet 10^4 \quad \bullet mole^{-1} \bullet joule$

4.30 For an isothermal process involving a fluid described by the Redlich-Kwong equation of state develop expressions for the changes in
(a) internal energy,
(b) enthalpy, and
(c) entropy
in terms of the initial temperature and the initial and final volumes.
For your information, the Redlich-Kwong equation of state is

$$P = \frac{RT}{\underline{V}-b} - \frac{a}{\sqrt{T}\cdot\underline{V}\cdot(\underline{V}+b)}$$

and

$$\int\frac{dx}{x(x+c)} = \frac{1}{c}\ln\left(\frac{x}{x+c}\right)$$

$$dU = \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]d\underline{V}$$

$$= \left[T\cdot\frac{R}{\underline{V}-b} + \frac{(1/2)at}{T^{3/2}\underline{V}(\underline{V}+b)} - \frac{RT}{\underline{V}-b} - \frac{a}{T^{1/2}\underline{V}(\underline{V}+b)}\right]d\underline{V}$$

$$= \frac{-adV}{2\sqrt{T}\underline{V}(\underline{V}+b)}$$

$$U(T,\underline{V}_2) - U(T,\underline{V}_1) = -\frac{a}{2\sqrt{T}}\int_{V_1}^{V_2}\frac{dV}{\underline{V}(\underline{V}+b)} = -\frac{a}{2\sqrt{T}b}\ln\left[\frac{\underline{V}_2}{\underline{V}_2+b}\frac{\underline{V}_1+b}{\underline{V}_1}\right]$$

$$\underline{H}(T,\underline{V}_2) - \underline{H}(T,\underline{V}_1) = \underline{U}(T,\underline{V}_2) - \underline{U}(T,\underline{V}_1) + P_2\underline{V}_2 - P_1\underline{V}_1$$

$$= -\frac{a}{2\sqrt{T}b}\ln\left[\frac{\underline{V}_2}{\underline{V}_1}\cdot\frac{(\underline{V}_1+b)}{(\underline{V}_2+b)}\right] + RT\left[\frac{\underline{V}_2}{\underline{V}_2-b} - \frac{\underline{V}_1}{\underline{V}_1-b}\right]$$

$$-\frac{a}{\sqrt{T}}\left[\frac{1}{\underline{V}_2+b} - \frac{1}{\underline{V}_1+b}\right]$$

$$d\underline{S} = \left(\frac{\partial P}{\partial T}\right)_V d\underline{V} = \left[\frac{R}{\underline{V}-b} + \frac{a}{2T^{3/2}\underline{V}(\underline{V}+b)}\right]d\underline{V}$$

$$\underline{S}(T,\underline{V}_2) - \underline{S}(T,\underline{V}_1) = R\ln\frac{\underline{V}_2-b}{\underline{V}_1-b} + \frac{a}{2T^{3/2}b}\ln\left[\frac{\underline{V}_2}{\underline{V}_1}\cdot\frac{(\underline{V}_1+b)}{(\underline{V}_2+b)}\right]$$

$$\underline{G}(T,\underline{V}_2) - \underline{G}(T,\underline{V}_1) = \left[\underline{H}(T,\underline{V}_2) - T\underline{S}(T,\underline{V}_2)\right] - \left[\underline{H}(T,\underline{V}_1) - T\underline{S}(T,\underline{V}_1)\right]$$

$$= -\frac{a}{2\sqrt{T}b}\ln\left[\frac{\underline{V}_2}{\underline{V}_1}\cdot\frac{(\underline{V}_1+b)}{(\underline{V}_2+b)}\right] + RT\left[\frac{\underline{V}_2}{\underline{V}_2-b} - \frac{\underline{V}_1}{\underline{V}_1-b}\right]$$

$$-\frac{a}{\sqrt{T}}\left[\frac{1}{\underline{V}_2+b} - \frac{1}{\underline{V}_1+b}\right]$$

$$- RT\ln\frac{\underline{V}_2-b}{\underline{V}_1-b} - \frac{a}{2\sqrt{T}b}\ln\left[\frac{\underline{V}_2}{\underline{V}_1}\cdot\frac{(\underline{V}_1+b)}{(\underline{V}_2+b)}\right]$$

$$= -\frac{a}{\sqrt{T}b}\ln\left[\frac{\underline{V}_2}{\underline{V}_1}\cdot\frac{(\underline{V}_1+b)}{(\underline{V}_2+b)}\right] + RT\left[\frac{\underline{V}_2}{\underline{V}_2-b} - \frac{\underline{V}_1}{\underline{V}_1-b}\right]$$

$$-\frac{a}{\sqrt{T}}\left[\frac{1}{\underline{V}_2+b} - \frac{1}{\underline{V}_1+b}\right] - RT\ln\left(\frac{\underline{V}_2+b}{\underline{V}_1+b}\right)$$

4.31
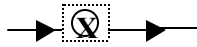
Joule-Thomson Expansion

$P_1 = 25 \text{ bar}$, $T_1 = 300°\text{C}$, $P_2 = 1 \text{ bar}$, $T_2 = ?$

(a) Ideal gas-enthalpy is independent of pressure $\Rightarrow T_2 = 300°\text{C}$

(b) van der Waals gas

$$\underline{H}_2 = \underline{H}_1 \Rightarrow \left(H_2 - \underline{H}_2^{IG}\right) + \left(\underline{H}_2^{IG} - \underline{H}_1^{IG}\right) - \left(\underline{H}_1 - \underline{H}_1^{IG}\right) = 0$$

$$\Rightarrow 0 = RT_2(Z_2 - 1) + \int_{\underline{V}=\infty}^{\underline{V}(T_2,P_1)} \left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P\right] d\underline{V} + \int_{T_1}^{T_2} C_p^* dT - RT_1(Z_1 - 1)$$

$$- \int_{\underline{V}=\infty}^{\underline{V}(T_1,P_1)} \left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P\right] d\underline{V} = 0$$

$$P = \frac{RT}{\underline{V}-b} - \frac{a}{\underline{V}^2}; \quad \left(\frac{\partial P}{\partial T}\right)_{\underline{V}} = \frac{R}{\underline{V}-b}; \quad T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P = \frac{RT}{\underline{V}-b} - \frac{RT}{\underline{V}-b} + \frac{a}{\underline{V}^2} = \frac{a}{\underline{V}^2}$$

$$\Rightarrow 0 = RT_2(Z_2 - 1) + a\int_{V=\infty}^{V_2} \frac{d\underline{V}}{\underline{V}^2} + \int_{T_1}^{T_2} C_p^V dT - RT_1(Z_1 - 1) - a\int_{V=\infty}^{V_1} \frac{d\underline{V}}{V^2}$$

$$0 = RT_2(Z_2 - 1) + a\int_{V=\infty}^{V_2} \frac{d\underline{V}}{\underline{V}^2} + \int_{T_1}^{T_2} C_p^V dT - RT_1(Z_1 - 1)$$

$$0 = P_2\underline{V}_2 - RT_2 - a\left(\frac{1}{\underline{V}_2} - \frac{1}{\underline{V}_1}\right) + \int_{T_1}^{T_2} \left(a + bT + cT^2 + dT^3\right) dT$$

$$- P_1\underline{V}_1 + RT_1$$

$$0 = P_2\underline{V}_2 - RT_2 - a\left(\frac{1}{\underline{V}_2} - \frac{1}{\underline{V}_1}\right) + a(T_2 - T_1) + \frac{b}{2}\left(T_2^2 - T_1^2\right)$$

$$+ \frac{c}{3}\left(T_2^3 - T_1^3\right) + \frac{d}{4}\left(T_2^4 - T_1^4\right) - P_1\underline{V}_1 + RT_1$$

Solved together with vdW EOS

$T = 575.07 \text{ K}$, $\approx 301.9°\text{C}$ (T increases?)

(c) Peng Robinson EOS

Thermodynamic properties relative to an ideal gas at 273.15 K and 1 bar.

$\hat{H}(300°\text{C}, 25 \text{ bar}) = 9.4363 \times 10^3 \text{ J/mol}$

After some trial and error

$\hat{H}(274.1°\text{C}, 1 \text{ bar}) = 9.4362 \times 10^3 \text{ J / mol}$ So the solution is $T=274.1°\text{C}$

Close enough

(d) Steam tables

$\hat{H}(300°\text{C}, 25 \text{ bar}) = 3008.8 \text{ kJ/kg}$

$\hat{H}(T = ?, 1 \text{ bar}) = 3008.8 \text{ kJ/kg}$

$\hat{H}(T = 250°\text{C}, 1 \text{ bar}) = 2974.3$

$\hat{H}(T = 300°\text{C}, 1 \text{ bar}) = 3074.3$

$\Rightarrow T \cong 267°\text{C} = 540 \text{ K}$

4.32 Note error in first printing. The problem statement should refer to

Problem 4.13, not the previous problem. The solution is available only as a Mathcad worksheet.

4.33 $A(N,V,T) = -kT \ln Q(N,V,T) = -kT \ln \left[\dfrac{f(T)^N V^N Z(N/V,T)^N}{N!} \right]$

$$= -NRT \ln f(T) - NkT \ln V - NkT \ln Z\left(\dfrac{N}{V}, T\right) + kT \ln N!$$

Stirling's approximation $\ln N! = N \ln N - N$

$$A(N,V,T) = -NkT \ln f(T) - NkT \ln V - kT \ln Z\left(\dfrac{N}{V}, T\right) + NkT \ln N - NkT$$

$$\left(\dfrac{\partial A}{\partial V}\right)_{T,N} = -P = -\dfrac{NkT}{V} - NkT\dfrac{\partial \ln Z(N/V,T)}{\partial (N/V)}\bigg|_T \dfrac{\partial (N/V)}{\partial V}\bigg|_T$$

$$P = \dfrac{NkT}{V} - \dfrac{N^2 kT}{V^2}\dfrac{\partial \ln Z(N/V,T)}{\partial (N/V)}\bigg|_T$$

$$\left(\dfrac{\partial A}{\partial T}\right)_{V,N} = -S = -Nk \ln f(T) - NkT\dfrac{d \ln f(T)}{dT} - Nk \ln V - k \ln Z\left(\dfrac{N}{V}, T\right)$$

$$- NkT\dfrac{\partial \ln Z(N/V,T)}{\partial T}\bigg|_{N,V} + Nk \ln N - kT$$

$$S = Nk \ln f(T) + NkT\dfrac{d \ln f(T)}{dT} - Nk \ln\left(\dfrac{N}{V}\right) + k \ln Z\left(\dfrac{N}{V}, T\right)$$

$$+ NkT\dfrac{\partial \ln Z(N/V,T)}{\partial T}\bigg|_{N,V} - kT$$

$$G\big|_{\text{molecule}} = \left(\dfrac{\partial A}{\partial N}\right)_{T,V} = -kT \ln f(T) - kT \ln V - kT\dfrac{\partial \ln Z(N/V,T)}{\partial (N/V)}\bigg|_V \dfrac{\partial (N/V)}{\partial N}\bigg|_V$$

$$- NkT \ln Z(N/V,T) + kT \ln N + kT - kT$$

$$G = N \cdot G\big|_{\text{molecule}} = -NkT \ln f(T) - NkT \ln V - \dfrac{NkT}{V}\dfrac{\partial \ln Z(N/V,T)}{\partial (N/V)}$$

$$+ NkT \ln N - NkT \ln Z\left(\dfrac{N}{V}, T\right)$$

As a check

$$G = A + PV = -NkT \ln f(T) - NkT \ln V - NkT \ln Z\left(\dfrac{N}{V}, T\right) + NkT \ln N$$

$$- NkT + \left[\dfrac{NkT}{V} - \dfrac{NkT}{V^2}\dfrac{\partial \ln Z(N/V,T)}{\partial (N/V)}\bigg|_T\right]V$$

$$= -NkT \ln f(T) - NkT \ln V - NkT \ln Z\left(\dfrac{N}{V}, T\right) + NkT \ln N$$

$$\cancel{-NkT} + \cancel{NkT} - \dfrac{NkT}{V}\dfrac{\partial \ln z(N/V, T)}{\partial (N/v)}\bigg|_T$$

$$= -NkT \ln f(T) - NkT \ln V - NkT \ln Z\left(\dfrac{N}{V}, T\right) + NkT \ln N$$

$$- \dfrac{NkT}{V}\dfrac{\partial \ln Z(N/V,T)}{\partial (N/V)}$$

which checks!

$$\left.\frac{\partial}{\partial T}\right|_{V,\,N}\left(\frac{A}{T}\right) = -\frac{U}{T^2}$$

$$= \left.\frac{\partial}{\partial T}\right|_{V,\,N}\left[-Nk\ln f(T) - Nk\ln V - Nk\ln Z\left(\frac{N}{V},T\right) + Nk\ln N - Nk\right]$$

$$= \left[-Nk\frac{d\ln f(T)}{dT} - Nk\left(\frac{\partial\ln Z(N/V,T)}{\partial T}\right)_{N,\,V}\right]$$

$$U = NkT^2\frac{d\ln f(T)}{dT} + NkT^2\left(\frac{\partial\ln Z(N/V,T)}{\partial T}\right)_{N,\,V}$$

$$C_V = \left(\frac{dU}{dT}\right)_{N,\,V} = 2NkT\frac{d\ln f(T)}{dT} + NkT^2\frac{d^2\ln f(T)}{dT^2}$$

$$+ 2NkT\left(\frac{\partial\ln Z(N/V,T)}{\partial T}\right)_{N,\,V} + NkT^2\left(\frac{\partial^2\ln Z(N/V,T)}{\partial T}\right)_{N,\,V}$$

$$H = U + PV$$

$$= NkT^2\frac{d\ln f(T)}{dT} + NkT^2\left(\frac{\partial\ln Z(N/V,T)}{\partial T}\right)_{N,V}$$

$$+ \frac{NkT}{V} - \frac{NkT}{V}\left.\frac{\partial\ln Z(N/V,T)}{\partial(N/V)}\right|_T$$

etc.

4.34 $\quad d\underline{H}^{\text{res}} = d\underline{H} - d\underline{H}^{\text{IG}} = C_P dT + \left[\underline{V} - T\left(\frac{\partial\underline{V}}{\partial T}\right)_P\right]dP - C_P^* dT$

$$= \left(C_P - C_P^*\right)dT + \left[\underline{V} - T\left(\frac{\partial\underline{V}}{\partial T}\right)_P\right]dP$$

$$d\underline{U}^{\text{res}} = \left(C_V - C_V^*\right)dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]d\underline{V}$$

$$d\underline{S} = \frac{C_V}{T}dT + \left(\frac{\partial P}{\partial T}\right)_V dV \Rightarrow d\underline{S}^{\text{res}} = \frac{C_V - C_V^*}{T}dT + \left[\left(\frac{\partial P}{\partial T}\right)_V - \frac{P}{T}\right]d\underline{V}$$

or $d\underline{S}^{\text{res}} = \dfrac{C_V - C_V^*}{T} - \left[\left(\dfrac{\partial\underline{V}}{\partial T}\right)_P - \dfrac{\underline{V}}{T}\right]dP$

$$d\underline{G}^{\text{res}} = d\underline{H}^{\text{res}} - d\left(TS^{\text{res}}\right) = d\underline{H}^{\text{res}} - Td\underline{S}^{\text{res}} - \underline{S}^{\text{res}}dT$$

$$= \left(C_P - C_P^*\right)dT + \left[\underline{V} - T\left(\frac{\partial\underline{V}}{\partial T}\right)_P\right]dP - \left(C_P - C_P^*\right)dT - \left[T\left(\frac{\partial\underline{V}}{\partial T}\right)_P - \underline{V}\right]dP$$

$$- \underline{S}^{\text{res}}dT$$

$$d\underline{G}^{\text{res}} = \underline{S}^{\text{res}}dT$$

$$\underline{H}(T,P)-\underline{H}^{IG}(T,P)= RT(Z-1)+\int_{\underline{V}=\infty}^{\underline{V}}\left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}}-P\right]d\underline{V}$$

$$P=\frac{RT}{\underline{V}-b}-\frac{a}{\underline{V}^{2}}$$

$$\left(\frac{\partial P}{\partial T}\right)_{\underline{V}}=\frac{R}{\underline{V}-b}$$

$$T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}}-P=\frac{RT}{\underline{V}-b}-\frac{RT}{\underline{V}-b}+\frac{a}{\underline{V}^{2}}=\frac{a}{\underline{V}^{2}}$$

$$\underline{H}(T,P)-\underline{H}^{IG}(T,P)= RT(Z-1)+\int_{\underline{V}=\infty}^{\underline{V}}\frac{a}{\underline{V}^{2}}d\underline{V}= RT(Z-1)-a\left[\frac{1}{\underline{V}}-\frac{1}{\infty}\right]$$

$$= RT(Z-1)-\frac{a}{\underline{V}}= RT(Z-1)-\frac{RT}{P}\frac{a}{\underline{V}}\cdot\frac{P}{RT}$$

$$= RT(Z-1)-\frac{aP}{ZRT}$$

$$\underline{H}(T,P)-\underline{H}^{IG}(T)= RT(Z-1)-\frac{aP}{ZRT}=\underline{H}^{res}$$

$$\underline{U}^{res}=\underline{U}(T,P)-\underline{U}^{IG}(T)=\underline{H}(T,\ P)-P\underline{V}-\left(\underline{H}^{IG}-P\underline{V}^{IG}\right)$$

$$=\underline{H}^{res}(T,P)-RT\frac{P\underline{V}}{RT}+\frac{P\underline{V}^{IG}}{RT}RT=\underline{H}^{res}(T,\ P)+RT(1-Z)$$

$$=\underline{H}^{res}(T,P)-RT(Z-1)=\frac{aP}{ZRT}$$

$$\underline{S}^{res}=\underline{S}(T,P)-\underline{S}^{IG}(T,P)=-\int_{\underline{V}=\infty}^{\underline{V}}\left[\left(\frac{\partial P}{\partial T}\right)_{\underline{V}}-\frac{R}{\underline{V}}\right]d\underline{V}$$

$$=-\int_{\underline{V}=\infty}^{\underline{V}}\left[\frac{R}{\underline{V}-b}-\frac{R}{\underline{V}}\right]d\underline{V}=-R\ln\frac{(\underline{V}-b)}{(\underline{V}\to\infty)-b}+R\ln\frac{\underline{V}}{(\underline{V}\to\infty)}$$

$$\underline{S}^{res}(T,P)=R\ln\frac{\underline{V}}{\underline{V}-b}=R\ln\frac{Z}{Z-B};\ B=\frac{Pb}{RT}$$

4.35 a) The Soave-Redlich-Kwong equation of state is

$$P=\frac{RT}{\underline{V}-b}-\frac{a(T)}{\underline{V}(\underline{V}-b)}$$

Rewrite this in the power series of $\underline{V}$

$$\underline{V}^{3}-\frac{RT}{P}\underline{V}^{2}+\left(-b^{2}-\frac{RT}{P}b-\frac{a(T)}{P}\right)\underline{V}-\frac{a(T)b}{P}=0$$

Notice that the three roots of volume at the critical point are identical so we can write

$$\left(\underline{V}-\underline{V}_{C}\right)^{3}=0\qquad\text{or}$$
$$\underline{V}^{3}-3\underline{V}_{C}\underline{V}^{2}+3\underline{V}_{C}^{2}\underline{V}-\underline{V}_{C}^{3}=0$$

At critical point, the second and fourth equations must be satisfied simultaneously. Consequently, the coefficients of each power of $\underline{V}$ must be the same. Thus,

$$3\underline{V}_C = \frac{RT_C}{P_C}$$

$$3\underline{V}_C^2 = -b^2 - \frac{RT_C}{P_C}b - \frac{a(T_C)}{P_C} \quad \text{and}$$

$$\underline{V}_C^3 = \frac{a(T_C)}{P_C}b$$

Solving the above three equations together for $a(T)$, b and $\underline{V}_C$, we get

$$\underline{V}_C = \frac{RT_C}{3P_C}$$

$$b = \left(\sqrt[3]{2}-1\right)\underline{V}_C = 0.08664\frac{RT_C}{P_C} \quad \text{and}$$

$$a(T_C) = \frac{P_C\underline{V}_C^3}{b} = 0.42748\frac{(RT_C)^2}{P_C}$$

Also

$$a(T) = a(T_C)\alpha(T) = 0.42748\frac{(RT_C)^2}{P_C}\alpha(T)$$

b) $$Z_C = \frac{P_C\underline{V}_C}{RT_C} = \frac{P_C\underline{V}_C}{RT_C}\frac{RT_C}{3P_C} = \frac{1}{3}$$

4.36 (also available as a Mathcad worksheet)

$$P = \frac{RT}{\underline{V}-b} - \frac{a(T)}{\underline{V}(\underline{V}+b)}$$

$$\underline{H}(T,P) - \underline{H}^{IG}(T,P) = RT(Z-1) + \int_{\underline{V}=\infty}^{\underline{V}}\left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P\right]d\underline{V}$$

$$\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} = \frac{R}{\underline{V}-b} - \frac{1}{\underline{V}(\underline{V}+b)}\frac{da(T)}{dT}$$

$$T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P = \frac{RT}{\underline{V}-b} - \frac{T}{\underline{V}(\underline{V}+b)}\frac{da(T)}{dT} - \frac{RT}{\underline{V}-b} + \frac{a}{\underline{V}(\underline{V}+b)}$$

$$= \frac{1}{\underline{V}(\underline{V}+b)}\left[a - T\frac{da(T)}{dT}\right]$$

So the integral to be done is

$$\int_{\underline{V}=\infty}^{\underline{V}}\frac{1}{\underline{V}(\underline{V}+b)}d\underline{V} = \int_{\underline{V}=\infty}^{\underline{V}}\frac{d\underline{V}}{\underline{V}(\underline{V}+b)} = \frac{1}{(-b)}\ln\left[\frac{1\cdot\underline{V}+b}{\underline{V}}\right]\Bigg|_{\underline{V}=\infty}^{\underline{V}}$$

$$= -\frac{1}{b}\ln\left[\frac{\underline{V}+b}{\underline{V}}\right] + \frac{1}{b}\ln\left[\frac{\underline{V}+b}{\underline{V}}\right]\Bigg|_{\underline{V}=\infty} = -\frac{1}{b}\ln\left[\frac{\underline{V}+b}{\underline{V}}\right]$$

So

$$\underline{H}(T,P) - \underline{H}^{IG}(T,P) = RT(Z-1) + \int_{\underline{V}=\infty}^{\underline{V}}\left[T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P\right]d\underline{V}$$

$$= RT(Z-1) - \frac{a - T(da/dT)}{b}\ln\left(\frac{\underline{V}+b}{\underline{V}}\right)$$

$$= RT(Z-1) + \frac{T(da/dT)-a}{b}\ln\left[\frac{Z+(Pb/RT)}{Z}\right]$$

$$= RT(Z-1) + \frac{T(da/dT)-a}{b}\ln\left[\frac{Z+B}{Z}\right]$$

$$\underline{S}(T,P) - \underline{S}^{IG}(T,P) = R\ln Z + \int_{\underline{V}=\infty}^{\underline{V}=ZRT/P}\left[\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - \frac{R}{\underline{V}}\right]d\underline{V}$$

$$\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - \frac{R}{\underline{V}} = \frac{R}{\underline{V}-b} - \frac{1}{\underline{V}(\underline{V}+b)}\frac{da}{dT} - \frac{R}{\underline{V}}$$

$$\int_{\underline{V}=\infty}^{\underline{V}=ZRT/P}\left[\frac{R}{\underline{V}-b} - \frac{1}{\underline{V}(\underline{V}+b)}\frac{da}{dT} - \frac{R}{\underline{V}}\right]d\underline{V}$$

$$= R\ln\frac{\underline{V}-b}{[\underline{V}-b]_{\underline{V}\to\infty}} - R\ln\frac{\underline{V}}{[\underline{V}]_{\underline{V}\to\infty}} + \frac{da}{dT}\frac{1}{b}\ln\frac{\underline{V}+b}{\underline{V}}$$

$$= R\ln\frac{\underline{V}-b}{\underline{V}} + \frac{da}{dT}\frac{1}{b}\ln\left[\frac{Z+(Pb/RT)}{Z}\right]$$

$$= R\ln\left(\frac{Z-B}{Z}\right) + \frac{da}{dT}\frac{1}{b}\ln\left[\frac{Z+B}{Z}\right]$$

$$\underline{S}(T,P) - \underline{S}^{IG}(T,P) = R\ln Z + R\ln\left(\frac{Z-B}{Z}\right) + \frac{da}{dT}\frac{1}{b}\ln\left[\frac{Z+B}{Z}\right]$$

$$= R\ln(Z-B) + \frac{da}{dT}\frac{1}{b}\ln\left[\frac{Z+B}{Z}\right]$$

$$\underline{G}^{res} = \underline{H}^{res} - T\underline{S}^{res} = RT(Z-1) - \frac{aP}{zRT} - RT\ln\frac{Z}{Z-B}$$

Redlich-Kwong

$$P = \frac{RT}{\underline{V}-b} - \frac{a}{\sqrt{T}\underline{V}(\underline{V}+b)}$$

$$\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} = \frac{R}{\underline{V}-b} + \frac{(1/2)a}{T^{3/2}\underline{V}(\underline{V}+b)}$$

$$T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P = \frac{RT}{\underline{V}-b} + \frac{(1/2)a}{\sqrt{T}\underline{V}(\underline{V}+b)} - \frac{RT}{\underline{V}-b} + \frac{a}{\sqrt{T}\underline{V}(\underline{V}+b)}$$

$$= \frac{(3/2)a}{\sqrt{T}\underline{V}(\underline{V}+b)} = \frac{3a}{2\sqrt{T}\underline{V}(\underline{V}+b)}$$

$$\underline{H}(T,P) - \underline{H}^{IG}(T,P) = RT(Z-1) + \int_{\underline{V}=\infty}^{\underline{V}} \frac{3a}{2\sqrt{T}} \frac{d\underline{V}}{\underline{V}(\underline{V}+b)}$$

$$= RT(Z-1) + \frac{3a}{2b\sqrt{T}} \ln \frac{\underline{V}}{\underline{V}+b}$$

$$= RT(Z-1) + \frac{3a}{2b\sqrt{T}} \ln \frac{Z}{Z+(bP/RT)}$$

$$= RT(Z-1) + \frac{3a}{2b\sqrt{T}} \ln \frac{Z}{Z+B}$$

$$\underline{U}(T,P) - \underline{U}^{IG}(T,P) = \frac{3a}{2b\sqrt{T}} \ln \frac{Z}{Z+B}$$

$$\underline{S}(T,P) - \underline{S}^{IG}(T,P) = - \int_{\underline{V}=\infty}^{\underline{V}} \left[\left(\frac{\P P}{\P T} \right)_{\underline{V}} - \frac{R}{\underline{V}} \right] d\underline{V}$$

$$= - \int_{\underline{V}=\infty}^{\underline{V}} \left[\frac{R}{\underline{V}-b} + \frac{(1/2)a}{T^{3/2}V(V+b)} - \frac{R}{\underline{V}} \right] d\underline{V}$$

$$= R \ln \frac{\underline{V}}{\underline{V}-b} - \frac{(1/2)a}{T^{3/2}b} \ln \frac{\underline{V}}{\underline{V}+b}$$

$$= R \ln \frac{Z}{Z-B} - \frac{a}{2T^{3/2}b} \ln \frac{Z}{Z+B}$$

4.37 (also available as a Mathcad worksheet)

Problem 4.37

Critical properties and heat capacity for oxygen:

$Tc := 154.6 \cdot K$ $\qquad$ $Pc := 5.046 \cdot 10^6 \cdot Pa$ $\qquad$ $\omega := 0.021$ $\qquad$ $Tref := 298.15 \cdot K$ $\qquad$ $Pref := 10^5 \cdot Pa$

$$Cp(T) := 25.460 \cdot \frac{joule}{mole \cdot K} + 1.519 \cdot 10^{-2} \cdot T \cdot \left(\frac{joule}{mole \cdot K^2}\right) - 0.715 \cdot 10^{-5} \cdot T^2 \cdot \left(\frac{joule}{mole \cdot K^3}\right) + 1.311 \cdot 10^{-9} \cdot T^3 \cdot \left(\frac{joule}{mole \cdot K^4}\right)$$

Soave-Redlich-Kwong Constants:

$$R := 8.31451 \cdot \frac{joule}{K \cdot mole} \qquad a1 := 0.42748 \cdot \left(\frac{R^2 \cdot Tc^2}{Pc}\right) \qquad \alpha(T) := \left[1 + \left(0.480 + 1.574 \cdot \omega - 0.176 \cdot \omega^2\right) \cdot \left(1 - \sqrt{\frac{T}{Tc}}\right)\right]^2$$

$$a(T) := a1 \cdot \alpha(T) \qquad b := 0.08664 \cdot \frac{R \cdot Tc}{Pc} \qquad b = 2.207 \cdot 10^{-5} \cdot m^3 \cdot mole^{-1}$$

(Initial guess for solver)

Temperature and Pressure:

$T := 173.15 \cdot K$ $\qquad\qquad$ $P := 1 \cdot 10^5 \cdot Pa$ $\qquad\qquad$ $V := 10^{-4} \cdot m^3 \cdot mole^{-1}$

Solve block for Volume:

Given $\qquad$ $P = \dfrac{R \cdot T}{V - b} - \dfrac{a(T)}{V \cdot (V + b)}$ $\qquad\qquad$ $V := Find(V)$

Calculation of Compressibility:

$$Z := \frac{P \cdot V}{R \cdot T}$$

Calculation of Enthalpy and Entropy:

$$HDEP := R \cdot T \cdot (Z - 1) + \frac{a(T) - \left(\dfrac{d}{dT} a(T)\right) \cdot T}{b} \cdot \ln\left(\frac{V}{V + b}\right) \qquad\qquad HIG := \int_{Tref}^{T} Cp(T)\,dT$$

$$SDEP := R \cdot \ln\left[\frac{Z \cdot (V - b)}{V}\right] - \frac{\dfrac{d}{dT} a(T)}{b} \cdot \ln\left(\frac{V}{V + b}\right) \qquad\qquad SIG := \int_{Tref}^{T} \frac{Cp(T)}{T}\,dT - R \cdot \ln\left(\frac{P}{Pref}\right)$$

$H := HIG + HDEP$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $S := SIG + SDEP$

Final Results:

$T = 173.15 \cdot K$ $\qquad$ $Z = 0.9952$

$P = 1 \cdot 10^5 \cdot Pa$ $\qquad$ $V = 0.014327 \quad \cdot m^3 \cdot mole^{-1}$

$\qquad\qquad\qquad\qquad$ $H = -3.60273 \cdot 10^3 \quad \cdot mole^{-1} \quad \cdot joule$

$\qquad\qquad\qquad\qquad$ $S = -15.62 \quad \cdot K^{-1} \cdot mole^{-1} \quad \cdot joule$

4.38 (also available as a Mathcad worksheet)

4.38 with the SRK equation

Property Data
(T in K, P in bar):
$\qquad$ $Tc := 126.2 \quad Pc := 33.94 \quad om := 0.04 \quad Cp_1 := 27.2 \quad Cp_2 := 4.2 \cdot 10^{-3}$

$$R := 0.00008314 \qquad kap := 0.480 + 1.574 \cdot om - 0.176 \cdot om \cdot om$$

Initial Conditions (Vt = total volume, m^3): $\qquad Ti := 170 \quad Pi := 100 \quad Vt := 0.15$

SRK Constants: $\qquad b := 0.08664 \cdot \dfrac{R \cdot Tc}{Pc} \qquad ac := 0.42748 \cdot \dfrac{R^2 \cdot Tc^2}{Pc}$

Initial temperature $\quad T := Ti$

Note that these are being defined as a function of temperature since we will need to interate on temperature later to obtain the final state of the system
$\qquad alf(T) := 1 \cdot \left[1 + kap \cdot \left(1 - \sqrt{\dfrac{T}{Tc}} \right) \right]^2$
$\qquad a(T) := ac \cdot alf(T)$

$$Da(T) := \frac{d}{dT} a(T)$$

Find initial molar volume and number of moles
Start with initial guess for volume, m³/mol
$\qquad V := \dfrac{R \cdot Ti}{Pi}$

Solve SRK EOS for initial volume $\qquad$ Given $\qquad Pi = \dfrac{R \cdot T}{V - b} - \dfrac{a(T)}{V \cdot (V + b)} \qquad Vi := Find(V)$

Initial molar volume and number of moles $\qquad Vi = 1.02 \cdot 10^{-4} \qquad Ni := \dfrac{Vt}{Vi} \qquad Ni = 1.471 \cdot 10^3$

Entropy departure at the initial conditions $\qquad DELSi := \left[R \cdot \ln \left[(Vi - b) \cdot \dfrac{Pi}{R \cdot T} \right] + \dfrac{Da(T)}{b} \cdot \ln \left(\dfrac{Vi + b}{Vi} \right) \right] \cdot 10^5$

Now consider final state $\qquad Nf := Ni - 10 \cdot 50 \quad Vf := \dfrac{0.15}{Nf} \qquad V := Vf$

Type out final number of moles and specific volume $\qquad Nf = 971.269 \qquad Vf = 1.544 \cdot 10^{-4}$

Final pressure, will change in course of solving for the final temperature $\qquad Pf(T) := \dfrac{R \cdot T}{V - b} - \dfrac{a(T)}{V \cdot (V + b)}$

Entropy departure at final conditions $\qquad DELS(T) := \left[R \cdot \ln \left[(V - b) \cdot \dfrac{Pf(T)}{R \cdot T} \right] + \dfrac{Da(T)}{b} \cdot \ln \left(\dfrac{V + b}{V} \right) \right] \cdot 10^5$

Solve for final temperature using S(final) - S(initial) = 0 $\qquad$ GIVEN

$$0 = Cp_1 \cdot \ln \left(\dfrac{T}{Ti} \right) + Cp_2 \cdot (T - Ti) - R \cdot 10^5 \cdot \ln \left(\dfrac{Pf(T)}{Pi} \right) + DELS(T) - DELSi$$

$\qquad T := FIND(T)$

Type out solution $\qquad V = 1.544 \cdot 10^{-4} \qquad\qquad T = 131.34 \qquad Pf(T) = 37.076$

4.39 (also available as a Mathcad worksheet)

Problem 4.39

Critical properties for carbon dioxide:

$Tc := 304.2$ K $\qquad Pc := 7.376 \cdot 10^6$ Pa $\qquad \omega := 0.225$

Soave-Redlich-Kwong Equation of State and Constants:

$R := 8.31451 \qquad \dfrac{joule}{K \cdot mol} \quad or \quad \dfrac{Pa \cdot m^3}{(K \cdot mol)} \qquad a1 := 0.42748 \cdot \left(\dfrac{R^2 \cdot Tc^2}{Pc} \right) \qquad b := 0.08664 \cdot \dfrac{R \cdot Tc}{Pc}$

$\alpha(T) := \left[1 + \left(0.480 + 1.574 \cdot \omega - 0.176 \cdot \omega^2 \right) \cdot \left(1 - \sqrt{\dfrac{T}{Tc}} \right) \right]^2 \qquad a(T) := a1 \cdot \alpha(T)$

$P(V, T) := \dfrac{R \cdot T}{V - b} - \dfrac{a(T)}{V \cdot (V + b)}$

Data given in the problem:

$T := (150 + 273.15)$ K $\qquad P1 := 50 \cdot 10^5$ Pa $\qquad P2 := 300 \cdot 10^5$ Pa $\qquad V1total := 100 \ m^3$

$V := R \cdot \dfrac{T}{P1} \qquad$ (Initial guess needed for solver)

Solving for the initial molar volume and the number of moles of carbon dioxide:

Given $\qquad P1 = P(V, T)$

$V1molar := Find(V) \qquad\qquad N := \dfrac{V1total}{V1molar} \qquad\qquad N = 1.518 \cdot 10^5 \qquad\qquad V1molar = 6.587 \cdot 10^{-4}$

Solving for the final molar volume and the final total volume:

$V := \dfrac{(R \cdot T)}{P2}$

Given $\qquad P2 = P(V, T)$

$V2molar := Find(V) \qquad\qquad V2molar = 9.805 \cdot 10^{-5}$

$V2total := V2molar \cdot N \qquad\qquad$ (i) $V2total = 14.885$

Calculating the amount of work done to compress the gas:

$Work := N \cdot \displaystyle\int_{V1molar}^{V2molar} -P(V, T) \, dV \qquad\qquad$ (ii) $Work = 8.823 \cdot 10^8 \qquad joule$

Since the temperature is constant, the change in enthalpy, H(T, P2) - H(T,P1), is just equal to Hdep(T,P2) - Hdep(T,P1) :

$Hdep(T, P) := R \cdot T \cdot \left(\dfrac{P \cdot V}{R \cdot T} - 1 \right) + \dfrac{a(T) - T \cdot \dfrac{d}{dT} a(T)}{b} \cdot \ln\left(\dfrac{V}{V + b} \right)$

$H(T, P) := Hdep(T, P) \qquad\qquad H(T, P2) = -4.382 \cdot 10^3 \qquad\qquad H(T, P1) = -7.314 \cdot 10^3$

$Q := N \cdot ((H(T, P2) - H(T, P1)) - (P2 \cdot V2molar - P1 \cdot V1molar)) - Work$

$Q = -3.837 \cdot 10^8 \qquad joule$

4.40 (also available as a Mathcad worksheet)

Problem 4.40

Critical properties and heat capacity for ethylene:

$Tc := 282.4$ K $Pc := 5.036 \cdot 10^6$ Pa $\omega := 0.085$

$Ca := 3.950$ $Cb := 15.628 \cdot 10^{-2}$ $Cc := -8.339 \cdot 10^{-5}$ $Cd := 17.657 \cdot 10^{-9}$

Soave-Redlich-Kwong Equation of State and Constants:

$$R := 8.31451 \quad \frac{J}{mol \cdot K} \qquad a1 := 0.42748 \cdot \left(\frac{R^2 \cdot Tc^2}{Pc}\right) \qquad \alpha(T) := \left[1 + \left(0.480 + 1.574 \cdot \omega - 0.176 \cdot \omega^2\right) \cdot \left(1 - \sqrt{\frac{T}{Tc}}\right)\right]^2$$

$$a(T) := a1 \cdot \alpha(T) \qquad b := 0.08664 \cdot \frac{R \cdot Tc}{Pc} \qquad P(V, T) := \frac{R \cdot T}{V - b} - \frac{a(T)}{V \cdot (V + b)}$$

$T1 := (100 + 273.15)$ K $P1 := 30 \cdot 10^5$ Pa

$T2 := (150 + 273.15)$ K $P2 := 20 \cdot 10^5$ Pa

$V := \frac{(R \cdot T1)}{P1}$ (Initial guess for solver)

Solving for the initial and final molar volume (Only one root is possible for each volume because both temperatures are above the critical temperature):

Given $P1 = P(V, T1)$

$V1 := Find(V)$ $V1 = 9.501 \cdot 10^{-4}$ m^3

Given $P2 = P(V, T1)$

$V2 := Find(V)$ $V2 = 1.467 \cdot 10^{-3}$ m^3

Defining the reference state as P=1 bar, and T=300 K :

$$Hig(T) := \int_{300}^{T} \left(Ca + Cb \cdot TT + Cc \cdot TT^2 + Cd \cdot TT^3\right) d TT$$

$$Hdep(T, P, V) := R \cdot T \cdot \left(\frac{P \cdot V}{R \cdot T} - 1\right) + \frac{a(T) - T \cdot \frac{d}{dT} a(T)}{b} \cdot \ln\left(\frac{V}{V + b}\right)$$

$H(T, P, V) := Hdep(T, P, V) + Hig(T)$

$Q := H(T2, P2, V2) - H(T1, P1, V1)$

$Q = 2.64 \cdot 10^3$ joule

4.41   (also available as a Mathcad worksheet)

Problem 4.41 Soave-Redlich Kwong EOS with MATHCAD

$mol := 1$ $bar := 101300 \cdot Pa$

$RE := 8.314 \cdot \dfrac{joule}{mol \cdot K}$ $RG := 0.00008314 \cdot \dfrac{bar \cdot m^3}{mol \cdot K}$

Property Data $Tc := 304.2 \cdot K$ $Pc := 73.76 \cdot bar$ $om := 0.225$
(T in K, P in bar):

$kap := 0.480 + 1.574 \cdot om - 0.176 \cdot om \cdot om$

Initial Conditions: $Ti := 400 \cdot K$ $Pi := 50 \cdot bar$

SRK Constants: $b := 0.08664 \cdot \dfrac{RG \cdot Tc}{Pc}$ $ac := 0.42748 \cdot \dfrac{RG^2 \cdot Tc^2}{Pc}$

Initial temperature $T := Ti$

Note that these are being defined as a
function of temperature since we will need to
interate on temperature later to obtain the final
state of the system

$alf(T) := 1 \cdot \left[1 + kap \cdot \left(1 - \sqrt{\dfrac{T}{Tc}} \right) \right]^2$ $a(T) := ac \cdot alf(T)$

$Da(T) := \dfrac{d}{dT} a(T)$

Heat capacity $Cp1 := 22.243 \cdot \dfrac{joule}{mol \cdot K}$ $Cp2 := 5.977 \cdot 10^{-2} \cdot \dfrac{joule}{mol \cdot K}$
constants

$Cp3 := -3.499 \cdot 10^{-5} \cdot \dfrac{joule}{mol \cdot K}$ $Cp4 := 7.464 \cdot 10^{-9} \cdot \dfrac{joule}{mol \cdot K}$

Find initial molar volume and number of moles $V := \dfrac{RG \cdot Ti}{Pi}$ $V = 6.6512 \bullet 10^{-4} \bullet m^3$
Start with initial guess for volume, m^3/mol

Solve SRK EOS for initial volume   Given $Pi = \dfrac{RG \cdot T}{V - b} - \dfrac{a(T)}{V \cdot (V + b)}$ $Vi := Find(V)$

$Vi = 6.09602 \bullet 10^{-4} \bullet m^3$

Entropy departure at the $DELSi := \left[\ln \left[(Vi - b) \cdot \dfrac{Pi}{RG \cdot T} \right] + \dfrac{Da(T)}{b \cdot RG} \cdot \ln \left(\dfrac{Vi + b}{Vi} \right) \right] \cdot RE$
initial conditions

$DELSi = -2.37467 \bullet K^{-1} \bullet joule$ $Zi := \dfrac{Pi \cdot Vi}{RG \cdot T}$ $Zi = 0.91653$

$DelHi := RE \cdot T \cdot (Zi - 1) + \dfrac{\left(T \cdot \dfrac{d}{dT} a(T) - a(T) \right)}{b} \cdot \ln \left(\dfrac{Zi + \dfrac{b \cdot Pi}{RG \cdot T}}{Zi} \right)$

$DelHi = -1.24253 \bullet 10^3 \bullet joule$

Final temperature is 300 K, and final pressure is unknown; will be found by equating the initial and final
entropies. Guess final temperature is 10 bar

$Pf := 10 \cdot bar$ $T := 300 \cdot K$ $V := \dfrac{RG \cdot T}{Pf}$ $V = 2.4942 \bullet 10^{-3} \bullet m^3$

Temperature part of ideal gas entropy change

$$ti := 400 \qquad tf := 300$$

$$DSidealT := Cp1 \cdot \ln\left(\frac{tf}{ti}\right) + Cp2 \cdot (tf - ti) + \frac{Cp3}{2} \cdot \left(tf^2 - ti^2\right) + \frac{Cp4}{3} \cdot \left(tf^3 - ti^3\right)$$

$$DSidealT = {}^{-}11.24332 \cdot K^{-1} \cdot joule$$

Note: To use the given and find commands for variable with different dimensions such as P and V, will have to convert to dimensionless variables so as not to have a units conflict. Define x=V/b and y=P/Pc

initial guess $\qquad x := \dfrac{V}{b} \qquad x = 83.95847 \qquad\qquad\qquad y := 0.5$

Given

$$y \cdot Pc = \frac{RG \cdot 300 \cdot K}{x \cdot b - b} - \frac{a(300 \cdot K)}{x \cdot b \cdot (x \cdot b + b)}$$

$$0 = DSidealT - RE \cdot \ln\left(\frac{y \cdot Pc}{Pi}\right) + \left[\ln\left[(x \cdot b - b) \cdot \frac{y \cdot Pc}{RG \cdot 300 \cdot K}\right] + \frac{Da(300 \cdot K)}{b \cdot RG} \cdot \ln\left(\frac{x+1}{x}\right)\right] \cdot RE - DELSi$$

$$Y := FIND(x, y) \qquad Y = \begin{bmatrix} 53.6541 \\ 0.19654 \end{bmatrix}$$

$$Vf := Y_0 \cdot b \qquad\qquad Vf = 1.59393 \cdot 10^{-3} \cdot m^3$$

$$Pf := Y_1 \cdot Pc \qquad\qquad Pf = 1.46849 \cdot 10^6 \cdot Pa$$

$$\frac{Pf}{bar} = 14.49643 \qquad \text{Fraction mass remaining in tank} = \quad \frac{Vi}{Vf} = 0.38245$$

4.42 (also available as a Mathcad worksheet. In fact, this file contain graphs and other information.)

Easier to work with $\left(\dfrac{\partial C_V}{\partial \underline{V}}\right)_T = T\left(\dfrac{\partial^2 P}{\partial T^2}\right)_V$ than with $\left(\dfrac{\partial C_P}{\partial P}\right)_T = -T\left(\dfrac{\partial^2 \underline{V}}{\partial T^2}\right)_P$.

$$C_V(V,T) - C_V(V = \infty, T) = C_V(V,T) - C_V^*(T) = \int_{\underline{V}=\infty}^{\underline{V}} T\left(\frac{\partial^2 P}{\partial T^2}\right) d\underline{V}$$

$$= 0.75\frac{a}{T^{3/2}} \ln\frac{\underline{V}+b}{\underline{V}}\Bigg|_{\underline{V}=\infty}^{\underline{V}} = 0.75\frac{a}{T^{3/2}} \ln\left(\frac{\underline{V}+b}{\underline{V}}\right)$$

So $C_V(V,T) = C_V^*(T) + 0.75\dfrac{a}{T^{3/2}b}\ln\left(\dfrac{V+b}{V}\right)$. Clearly as $V \to \infty$ (ideal gas) we

recover $C_V = C_V^*$.

Procedure: Choose collection of V's

Calculate $C_V - C_V^*$ for given V and T

Calculate P from RK EOS get $C_V - C_V^*$ vs. P

Next use

$$C_P = C_V - T\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V^2 = C_V - T\frac{(\partial P/\partial T)_V^2}{(\partial P/\partial V)_T}$$

to convert from C_V to C_P. Have done both parts using MATHCAD. See the MATHCAD F file.

4.43   (also available as a Mathcad worksheet)

a) $P = \dfrac{RT}{V-b} - \dfrac{a}{\sqrt{T}V(V+b)}$; $\dfrac{PV}{RT} = 1 + \dfrac{B}{V} + \dfrac{C}{V^2} + \cdots = Z$

$Z = \dfrac{PV}{RT} = \dfrac{V}{V-b} - \dfrac{V}{RT}\dfrac{a}{\sqrt{T}V(V+b)} = \dfrac{V}{V-b} - \dfrac{a}{RT^{3/2}(V+b)}$

$\quad = \dfrac{1}{1-b/V} - \dfrac{a/V}{RT^{3/2}(1+b/V)} = \dfrac{1}{1-b/V} - \dfrac{a/V}{RT^{3/2}(1+b/V)}$

Now expanding in a power series in $\dfrac{1}{V}$

$Z = 1 + b/V - \dfrac{a/V}{RT^{3/2}} = 1 + \left(b - \dfrac{a}{RT^{3/2}}\right)\dfrac{1}{V}$

$B = b - \dfrac{a}{RT^{3/2}}$; $B = 0$; $b = \dfrac{a}{RT_B^{3/2}}$

$T_B^{3/2} = \dfrac{a}{bR} \Rightarrow T_B = \left(\dfrac{a}{bR}\right)^{2/3} = 876.5\text{ K}$

b) Using the Redlich-Kwong parameters

$T_B = \left(\dfrac{a}{bR}\right)^{2/3} = 876.5\text{ K}$

4.44   (also available as a Mathcad worksheet)

$Z = \dfrac{V}{V-b} - \dfrac{a}{RT^{3/2}(V+b)}$

$$\left(\frac{\partial Z}{\partial P}\right)_T = \frac{1}{\underline{V}-b}\left(\frac{\partial \underline{V}}{\partial P}\right)_T - \frac{\underline{V}}{(\underline{V}-b)^2}\left(\frac{\partial \underline{V}}{\partial P}\right)_T + \frac{a}{RT^{3/2}(V+b)^2}\left(\frac{\partial \underline{V}}{\partial P}\right)_T$$

$$P = \frac{RT}{\underline{V}-b} - \frac{a}{\sqrt{T}\left(V^2+b\underline{V}\right)}$$

$$\left(\frac{\partial P}{\partial \underline{V}}\right)_T = -\frac{RT}{(\underline{V}-b)^2} + \frac{a}{\sqrt{T}\left(\underline{V}^2+b\underline{V}\right)^2}\cdot(2\underline{V}+b)$$

$$\lim_{\substack{P\to 0 \\ \underline{V}\to\infty}}\left(\frac{\partial P}{\partial \underline{V}}\right)_T = 0\ ;\ \lim_{\substack{P\to\infty \\ \underline{V}\to\infty}}\left(\frac{\partial P}{\partial \underline{V}}\right)_T = \infty$$

$$\lim_{\substack{P\to 0 \\ \underline{V}\to\infty}}\left(\frac{\partial Z}{\partial P}\right)_T = 0 = \left[\frac{1}{\underline{V}-b} - \frac{\underline{V}}{(\underline{V}-b)^2} + \frac{a}{RT^{3/2}(\underline{V}+b)^2}\right]\left(\frac{\partial \underline{V}}{\partial P}\right)_T$$

$$\left(\frac{\partial Z}{\partial P}\right)_T = \frac{[1/(\underline{V}-b)] - \{\underline{V}/[(\underline{V}-b)^2]\} + \{a/[RT^{3/2}(\underline{V}+b)^2]\}}{\{-RT/[(\underline{V}-b)^2]\} + \{a/[\sqrt{T}(\underline{V}^2+b\underline{V})^2]\}(2\underline{V}+b)}$$

$$\lim_{\substack{P\to\infty \\ \underline{V}\to b}}\left(\frac{\partial Z}{\partial P}\right)_T = \frac{[\underline{V}-b-\underline{V}]/[(\underline{V}-b)^2]}{-RT/[(\underline{V}-b)^2]} = \frac{b}{RT}$$

$$\lim_{\substack{P\to 0 \\ \underline{V}\to\infty}}\left(\frac{\partial Z}{\partial P}\right)_T = \frac{[1/\underline{V}]-[1/\underline{V}]+[a/(RT^{3/2}\underline{V})]}{[-RT/(\underline{V})^2]+[a/(\sqrt{T}\underline{V}^4)]\cdot 2\underline{V}}$$

$$= \frac{a/(RT^{3/2}\underline{V}^2)}{-RT/\underline{V}^2} = -\frac{a\underline{V}^2}{RT^{3/2}\underline{V}^2} = -\frac{a}{RT^{3/2}}$$

4.45 a) The Redlich-Kwong equation of state is

$$P = \frac{RT}{\underline{V}-b} - \frac{a}{\sqrt{T}\underline{V}(\underline{V}+b)}$$

which we rewrite as follows

$$\frac{P\underline{V}}{RT} = \frac{\underline{V}}{\underline{V}-b} - \frac{a}{RT^{1.5}(\underline{V}+b)} \quad \text{so that}$$

$$\frac{P\underline{V}}{RT} - 1 = \frac{\underline{V}}{\underline{V}-b} - 1 - \frac{a}{RT^{1.5}(\underline{V}+b)} = \frac{b}{\underline{V}-b} - \frac{a}{RT^{1.5}(\underline{V}+b)} \quad \text{and}$$

$$\underline{V}\left(\frac{P\underline{V}}{RT}-1\right) = b\frac{\underline{V}}{\underline{V}-b} - \frac{a}{RT^{1.5}}\frac{\underline{V}}{\underline{V}+b}$$

$$\text{Lim}_{P\to 0}\underline{V}\left(\frac{P\underline{V}}{RT}-1\right) = \text{Lim}_{\underline{V}\to\infty}\underline{V}\left(\frac{P\underline{V}}{RT}-1\right) = \text{Lim}_{\underline{V}\to\infty}\left[b\frac{\underline{V}}{\underline{V}-b} - \frac{a}{RT^{1.5}}\frac{\underline{V}}{\underline{V}+b}\right] = b - \frac{a}{RT^{1.5}} = B(T)$$

To proceed further, we now need to have expressions for a and b in terms of the critical properties. To obtain these we proceed as in Problem 4.35 and rewrite this in the power series of $\underline{V}$

$$\underline{V}^3 - \frac{RT}{P}\underline{V}^2 + \left(-b^2 - \frac{RT}{P}b - \frac{a}{\sqrt{T}P}\right)\underline{V} - \frac{ab}{\sqrt{T}P} = 0$$

Notice that the three roots of volume at the critical point are identical so we can write

$$\left(\underline{V} - \underline{V}_C\right)^3 = 0 \qquad \text{or}$$
$$\underline{V}^3 - 3\underline{V}_C\underline{V}^2 + 3\underline{V}_C^2\underline{V} - \underline{V}_C^3 = 0$$

At critical point, the second and fourth equations must be satisfied simultaneously. Consequently, the coefficients of each power of $\underline{V}$ must be the same. Thus,

$$3\underline{V}_C = \frac{RT_C}{P_C}$$

$$3\underline{V}_C^2 = -b^2 - \frac{RT_C}{P_C}b - \frac{a}{\sqrt{T_C}P_C} \qquad \text{and}$$

$$\underline{V}_C^3 = \frac{a}{\sqrt{T_C}P_C}b$$

Solving the above three equations together for $a(T)$, b and $\underline{V}c$, we get

$$\underline{V}_C = \frac{RT_C}{3P_C}$$

$$b = \left(\sqrt[3]{2} - 1\right)\underline{V}_C = 0.08664\frac{RT_C}{P_C} \qquad \text{and}$$

$$a = 0.42748\frac{R^2 T_C^{2.5}}{P_C}$$

So $B(T) = b - \dfrac{a}{RT^{1.5}} = 0.08664\dfrac{RT_C}{P_C} - 0.42748\dfrac{RT_C^{2.5}}{P_C T^{1.5}}$

For n-pentane, T_C=469.6 K and P_C = 33.74 bar

The resulting virial coefficient as a function of temperature is shown below.
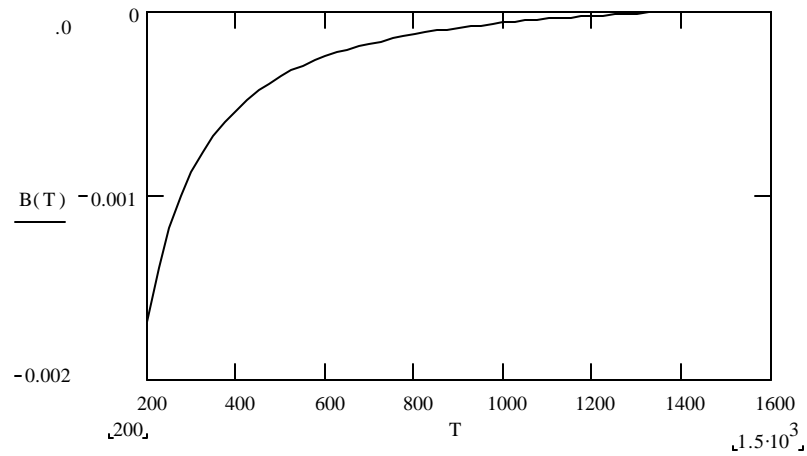
4.46   Inversion temperature $\mu = 0 = \left(\dfrac{\partial T}{\partial P}\right)_{\underline{H}} = -\dfrac{\underline{V}}{C_P}[1 - T\alpha] \Rightarrow \alpha T = 1$

$\alpha = \dfrac{1}{\underline{V}}\left(\dfrac{\partial \underline{V}}{\partial T}\right)_P$ but $\left(\dfrac{\partial \underline{V}}{\partial T}\right)_P\left(\dfrac{\partial P}{\partial \underline{V}}\right)_T\left(\dfrac{\partial T}{\partial P}\right)_{\underline{V}} = -1$ by triple product rule.

$$\left(\dfrac{\partial \underline{V}}{\partial T}\right)_P = \dfrac{-1}{(\partial P/\partial \underline{V})_T(\partial T/\partial P)_{\underline{V}}} = -\dfrac{(\partial P/\partial T)_{\underline{V}}}{(\partial P/\partial \underline{V})_T}$$

(a) vdW EOS; $P = \dfrac{RT}{\underline{V} - b} - \dfrac{a}{\underline{V}^2}$; $\left(\dfrac{\partial P}{\partial T}\right)_{\underline{V}} = \dfrac{R}{\underline{V} - b}$

$\left(\dfrac{\partial P}{\partial \underline{V}}\right)_T = -\dfrac{RT}{(\underline{V} - b)^2} + \dfrac{2a}{\underline{V}^3}$

$\left(\dfrac{\partial \underline{V}}{\partial T}\right)_P = \dfrac{-R/(\underline{V} - b)}{\left\{(-RT)\big/\big[(\underline{V} - b)^2\big]\right\} + \big[2a/\underline{V}^3\big]}$

$\alpha = \dfrac{1}{\underline{V}}\left(\dfrac{\partial \underline{V}}{\partial T}\right)_P = \dfrac{\left\{-R\big/\big[\underline{V}(\underline{V} - b)\big]\right\}}{\left\{-RT\big/\big[(\underline{V} - b)^2\big]\right\} + \big[2a/\underline{V}^3\big]}$

$T\alpha = 1$; $\dfrac{-RT\big/\big[\underline{V}(\underline{V} - b)\big]}{\left\{-RT\big/\big[(\underline{V} - b)^2\big]\right\} + \big[2a/\underline{V}^3\big]} = 1$

$$\frac{RT}{\underline{V}(\underline{V}-b)} = \frac{RT}{(\underline{V}-b)^2} - \frac{2a}{\underline{V}^3}$$

$$TR\left[\frac{1}{\underline{V}(\underline{V}-b)} - \frac{1}{(\underline{V}-b)^2}\right] = -\frac{2a}{\underline{V}^3}$$

$$\frac{TR}{\underline{V}(\underline{V}-b)^2}[V-b-V] = -\frac{2a}{\underline{V}^3}$$

$$\frac{bRT}{\underline{V}(\underline{V}-b)^2} = \frac{2a}{\underline{V}^3}$$

$$T = \frac{2a}{bR}\frac{(\underline{V}-b)^2}{\underline{V}^2} = \frac{2a}{bR}\left(1-\frac{b}{\underline{V}}\right)^2 \tag{1}$$

also $P = \dfrac{RT}{\underline{V}-b} - \dfrac{a}{\underline{V}^2}$ (2)

Choose V

Calculate T_{inv} from Eqn. (1)

Calculate P from Eqn. (2)

Solution done with MATHCAD (see MATHCAD worksheet).

(b) RK EOS

$$P = \frac{RT}{\underline{V}-b} - \frac{a}{\sqrt{T}\underline{V}(\underline{V}+b)}$$

$$\left(\frac{\partial P}{\partial \underline{V}}\right)_T = -\frac{RT}{(\underline{V}-b)^2} + \frac{a}{\sqrt{T}\underline{V}^2(\underline{V}+b)} + \frac{a}{\sqrt{T}\underline{V}(\underline{V}+b)^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} = \frac{R}{\underline{V}-b} + \frac{(1/2)a}{T^{3/2}\underline{V}(\underline{V}+b)}$$

$$\boldsymbol{a} = \frac{1}{\underline{V}}\left(\frac{\partial \underline{V}}{\partial T}\right)_P = -\frac{1}{\underline{V}}\frac{(\partial P/\partial T)_{\underline{V}}}{(\partial P/\partial \underline{V})_T}$$

$$= \frac{1}{\underline{V}}\frac{-\{[R/(\underline{V}-b)]+[(1/2)a]/[T^{3/2}\underline{V}(\underline{V}+b)]\}}{-\{RT/[(\underline{V}-b)^2]\}+\{a/[\sqrt{T}\underline{V}^2(\underline{V}+b)]\}+\{a/[\sqrt{T}\underline{V}(\underline{V}+b)^2]\}}$$

$$T\boldsymbol{a} = 1$$

$$\frac{-RT}{\underline{V}(\underline{V}-b)} - \frac{(1/2)a}{T^{1/2}\underline{V}^2(\underline{V}+b)} = -\frac{RT}{(\underline{V}-b)^2} + \frac{a}{\sqrt{T}\underline{V}^2(\underline{V}+b)} + \frac{a}{\sqrt{T}\underline{V}(\underline{V}+b)^2}$$

$$-\frac{RT}{\underline{V}-b}\left[\frac{1}{\underline{V}} - \frac{1}{\underline{V}-b}\right] = \frac{a}{\sqrt{T}\underline{V}(\underline{V}+b)}\left[\frac{1}{\underline{V}} + \frac{1}{\underline{V}+b} + \frac{1/2}{\underline{V}}\right]$$

$$-\frac{RT}{\underline{V}-b}\left[\frac{\underline{V}-b-\underline{V}}{\underline{V}(\underline{V}-b)}\right] = \frac{RTb}{\underline{V}(\underline{V}-b)^2} = \frac{a}{\sqrt{T}\underline{V}(\underline{V}+b)}\left[\frac{(3/2)(\underline{V}+b)+\underline{V}}{\underline{V}(\underline{V}+b)}\right]$$

$$\frac{RTb}{V(V-b)^2} = \frac{a}{2\sqrt{T}V(V+b)}\frac{5V+3b}{V(V+b)}$$

$$\frac{RTb}{(V-b)^2} = \frac{a(5V+3b)}{2\sqrt{T}V(V+b)^2}$$

$$T^{3/2} = \frac{a(5V+3b)}{2V(V+b)^2}\frac{(V-b)^2}{Rb}$$

$$T = \left\{\frac{a}{2Rb}\left[5+3\frac{b}{V}\right]\frac{(V-b)^2}{(V+b)^2}\right\}^{2/3}$$

4.47   Sorry, in the first printing this problem was misplaced. It is Problem 5.47, and the solution appears in Chapter 5 of the solution manual.

The replacement problem is
"Repeat the calculation of Problem 4.31 with the Soave version of the Redlich-Kwong equation."
The solution is as follows:
   Using a Mathcad program for the Soave-Redlich-Kwong EOS we find
   $\underline{H}(300°\,C,\ 25\ bar) = 9.45596 \times 10^3$ J/mol

   (relative to ideal gas at 273.15 K and 1 bar).
   Now by trial and error until enthalpies match
   $$\underline{H}(274.5°\,C,\ 1\ bar) = 9.45127 \times 10^3$$
   $$\underline{H}(274.6°C,\ 1\ bar) = 9.45486 \times 10^3 \qquad \Rightarrow T = 274.6°C$$
                  Close enough

Note that this solution is only very slightly different from that obtained with the Peng-Robinson equation (274.1oC compared to 274.6oC obtained here).

4.48   (also available as a Mathcad worksheet)

Problem 4.48   Peng-Robinson EOS with MATHCAD

$mol := 1$ $bar := 101300 \cdot Pa$ $RE := 8.314 \cdot \dfrac{joule}{mol \cdot K}$ $RG := 0.00008314 \cdot \dfrac{bar \cdot m^3}{mol \cdot K}$

Property Data $Tc := 5.19 \cdot K$ $Pc := 2.27 \cdot bar$ $om := -0.387$ $Cp := 2.5 \cdot RE$
(T in K, P in bar):
                                        $kap := 0.37464 + 1.54226 \cdot om - 0.26992 \cdot om \cdot om$

Initial Conditions and total volume Vt: $Ti := 298 \cdot K$ $Pi := 400 \cdot bar$ $Vt := 0.045 \cdot m^3$

Peng-Robinson Constants: $b := 0.07780 \cdot \dfrac{RG \cdot Tc}{Pc}$ $ac := 0.45724 \cdot \dfrac{RG^2 \cdot Tc^2}{Pc}$

Initial temperature $T := Ti$

Note that these are being defined as a
function of temperature since we will need to $alf(T) := 1 \cdot \left[1 + kap \cdot \left\{1 - \sqrt{\dfrac{T}{Tc}}\right\}\right]^2$
interate on temperature later to obtain the final
state of the system $a(T) := ac \cdot alf(T)$

                                                                           $Da(T) := \dfrac{d}{dT} a(T)$

Find initial molar volume and number of moles
Start with initial guess for volume, m^3/mol

$$V := \frac{RG \cdot Ti}{Pi}$$

$$V = 6.19393 \cdot 10^{-5} \cdot m^3$$

Solve P-R EOS for initial volume   Given

$$Pi = \frac{RG \cdot T}{V - b} - \frac{a(T)}{V \cdot (V + b) + b \cdot (V - b)}$$

$$Vi := Find(V)$$

Initial molar volume and number of moles

$$Vi = 7.10667 \cdot 10^{-5} \cdot m^3$$

$$N := \frac{Vt}{Vi}$$

$$N = 633.20762$$

Entropy departure at the initial conditions

$$DELSi := \left[\ln\left[(Vi - b) \cdot \frac{Pi}{RG \cdot T} \right] + \frac{Da(T)}{2 \cdot \sqrt{2} \cdot b \cdot RG} \cdot \ln\left[\frac{Vi + \left(1 + \sqrt{2}\right) \cdot b}{Vi + \left(1 - \sqrt{2}\right) \cdot b} \right] \right] \cdot RE$$

$$DELSi = 0.0151 \cdot K^{-1} \cdot joule$$

$$Zi := \frac{Pi \cdot Vi}{RG \cdot T}$$

$$Zi = 1.14736$$

$$DelHi := RE \cdot T \cdot (Zi - 1) + \frac{T \cdot \frac{d}{dT} a(T) - a(T)}{2 \cdot \sqrt{2} \cdot b} \cdot \ln\left[\frac{Zi + \left(1 + \sqrt{2}\right) \cdot \frac{b \cdot Pi}{RG \cdot T}}{Zi + \left(1 - \sqrt{2}\right) \cdot \frac{b \cdot Pi}{RG \cdot T}} \right]$$

$$DelHi = 274.27781 \cdot joule$$

Final pressure is 1.013 bar, and final temperature is unknown; will be found by equating the initial and final entropies. Guess final temperature is 30 K

$$Pf := 1.013 \cdot bar \qquad T := 25.7 \cdot K \qquad V := \frac{RG \cdot T}{Pf}$$

$$V = 2.10928 \cdot 10^{-3} \cdot m^3$$

Note: To use the given and find command for variables with different dimensions such as T and V, will have to convert to dimensionless variables so as not to get a units conflict. Define x=V/b, y=T/Tc

initial guess $x := 10 \quad y := 5$

Given

$$Pf = \frac{RG \cdot y \cdot Tc}{x \cdot b - b} - \frac{a(y \cdot Tc)}{x \cdot b \cdot (x \cdot b + b) + b \cdot (x \cdot b - b)}$$

$$0 = Cp \cdot \ln\left(\frac{y \cdot Tc}{Ti}\right) - RE \cdot \ln\left(\frac{Pf}{Pi}\right) + \left[RE \cdot \ln\left[(x \cdot b - b) \cdot \frac{Pf}{RG \cdot y \cdot Tc} \right] + \frac{Da(y \cdot Tc) \cdot RE}{2 \cdot \sqrt{2} \cdot b \cdot RG} \cdot \ln\left[\frac{x \cdot b + \left(1 + \sqrt{2}\right) \cdot b}{x \cdot b + \left(1 - \sqrt{2}\right) \cdot b} \right] \right] - DELSi$$

$$Y := FIND(x, y) \qquad Y = \begin{bmatrix} 150.89161 \\ 5.27265 \end{bmatrix}$$

$$V := Y_0 \cdot b \qquad V = 2.2315 \cdot 10^{-3} \cdot m^3 \quad Tf := Y_1 \cdot Tc \qquad Tf = 27.36506 \cdot K \qquad \text{Final temperature}$$

$$Zf := \frac{Pf \cdot V}{RG \cdot T} \qquad Zf = 1.05794$$

$$DelHf := RE \cdot Tf \cdot (Zf - 1) + \frac{Tf \cdot \dfrac{d}{dTf}a(Tf) - a(Tf)}{2 \cdot \sqrt{2} \cdot b} \cdot \ln\left[\frac{Zf + \left(1 + \sqrt{2}\right) \cdot \dfrac{b \cdot Pf}{RG \cdot Tf}}{Zf + \left(1 - \sqrt{2}\right) \cdot \dfrac{b \cdot Pf}{RG \cdot Tf}}\right]$$

DelHf = 11.61232 •joule

Uf - Ui = (Hf - Zf*R*Tf) - (Hi - Zi*R*Ti) = Hf - Hi - Zf*R*Tf + Zi*R*Ti
   = (Hf-HfIG) + HfIG -(Hi - HiIG) -HiIG - Zf*R*Tf + Zi*R*Ti
   = DelHf - DelHi + Cp*(Tf-Ti) - Zf*R*Tf + Zi*R*Ti

$$DelU := (DelHf - DelHi + Cp \cdot (Tf - Ti) - Zf \cdot RE \cdot Tf + Zi \cdot RE \cdot Ti) \cdot N$$

DelU = $-2.08062 \cdot 10^6$ •joule

$$TNTeq := -\frac{DelU}{4600000 \cdot \dfrac{joule}{kg}} \qquad\qquad TNTeq = 0.45231 \cdot kg$$

4.49   (also available as a Mathcad worksheet)

PENG-ROBINSON EQUATION OF STATE CALCULATION   **Nitrogen**

The Property Data should be as follows
Tc (in K), Pc (in bar), omega, Tb (in K)
Cp1, Cp2, Cp3, Cp4   (In eqn Cp=Cp0+Cp1*T+Cp2*T^2+Cp3*T^3)
Tref (in K), Pref (in bar)   (reference conditions)

Note that in the 1st and 2nd printings, carbon dioxide was used as the fluid. This gave
unreasonable answers when this problem was revisited with the Peng-Robinson eqn.
of state, as both the initial and final states were found to be in the liquid state. Therefore
from the 3rd printing on, the fluid has been changed to nitrogen.

$i := 0, 1 .. 3$ $R := 0.00008314$

$Cp_0 := 28.883$ $Cp_1 := -0.157 \cdot 10^{-2}$ $Cp_2 := 0.808 \cdot 10^{-5}$ $Cp_3 := -2.871 \cdot 10^{-9}$

$Tc := 126.2$ $Pc := 33.94$ $om := 0.04$

$Trs := 273.15$ $Prs := 1.0$

$kap := 0.37464 + 1.54226 \cdot om - 0.26992 \cdot om \cdot om$

Peng-Robinson Constants: $b := 0.07780 \cdot \dfrac{R \cdot Tc}{Pc}$ $ac := 0.45724 \cdot \dfrac{R^2 \cdot Tc^2}{Pc}$

Input temperature and pressure of calculation $T := 298.15$ K, $P := 140$ bar

$$alf(T) := 1 \cdot \left[1 + kap \cdot \left(1 - \sqrt{\frac{T}{Tc}} \right) \right]^2 \qquad a(T) := ac \cdot alf(T) \qquad CA(T,P) := \frac{a(T) \cdot P}{(R \cdot T)^2} \qquad CB(T,P) := \frac{P \cdot b}{R \cdot T}$$

$$Da(T) := \frac{d}{dT} a(T)$$

$$Z(T,P) := \begin{array}{|l}
A \leftarrow CA(T,P) \\
B \leftarrow CB(T,P) \\
\\
V \leftarrow \begin{bmatrix} -\left(A \cdot B - B^2 - B^3\right) \\ A - 3 \cdot B^2 - 2 \cdot B \\ -(1 - B) \\ 1 \end{bmatrix} \\
\\
ZZ \leftarrow polyroots(V) \\
\text{for } i \in 0..2 \\
\quad \left(ZZ_i \leftarrow 0 \right) \text{ if } \left(Im\left(ZZ_i\right) \neq 0 \right) \\
ZZ \leftarrow sort(ZZ) \\
ZZ_0 \leftarrow ZZ_2 \text{ if } \left(\left| ZZ_0 \right| < 10^{-5} \right) \\
ZZ_2 \leftarrow ZZ_0 \text{ if } \left(\left| ZZ_2 \right| < 10^{-5} \right) \\
ZZ
\end{array}$$

Vector of coefficients in the PR equation in the form
0=-(A*B-B^2-B^3)+(A-3*B^2-2*B)*Z-(1-B)*Z^2+Z^3

Solution to the cubic

Set any imaginary roots to zero
Sort the roots

Set the value of any imaginary roots to value of the real root

Calculate molar volumes

$$VL(T,P) := \frac{Z(T,P)_0 \cdot R \cdot T}{P} \cdot 10^3 \qquad VV(T,P) := \frac{Z(T,P)_2 \cdot R \cdot T}{P} \cdot 10^3$$

Fugacity expressions [actually ln(f/P)] for the liquid fl and vapor fv

$$fl(T,P) := \left(Z(T,P)_0 - 1 \right) - \ln\left(Z(T,P)_0 - CB(T,P) \right) - \frac{CA(T,P)}{2 \cdot \sqrt{2} \cdot CB(T,P)} \cdot \ln\left[\frac{Z(T,P)_0 + \left(1 + \sqrt{2}\right) \cdot CB(T,P)}{Z(T,P)_0 + \left(1 - \sqrt{2}\right) \cdot CB(T,P)} \right]$$

$$fv(T,P) := \left(Z(T,P)_2 - 1 \right) - \ln\left(Z(T,P)_2 - CB(T,P) \right) - \frac{CA(T,P)}{2 \cdot \sqrt{2} \cdot CB(T,P)} \cdot \ln\left[\frac{Z(T,P)_2 + \left(1 + \sqrt{2}\right) \cdot CB(T,P)}{Z(T,P)_2 + \left(1 - \sqrt{2}\right) \cdot CB(T,P)} \right]$$

$phil(T,P) := \exp(fl(T,P))$ $phiv(T,P) := \exp(fv(T,P))$

$fugl(T,P) := P \cdot phil(T,P)$ $fugv(T,P) := P \cdot phiv(T,P)$

Residual entropy for liquid (DELSL) and vapor (DELSV) phases

$$\text{DELSL}(T, P) := \left[R \cdot \ln\left(Z(T, P)_0 - CB(T, P) \right) + \frac{Da(T)}{2 \cdot \sqrt{2} \cdot b} \cdot \ln\left[\frac{Z(T, P)_0 + \left(1 + \sqrt{2}\right) \cdot CB(T, P)}{Z(T, P)_0 + \left(1 - \sqrt{2}\right) \cdot CB(T, P)} \right] \right] \cdot 10^5$$

$$\text{DELSV}(T, P) := \left[R \cdot \ln\left(Z(T, P)_2 - CB(T, P) \right) + \frac{Da(T)}{2 \cdot \sqrt{2} \cdot b} \cdot \ln\left[\frac{Z(T, P)_2 + \left(1 + \sqrt{2}\right) \cdot CB(T, P)}{Z(T, P)_2 + \left(1 - \sqrt{2}\right) \cdot CB(T, P)} \right] \right] \cdot 10^5$$

Residual enthalpy for liquid (DELHL) and vapor (DELHV) phases

$$\text{DELHL}(T, P) := \left[R \cdot T \cdot \left(Z(T, P)_0 - 1 \right) + \frac{T \cdot Da(T) - a(T)}{2 \cdot \sqrt{2} \cdot b} \cdot \ln\left[\frac{Z(T, P)_0 + \left(1 + \sqrt{2}\right) \cdot CB(T, P)}{Z(T, P)_0 + \left(1 - \sqrt{2}\right) \cdot CB(T, P)} \right] \right] \cdot 10^5$$

$$\text{DELHV}(T, P) := \left[R \cdot T \cdot \left(Z(T, P)_2 - 1 \right) + \frac{T \cdot Da(T) - a(T)}{2 \cdot \sqrt{2} \cdot b} \cdot \ln\left[\frac{Z(T, P)_2 + \left(1 + \sqrt{2}\right) \cdot CB(T, P)}{Z(T, P)_2 + \left(1 - \sqrt{2}\right) \cdot CB(T, P)} \right] \right] \cdot 10^5$$

Ideal gas properties changes relative to the reference state

$$\text{DELHIG}(T) := Cp_0 \cdot (T - Trs) + \frac{Cp_1 \cdot \left(T^2 - Trs^2\right)}{2} + \frac{Cp_2 \cdot \left(T^3 - Trs^3\right)}{3} + \frac{Cp_3 \cdot \left(T^4 - Trs^4\right)}{4}$$

$$\text{DELSIG}(T, P) := Cp_0 \cdot \ln\left(\frac{T}{Trs}\right) + Cp_1 \cdot (T - Trs) + \frac{Cp_2 \cdot \left(T^2 - Trs^2\right)}{2} + \frac{Cp_3 \cdot \left(T^3 - Trs^3\right)}{3} - R \cdot 10^5 \cdot \ln\left(\frac{P}{Prs}\right)$$

Total entropy and enthalpy relative to ideal gas reference state

$$SL(T, P) := \text{DELSIG}(T, P) + \text{DELSL}(T, P) \qquad SV(T, P) := \text{DELSIG}(T, P) + \text{DELSV}(T, P)$$

$$HL(T, P) := \text{DELHIG}(T) + \text{DELHL}(T, P) \qquad HV(T, P) := \text{DELHIG}(T) + \text{DELHV}(T, P)$$

SUMMARY OF RESULTS

T = 298.15   **K**   **Pressure, bar**   P = 140

	LIQUID	VAPOR
Compressibility	$Z(T,P)_0 = 0.99907$	$Z(T,P)_2 = 0.99907$
Enthalpy, J/mol	$HL(T,P) = {}^-96.20674$	$HV(T,P) = {}^-96.20674$
Entropy, J/mol K	$SL(T,P) = {}^-41.04818$	$SV(T,P) = {}^-41.04818$
Fugacity coefficient	$phil(T,P) = 0.97024$	$phiv(T,P) = 0.97024$
Fugacity, bar	$fugl(T,P) = 135.83299$	$fugv(T,P) = 135.83299$
Volume, m^3/kmol	$VL(T,P) = 0.17689$	$VV(T,P) = 0.17689$

Number of moles initially $\qquad N := \dfrac{\left[3.1416 \cdot (.01)^2 \cdot .06\right]}{VV(T,P)} \cdot 1000 \qquad N = 0.10656$

$Tf := 100 \qquad Pf := 1.103$

Given

$$SV(Tf, Pf) = -41.04818 \qquad Tf := find(Tf) \qquad Tf = 69.36841$$

$Tf = 69.36841$**K** $\qquad$ **Pressure, bar** $\quad Pf = 1.103$

	LIQUID	VAPOR
Compressibility	$Z(Tf, Pf)_0 = 5.61855 \cdot 10^{-3}$	$Z(Tf, Pf)_2 = 0.94081$
Enthalpy, J/mol	$HL(Tf, Pf) = {}^-1.16967 \cdot 10^4$	$HV(Tf, Pf) = {}^-5.96312 \cdot 10^3$
Entropy, J/mol K	$SL(Tf, Pf) = {}^-114.62977$	$SV(Tf, Pf) = {}^-41.04818$
Fugacity coefficient	$phil(Tf, Pf) = 0.31698$	$phiv(Tf, Pf) = 0.94395$
Fugacity, bar	$fugl(Tf, Pf) = 0.34963$	$fugv(Tf, Pf) = 1.04117$
Volume, m^3/kmol	$VL(Tf, Pf) = 0.02938$	$VV(Tf, Pf) = 4.91926$

$U(T,P) := HV(T,P) - 140 \cdot \dfrac{0.17689}{100} \qquad U(T,P) = {}^-96.45439$

$U(Tf, Pf) := HV(Tf, Pf) - 1.013 \cdot \dfrac{4.91926}{100} \qquad U(Tf, Pf) = {}^-5.96317 \cdot 10^3$

$W := N \cdot (U(Tf, Pf) - U(T,P)) \qquad W = {}^-625.17152$

$G := \dfrac{{}^-W}{4600} \qquad G = 0.13591 \quad$ grams of TNT

PENG-ROBINSON EQUATION OF STATE CALCULATION   **Carbon dioxide**

The Property Data should be as follows
Tc (in K), Pc (in bar), omega, Tb (in K)
Cp1, Cp2, Cp3, Cp4   **(In eqn Cp=Cp0+Cp1*T+Cp2*T^2+Cp3*T^3)**
Tref (in K), Pref (in bar)   **(reference conditions)**

Note that in the 1st and 2nd printings, carbon dioxide was used as the fluid. This gave
unreasonable answers when this problem was revisited with the Peng-Robinson eqn.
of state, as both the initial and final states were found to be in the liquid state. Therefore
from the 3rd printing on, the fluid has been changed to nitrogen.

$i := 0, 1..3$ $R := 0.00008314$

$Cp_0 := 22.243$ $Cp_1 := 5.977 \cdot 10^{-2}$ $Cp_2 := -3.499 \cdot 10^{-5}$ $Cp_3 := 7.464 \cdot 10^{-9}$

$Tc := 304.2$ $Pc := 73.76$ $om := 0.225$

$Trs := 273.15$ $Prs := 1.0$

         $kap := 0.37464 + 1.54226 \cdot om - 0.26992 \cdot om \cdot om$

Peng-Robinson Constants: $b := 0.07780 \cdot \dfrac{R \cdot Tc}{Pc}$ $ac := 0.45724 \cdot \dfrac{R^2 \cdot Tc^2}{Pc}$

Input temperature and pressure of calculation $T := 298.15$ **K,** $P := 140$ **bar**

$alf(T) := 1 \cdot \left[1 + kap \cdot \left(1 - \sqrt{\dfrac{T}{Tc}} \right) \right]^2$ $a(T) := ac \cdot alf(T)$ $CA(T,P) := \dfrac{a(T) \cdot P}{(R \cdot T)^2}$ $CB(T,P) := \dfrac{P \cdot b}{R \cdot T}$

                     $Da(T) := \dfrac{d}{dT} a(T)$

$Z(T,P) :=$
$\begin{array}{l}
A \leftarrow CA(T,P) \\
B \leftarrow CB(T,P) \\
V \leftarrow \begin{bmatrix} -(A \cdot B - B^2 - B^3) \\ A - 3 \cdot B^2 - 2 \cdot B \\ -(1 - B) \\ 1 \end{bmatrix} \\
ZZ \leftarrow polyroots(V) \\
\text{for } i \in 0..2 \\
\quad (ZZ_i \leftarrow 0) \text{ if } (Im(ZZ_i) \neq 0) \\
ZZ \leftarrow sort(ZZ) \\
ZZ_0 \leftarrow ZZ_2 \text{ if } \left(|ZZ_0| < 10^{-5} \right) \\
ZZ_2 \leftarrow ZZ_0 \text{ if } \left(|ZZ_2| < 10^{-5} \right) \\
ZZ
\end{array}$

                                     Vector of coefficients in the PR equation
                                       in the form
                                       0=-(A*B-B^2-B^3)+(A-3*B^2-2*B)*Z-(1-B)*Z^2+Z^3

                                       Solution to the cubic

                                       Set any imaginary roots to zero
                                       Sort the roots

                                       Set the value of any imaginary roots
                                       to value of the real root

Calculate molar volumes

                $VL(T,P) := \dfrac{Z(T,P)_0 \cdot R \cdot T}{P} \cdot 10^3$ $VV(T,P) := \dfrac{Z(T,P)_2 \cdot R \cdot T}{P} \cdot 10^3$

Fugacity expressions [actually ln(f/P)] for the liquid fl and vapor fv

$$fl(T,P) := \left(Z(T,P)_0 - 1\right) - \ln\left(Z(T,P)_0 - CB(T,P)\right) - \frac{CA(T,P)}{2 \cdot \sqrt{2} \cdot CB(T,P)} \cdot \ln\left[\frac{Z(T,P)_0 + \left(1+\sqrt{2}\right) \cdot CB(T,P)}{Z(T,P)_0 + \left(1-\sqrt{2}\right) \cdot CB(T,P)}\right]$$

$$fv(T,P) := \left(Z(T,P)_2 - 1\right) - \ln\left(Z(T,P)_2 - CB(T,P)\right) - \frac{CA(T,P)}{2 \cdot \sqrt{2} \cdot CB(T,P)} \cdot \ln\left[\frac{Z(T,P)_2 + \left(1+\sqrt{2}\right) \cdot CB(T,P)}{Z(T,P)_2 + \left(1-\sqrt{2}\right) \cdot CB(T,P)}\right]$$

$$phil(T,P) := \exp(fl(T,P)) \qquad phiv(T,P) := \exp(fv(T,P))$$

$$fugl(T,P) := P \cdot phil(T,P) \qquad fugv(T,P) := P \cdot phiv(T,P)$$

Residual entropy for liquid (DELSL) and vapor (DELSV) phases

$$DELSL(T,P) := \left[R \cdot \ln\left(Z(T,P)_0 - CB(T,P)\right) + \frac{Da(T)}{2 \cdot \sqrt{2} \cdot b} \cdot \ln\left[\frac{Z(T,P)_0 + \left(1+\sqrt{2}\right) \cdot CB(T,P)}{Z(T,P)_0 + \left(1-\sqrt{2}\right) \cdot CB(T,P)}\right]\right] \cdot 10^5$$

$$DELSV(T,P) := \left[R \cdot \ln\left(Z(T,P)_2 - CB(T,P)\right) + \frac{Da(T)}{2 \cdot \sqrt{2} \cdot b} \cdot \ln\left[\frac{Z(T,P)_2 + \left(1+\sqrt{2}\right) \cdot CB(T,P)}{Z(T,P)_2 + \left(1-\sqrt{2}\right) \cdot CB(T,P)}\right]\right] \cdot 10^5$$

Residual enthalpy for liquid (DELHL) and vapor (DELHV) phases

$$DELHL(T,P) := \left[R \cdot T \cdot \left(Z(T,P)_0 - 1\right) + \frac{T \cdot Da(T) - a(T)}{2 \cdot \sqrt{2} \cdot b} \cdot \ln\left[\frac{Z(T,P)_0 + \left(1+\sqrt{2}\right) \cdot CB(T,P)}{Z(T,P)_0 + \left(1-\sqrt{2}\right) \cdot CB(T,P)}\right]\right] \cdot 10^5$$

$$DELHV(T,P) := \left[R \cdot T \cdot \left(Z(T,P)_2 - 1\right) + \frac{T \cdot Da(T) - a(T)}{2 \cdot \sqrt{2} \cdot b} \cdot \ln\left[\frac{Z(T,P)_2 + \left(1+\sqrt{2}\right) \cdot CB(T,P)}{Z(T,P)_2 + \left(1-\sqrt{2}\right) \cdot CB(T,P)}\right]\right] \cdot 10^5$$

Ideal gas properties changes relative to the reference state

$$DELHIG(T) := Cp_0 \cdot (T - Trs) + \frac{Cp_1 \cdot \left(T^2 - Trs^2\right)}{2} + \frac{Cp_2 \cdot \left(T^3 - Trs^3\right)}{3} + \frac{Cp_3 \cdot \left(T^4 - Trs^4\right)}{4}$$

$$DELSIG(T,P) := Cp_0 \cdot \ln\left(\frac{T}{Trs}\right) + Cp_1 \cdot (T - Trs) + \frac{Cp_2 \cdot \left(T^2 - Trs^2\right)}{2} + \frac{Cp_3 \cdot \left(T^3 - Trs^3\right)}{3} - R \cdot 10^5 \cdot \ln\left(\frac{P}{Prs}\right)$$

Total entropy and enthalpy relative to ideal gas reference state

$$SL(T, P) := DELSIG(T, P) + DELSL(T, P) \qquad SV(T, P) := DELSIG(T, P) + DELSV(T, P)$$

$$HL(T, P) := DELHIG(T) + DELHL(T, P) \qquad HV(T, P) := DELHIG(T) + DELHV(T, P)$$

SUMMARY OF RESULTS

T = 298.15   K   **Pressure, bar**   P = 140

	LIQUID	**VAPOR**
Compressibility	$Z(T, P)_0 = 0.29126$	$Z(T, P)_2 = 0.29126$
Enthalpy, J/mol	$HL(T, P) = -1.03464 \cdot 10^4$	$HV(T, P) = -1.03464 \cdot 10^4$
Entropy, J/mol K	$SL(T, P) = -67.27151$	$SV(T, P) = -67.27151$
Fugacity coefficient	$phil(T, P) = 0.365$	$phiv(T, P) = 0.365$
Fugacity, bar	$fugl(T, P) = 51.09983$	$fugv(T, P) = 51.09983$
Volume, m^3/kmol	$VL(T, P) = 0.05157$	$VV(T, P) = 0.05157$

Number of moles initially $N := \dfrac{\left[3.1416 \cdot (.01)^2 \cdot .06\right]}{VL(T, P)} \cdot 1000$ N = 0.36552

Tf := 50   Pf := 1.013

Given

$$SL(Tf, Pf) = SL(T, P)$$
$$Tf := find(Tf) \qquad Tf = 277.04181$$

Tf = 277.04181   K   **Pressure, bar**   Pf = 1.013

	LIQUID	**VAPOR**
Compressibility	$Z(Tf, Pf)_0 = 2.52794 \cdot 10^{-3}$	$Z(Tf, Pf)_2 = 0.99308$
Enthalpy, J/mol	$HL(Tf, Pf) = -1.10995 \cdot 10^4$	$HV(Tf, Pf) = 93.98326$
Entropy, J/mol K	$SL(Tf, Pf) = -67.27151$	$SV(Tf, Pf) = 0.2929$
Fugacity coefficient	$phil(Tf, Pf) = 26.04907$	$phiv(Tf, Pf) = 0.99311$
Fugacity, bar	$fugl(Tf, Pf) = 26.3877$	$fugv(Tf, Pf) = 1.00603$
Volume, m^3/kmol	$VL(Tf, Pf) = 0.05748$	$VV(Tf, Pf) = 22.58025$

$$U(T, P) := HV(T, P)$$

$$U(T, P) = -1.03464 \cdot 10^4$$

$$U(Tf, Pf) := HV(Tf, Pf)$$

$$U(Tf, Pf) = 93.98326$$

$$W := N \cdot (U(Tf, Pf) - U(T, P))$$ $$W = 3.81613 \cdot 10^3$$

$$G := \frac{-W}{4600}$$ $$G = -0.82959$$ grams of TNT

Note that this answer does not make sense. The reason is that with carbon dioxide, but the initial and final states would be liquid. Therefore, carbon dioxide is a poor choice of fluid for this problem, and also problem 3.44. In the third and later printings, nitrogen is used.

4.50 We start from

$$d\underline{S} = C_V dT + \left(\frac{\partial P}{\partial T}\right)_V d\underline{V}$$

Since the entropy at 0 K is not a function of temperature, it follows that $C_V = 0$. Also, since the entropy is not a function of specific volume, it follows that

$$\left(\frac{\partial P}{\partial T}\right)_V = 0$$

However, by the triple product rule

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial \underline{V}}{\partial P}\right)_T \left(\frac{\partial T}{\partial \underline{V}}\right)_P = -1 \quad \text{or}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial \underline{V}}\right)_T \left(\frac{\partial \underline{V}}{\partial T}\right)_P = 0$$

but from the thermodynamic stability condition

$$\left(\frac{\partial P}{\partial \underline{V}}\right)_T < 0$$

which implies that

$$\left(\frac{\partial \underline{V}}{\partial T}\right)_P = 0 \quad \text{and} \quad \boldsymbol{a} = \frac{1}{\underline{V}}\left(\frac{\partial \underline{V}}{\partial T}\right)_P = 0$$

4.51 Rewrite the Clausius equation as

$$\underline{V} = \frac{RT}{P} + b \quad \text{Then} \left(\frac{\partial \underline{V}}{\partial T}\right)_P = \frac{R}{T};$$

$$\left(\frac{\partial^2 \underline{V}}{\partial T^2}\right)_P = 0 \text{ (which means } C_P \text{ is independent of pressure and equal to } C_P^*)$$

and $\underline{V} - T\left(\frac{\partial \underline{V}}{\partial T}\right)_P = b$

a) Therefore

$$\Delta \underline{H} = \underline{H}(T_2, P_2) - \underline{H}(T_1, P_1) = \int_{T_1}^{T_2} C_P^*(T)dT + \int_{P_1}^{P_2} b\,dP = 0 \text{ or}$$

$$a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{g}{3}(T_2^3 - T_1^3) + b(P_2 - P_1) = 0$$

is the line of constant enthalpy.

b)

$$\Delta \underline{S} = \underline{S}(T_2, P_2) - \underline{S}(T_1, P_1) = \int_{T_1}^{T_2} \frac{C_P^*(T)}{T}dT - \int_{P_1}^{P_2} \left(\frac{\partial \underline{V}}{\partial T}\right)_P dP = 0$$

$$= \int_{T_1}^{T_2} \frac{C_P^*(T)}{T}dT - \int_{P_1}^{P_2} \frac{R}{P}dP = 0$$

or

$$a\ln\frac{T_2}{T_1} + b(T_2 - T_1) + \frac{g}{2}(T_2^2 - T_1^2) - R\ln\frac{P_2}{P_1} = 0$$

is the line of constant entropy.

c) For the fluid to have a Joule-Thomson inversion temperature
$$m = \left(\frac{\partial T}{\partial P}\right)_H$$ must undergo a sign change. However

$$m = \left(\frac{\partial T}{\partial P}\right)_H = -\frac{\left[\underline{V} - T\left(\frac{\partial \underline{V}}{\partial T}\right)_P\right]}{C_P} = -\frac{\frac{RT}{P} + b - T\frac{R}{P}}{C_P} = -\frac{b}{C_P}$$

This is always negative, so the Clausius does not have a Joule-Thomson inversion temperature.

5

5.1 (also available as a Mathcad worksheet)

(a) $\hat{G} = \hat{H} - TS$ at $P = 2.5$ MPa and $T = 223.99°\text{C} = 497.14$ K

$$\left. \begin{array}{l} \hat{G}^V = \hat{H}^V - T\hat{S}^V = 2803.1 - 497.14 \times 6.2575 = -307.8 \ \text{J/g} \\ \hat{G}^L = \hat{H}^L - T\hat{S}^L = 962.11 - 497.14 \times 2.5547 = -307.9 \ \text{J/g} \end{array} \right\} \begin{array}{l} \text{equal with} \\ \text{the accuracy} \\ \text{of tables} \end{array}$$

(b)

$T(°\text{C})$	$T(\text{K})$	$\hat{H}^V$	$-$	$T\hat{S}^V$		$\hat{G}^L$
225	498.15	2806.3	$-$	$498.15 \times 6.2639 =$	-314.1	J/g
250	523.15	2880.1	$-$	$523.15 \times 6.4085 =$	-472.5	
300	573.15	3008.8	$-$	$573.15 \times 6.6438 =$	-799.1	
350	623.15	3126.3	$-$	$623.15 \times 6.8403 =$	-1136.2	
400	673.15	3239.3	$-$	$673.15 \times 7.0148 =$	-1482.7	

(Note: All Gibbs free energies are relative to the internal energy and entropy of the liquid phase being zero at the triple point. Since $\hat{H}^L \sim \hat{U}^L$, and $\hat{G}^L = \hat{H}^L - T\hat{S}^L$, we have that $\hat{G}^L = 0$ at the triple point.)

(c)

$T(°\text{C})$	$T(\text{K})$	$\hat{H}^L$	$-$	$T\hat{S}^L$		$\hat{G}^V$
160	433.15	675.55	$-$	$433.15 \times 1.9427 =$	-165.9	J/g
170	443.15	719.21	$-$	$443.15 \times 2.0419 =$	-185.7	
180	453.15	763.22	$-$	$453.15 \times 2.1396 =$	-206.3	
190	463.15	807.62	$-$	$463.15 \times 2.2359 =$	-227.9	
200	473.15	852.45	$-$	$473.15 \times 2.3309 =$	-250.4	
210	483.15	897.76	$-$	$483.15 \times 2.4248 =$	-273.8	

RESULTS

(d)

$T(°\text{C})$	150	160	180	200	220	224
$\hat{V}(\text{m}^3/\text{kg})$	0.001091	0.001102	0.001127	0.001157	0.001190	0.001197

to
0.07998

$T(°\text{C})$	225	250	300	350	400
$\hat{V}(\text{m}^3/\text{kg})$	0.08027	0.08700	0.09890	0.10976	0.12010

(e) Will compute C_P from $C_P \sim \left(\dfrac{\Delta \hat{H}}{\Delta T} \right)_P = \dfrac{\hat{H}(T + \Delta T) - \hat{H}(T)}{\Delta T}$

$T(°C)$	150	170	180	190	200	210	224
							4.6225
$C_P(kJ/kg\ K)$	4.328	4.392	4.430	4.472	4.518	4.572	to
							3.200

$T(°C)$	250	300	350	400
$C_P(kJ/kg\ K)$	2.952	2.574	2.350	2.260

These results are plotted below.
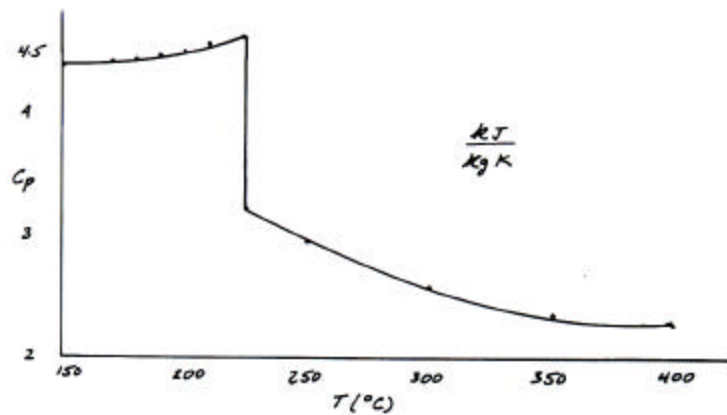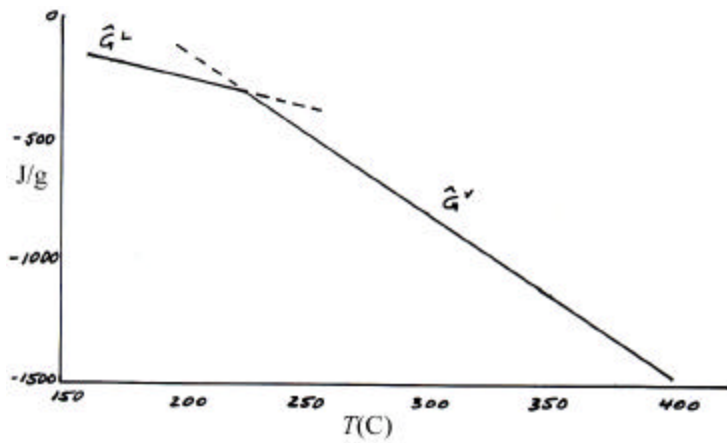
5.2   Closed system energy balance: $\dfrac{dU}{dt} = \dot{Q} - P\dfrac{dV}{dt}$

Closed system entropy balance: $\dfrac{dS}{dt} = \dfrac{\dot{Q}}{T} + \dot{S}_{gen}$

(a) System at constant volume and constant entropy

$$\frac{dV}{dt} = 0 \ \text{ and } \ \frac{dS}{dt} = 0$$

$$\Rightarrow \frac{dU}{dt} = \dot{Q} \ \text{ and } \ 0 = \frac{\dot{Q}}{T} + \dot{S}_{gen} \Rightarrow \dot{Q} = -T\dot{S}_{gen}$$

$$\text{and } \frac{dU}{dt} = -T\dot{S}_{\text{gen}} \, ; \ T > 0 \, ; \ \dot{S}_{\text{gen}} \geq 0$$

$$\Rightarrow \frac{dU}{dt} \leq 0 \ \text{ or } \ U = \text{minimum at equilibrium at constant } V \text{ and } S.$$

(b) System at constant entropy and pressure again $\dot{Q} = -T\dot{S}_{\text{gen}}$.

Now $\dfrac{dP}{dt} = 0 \Rightarrow P\dfrac{dV}{dt} = \dfrac{d}{dt}(PV)$. Thus

$$\frac{dU}{dt} = \dot{Q} - P\frac{dV}{dt} = -T\dot{S}_{\text{gen}} - \frac{d}{dt}(PV)$$

and

$$\frac{dU}{dt} + \frac{d}{dt}(PV) = \frac{d}{dt}(U + PV) = \frac{dH}{dt} = -T\dot{S}_{\text{gen}} \leq 0$$

Therefore, enthalpy is a minimum at equilibrium at constant S and P.

5.3 (a) The condition for equilibrium at constant T and V is that the Helmholtz free energy A shall be a minimum.

i) Equilibrium analysis (following analysis in text)

$$dA^{\mathrm{I}} = \left(\frac{\partial A^{\mathrm{I}}}{\partial T^{\mathrm{I}}}\right)_{V,M} dT^{\mathrm{I}} + \left(\frac{\partial A^{\mathrm{I}}}{\partial V^{\mathrm{I}}}\right)_{T,M} dV^{\mathrm{I}} + \left(\frac{\partial A^{\mathrm{I}}}{\partial M^{\mathrm{I}}}\right)_{T,V} dM^{\mathrm{I}}$$

but $dT^{\mathrm{I}} = 0$, since temperature is fixed, and

$$\left(\frac{\partial A^{\mathrm{I}}}{\partial V^{\mathrm{I}}}\right)_{T,M} = -P^{\mathrm{I}} \ \text{ and } \ \left(\frac{\partial A^{\mathrm{I}}}{\partial M^{\mathrm{I}}}\right)_{T,V} = \hat{G}^{\mathrm{I}}$$

Thus, following the analysis in the text, we obtain

$$dA = -\left(P^{\mathrm{I}} - P^{\mathrm{II}}\right)dV^{\mathrm{I}} + \left(\hat{G}^{\mathrm{I}} - \hat{G}^{\mathrm{II}}\right)dM^{\mathrm{I}} \Rightarrow P^{\mathrm{I}} = P^{\mathrm{II}} \text{ and } \hat{G}^{\mathrm{I}} - \hat{G}^{\mathrm{II}}$$

ii) Stability analysis:
Here again we follow analysis in Sec. 5.2—and find

$$\frac{1}{2}d^2 A = A_{VV}(dV)^2 + 2A_{VM}(dV)(dM) + A_{MM}(dM)^2 \geq 0$$

This can be rewritten as

$$\frac{1}{2}d^2 A = q_1(dx_1)^2 + q_2(dx_2)^2 \geq 0$$

where

$$q_1 = A_{VV} \, ; \ q_2 = \frac{A_{MM} A_{VV} - A_{VM}^2}{A_{VV}} = A_{MM} - \frac{A_{VM}^2}{A_{VV}}$$

and

$$dx_1 = dV + \frac{A_{VM}}{A_{VV}} dM \ , \ \ dx_2 = dM$$

Thus, $\boldsymbol{q}_1 \geq 0$ and $\boldsymbol{q}_2 \geq 0$

$$\boldsymbol{q}_1 = \left(\frac{\partial^2 A}{\partial V^2} \right)_{T,M} = \frac{\partial}{\partial V} \bigg|_{T,M} \left(\frac{\partial A}{\partial V} \right)_{T,M} = \frac{\partial}{\partial V} \bigg|_{T,M} (-P) \Rightarrow -\left(\frac{\partial P}{\partial V} \right)_{T,M} \geq 0$$

$$\text{or} \ \left(\frac{\partial P}{\partial V} \right)_{T,M} \leq 0 \ \text{ as previously found}$$

$$\boldsymbol{q}_2 = A_{MM} - \frac{A_{VM}^2}{A_{VV}} \geq 0$$

$$A_{VV} = -\left(\frac{\partial P}{\partial V} \right)_{T,M} \ ; \ \ A_{VM} = \frac{\partial}{\partial M} \left(\frac{\partial A}{\partial V} \right)_{T,M} = -\left(\frac{\partial P}{\partial M} \right)_{T,V} \ ;$$

$$A_{MM} = \frac{\partial}{\partial M} \bigg|_{T,V} \left(\frac{\partial A}{\partial M} \right)_{T,V} = \left(\frac{\partial \hat{G}}{\partial M} \right)_{T,V}$$

Now be Eqn. (4.8-17) on a mass basis

$$\left(\frac{\partial \hat{G}}{\partial M} \right)_{T,V} = \frac{1}{M} \left[\left(\frac{\partial G}{\partial M} \right)_{T,V} - \hat{G} \right]$$

Also, $dG = VdP - SdT + \hat{G}dM \Rightarrow \left(\frac{\partial G}{\partial M} \right)_{T,V} = V \left(\frac{\partial P}{\partial M} \right)_{T,V} + \hat{G}$ and

$$\left(\frac{\partial \hat{G}}{\partial M} \right)_{T,V} = \frac{1}{M} V \left(\frac{\partial P}{\partial M} \right)_{T,V} = \hat{V} \left(\frac{\partial P}{\partial M} \right)_{T,V} = A_{MM}$$

so

$$A_{MM} - \frac{A_{VM}^2}{A_{VV}} = \hat{V} \left(\frac{\partial P}{\partial M} \right)_{T,V} - \frac{\left[-(\partial P / \partial M)_{T,V} \right]^2}{-(\partial P / \partial V)_{T,M}}$$

$$= \left(\frac{\partial P}{\partial M} \right)_{T,V} \left[\hat{V} + \left(\frac{\partial V}{\partial P} \right)_{T,M} \left(\frac{\partial P}{\partial M} \right)_{T,V} \right]$$

$$= \left(\frac{\partial P}{\partial M} \right)_{T,V} \left[\hat{V} - \left(\frac{\partial V}{\partial M} \right)_{T,P} \right] \begin{array}{l} \text{by the triple product} \\ \text{rule; Eqn. (4.1-6)} \end{array}$$

Since

$$\left(\frac{\partial V}{\partial M} \right)_{T,P} = \hat{V} \Rightarrow A_{MM} - \frac{A_{VM}^2}{A_{VV}} = \boldsymbol{q}_2 = 0!$$

(b) The Gibbs free energy must be a minimum for a system constrained at constant T and P

i)   Equilibrium analysis

$$dG^{\mathrm{I}} = \left(\frac{\partial G^{\mathrm{I}}}{\partial T^{\mathrm{I}}}\right)_{P,M} dT^{\mathrm{I}} + \left(\frac{\partial G^{\mathrm{I}}}{\partial P^{\mathrm{I}}}\right)_{T,M} dP^{\mathrm{I}} + \left(\frac{\partial G^{\mathrm{I}}}{\partial M^{\mathrm{I}}}\right)_{T,P} dM^{\mathrm{I}}$$

Since T and P are fixed,

$$dG^{\mathrm{I}} = \left(\frac{\partial G^{\mathrm{I}}}{\partial M^{\mathrm{I}}}\right)_{T,P} dM^{\mathrm{I}} = \hat{G}^{\mathrm{I}} dM^{\mathrm{I}}$$

Thus

$$dG = \left(\hat{G}^{\mathrm{I}} - \hat{G}^{\mathrm{II}}\right) dM^{\mathrm{I}} = 0 \quad \text{and} \quad \hat{G}^{\mathrm{I}} = \hat{G}^{\mathrm{II}}$$

ii)   Stability analysis

$$\frac{1}{2}d^2 G = G_{MM}(dM)^2 = \left(\frac{\partial^2 G}{\partial M^2}\right)_{T,P} (dM)^2 > 0$$

Now

$$\left(\frac{\partial^2 G}{\partial M^2}\right)_{T,P} = \left(\frac{\partial \hat{G}}{\partial M}\right)_{T,P} \overset{\text{Eqn.}}{\underset{4.9\text{-}10}{\Rightarrow}} \frac{1}{M}\left[\left(\frac{\partial G}{\partial M}\right)_{T,P} - \hat{G}\right] = \frac{1}{M}\left[\hat{G} - \hat{G}\right]$$

Thus $G_{MM} \equiv 0$, and stability analysis gives no useful information.

5.4   (a)   At constant M, T and V, A should be a minimum. For a vapor-liquid mixture at constant M, T and V we have:

$$A = A^{\mathrm{L}} + A^{\mathrm{V}}$$

and at equilibrium $dA = 0 = dA^{\mathrm{L}} + dA^{\mathrm{V}}$. Thus

$$dA = 0 = \left\{-P^{\mathrm{L}}dV^{\mathrm{L}} - S^{\mathrm{L}}dT^{\mathrm{L}} + \hat{G}^{\mathrm{L}}dM^{\mathrm{L}}\right\} + \left\{-P^{\mathrm{V}}dV^{\mathrm{V}} - S^{\mathrm{V}}dT^{\mathrm{V}} + \hat{G}^{\mathrm{V}}dM^{\mathrm{V}}\right\}$$

but

$$M = \text{constant} \Rightarrow dM^{\mathrm{L}} + dM^{\mathrm{V}} = 0 \text{ or } dM^{\mathrm{L}} = -dM^{\mathrm{V}}$$
$$V = \text{constant} \Rightarrow dV^{\mathrm{L}} + dV^{\mathrm{V}} = 0 \text{ or } dV^{\mathrm{L}} = -dV^{\mathrm{V}}$$
$$T = \text{constant} \Rightarrow dT^{\mathrm{L}} + dT^{\mathrm{V}} = 0$$
$$\Rightarrow dA = -\left(P^{\mathrm{L}} - P^{\mathrm{V}}\right)dV^{\mathrm{L}} + \left(\hat{G}^{\mathrm{L}} - \hat{G}^{\mathrm{V}}\right)dM^{\mathrm{L}} = 0$$

Since dV^{L} and dM^{L} are independent variations, we have that

$$P^{\mathrm{L}} = P^{\mathrm{V}} ; \text{ and } \hat{G}^{\mathrm{L}} = \hat{G}^{\mathrm{V}}$$

also $T^{\mathrm{L}} = T^{\mathrm{V}}$ by constraint that T is constant and uniform.

(b)   At constant M, T, and P, $G = \text{minimum}$ or $dG = 0$ or equilibrium.

$$dG = \left\{V^{\mathrm{L}}dP^{\mathrm{L}} - S^{\mathrm{L}}dT^{\mathrm{L}} + \hat{G}^{\mathrm{L}}dM^{\mathrm{L}}\right\} + \left\{V^{\mathrm{V}}dP^{\mathrm{V}} - S^{\mathrm{V}}dT^{\mathrm{V}} + \hat{G}^{\mathrm{V}}dM^{\mathrm{V}}\right\}$$

$$\text{and } M = \text{constant} \Rightarrow dM^{\mathrm{L}} = -dM^{\mathrm{V}}$$

$$P = \text{constant} \Rightarrow dP^{\mathrm{L}} = dP^{\mathrm{V}} = 0$$

$$T = \text{constant} \Rightarrow dT^{\mathrm{L}} = dT^{\mathrm{V}} = 0$$

$$\Rightarrow dG = \hat{G}^{\mathrm{L}}dM^{\mathrm{L}} + \hat{G}^{\mathrm{V}}dM^{\mathrm{V}} = \left(\hat{G}^{\mathrm{V}} - \hat{G}^{\mathrm{L}}\right)dM^{\mathrm{L}} = 0$$

or $\hat{G}^{\mathrm{L}} = \hat{G}^{\mathrm{V}}$ for vapor-liquid equilibrium at constant T and P.

(Also, T and P are uniform—this is implied by constraints.)

5.5 From Sec. 4.2 we have

$$C_{\mathrm{P}} = C_{\mathrm{V}} - T\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V^2 = C_{\mathrm{V}} - T\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T$$

It is the last form of the equation which is useful here now $T > 0$ and $(\partial V/\partial T)_P^2 \geq 0$. However

$$\left(\frac{\partial P}{\partial V}\right)_T \begin{cases} < 0 \\ = 0 \text{ at critical point or limit of stability} \end{cases}$$

Thus $C_{\mathrm{P}} > C_{\mathrm{V}}$ in general; except that $C_{\mathrm{P}} = C_{\mathrm{V}}$

i)   at the critical point or limit of stability of a single phase.
ii) For the substances with zero valuer (or very small value) of the coefficient of thermal expansion $\alpha = (1/\underline{V})(\partial \underline{V}/\partial T)_P$ such as liquids and solids away from the critical point.

5.6 Stability conditions for a fluid are

$$C_{\mathrm{V}} > 0 \text{ and } \left(\frac{\partial P}{\partial \underline{V}}\right)_T < 0$$

for a fiber these translate to

$$C_{\mathrm{L}} > 0 \text{ and } \left(\frac{\partial F}{\partial L}\right)_T > 0$$

Now $C_{\mathrm{L}} = \alpha + \beta T$; if $C_{\mathrm{L}} > 0$ for all T, then $C_{\mathrm{L}} > 0$ at $T \Rightarrow 0$ implies $\alpha > 0$; $C_{\mathrm{L}} > 0$ as $T \to \infty$ implies $\beta > 0$. Also, $(\partial F/\partial L)_T = \gamma T > 0$ since $T > 0$, this implies $\gamma > 0$.

5.7 $d\underline{U} = Td\underline{S} - Pd\underline{V} \Rightarrow d\underline{S} = \dfrac{1}{T}d\underline{U} + \dfrac{P}{T}d\underline{V}$

Thus $\left(\dfrac{\partial \underline{S}}{\partial \underline{U}}\right)_V = \dfrac{1}{T}$ and $\left(\dfrac{\partial \underline{S}}{\partial \underline{V}}\right)_U = \dfrac{P}{T}$. These relations, together with the equation

$$\underline{S} = \underline{S}^{\circ} + \alpha \ln \frac{\underline{U}}{\underline{U}^{\circ}} + \beta \ln \frac{\underline{V}}{\underline{V}^{\circ}} \tag{1}$$

will be used to derive the required equation.

[Note that Eqn. (1), which is of the form $\underline{S} = \underline{S}(\underline{U},\underline{V})$ is a fundamental equation of state , in the sense of Sec. 4.2.]

(a) $\left(\dfrac{\partial \underline{S}}{\partial \underline{U}}\right)_V = a\left(\dfrac{\underline{U}}{\underline{U}^\circ}\right)^{-1}\dfrac{1}{\underline{U}^\circ} = \dfrac{a}{\underline{U}} = \dfrac{1}{T} \Rightarrow \underline{U} = aT$ (2)

(b) $\left(\dfrac{\partial \underline{S}}{\partial \underline{V}}\right)_U = \dfrac{P}{T} = b\dfrac{\underline{V}^\circ}{\underline{V}}\cdot\dfrac{1}{\underline{V}^\circ} = \dfrac{b}{\underline{V}}$. Thus $P\underline{V} = bT$. (3)

[Clearly, the fluid with an equation of state given by (1) is an ideal gas with constant heat capacity]

(c) Stability criteria:

$$\left(\dfrac{\partial^2 \underline{S}}{\partial \underline{U}\,\partial \underline{V}}\right)^2 < \left(\dfrac{\partial^2 \underline{S}}{\partial \underline{V}^2}\right)_U\left(\dfrac{\partial^2 \underline{S}}{\partial \underline{U}^2}\right)_V \text{ and } \left(\dfrac{\partial^2 \underline{S}}{\partial \underline{V}^2}\right)_U < 0 \; ; \left(\dfrac{\partial^2 \underline{S}}{\partial \underline{U}^2}\right)_V < 0$$

Now

$$\left.\begin{aligned}
\left(\dfrac{\partial^2 \underline{S}}{\partial \underline{U}^2}\right)_V &= \dfrac{\partial}{\partial \underline{U}}\bigg|_V \dfrac{a}{\underline{U}} = -\dfrac{a}{\underline{U}^2} < 0 \Rightarrow a > 0 \\[2ex]
\left(\dfrac{\partial^2 \underline{S}}{\partial \underline{V}^2}\right)_U &= \dfrac{\partial}{\partial \underline{V}}\bigg|_U \dfrac{b}{\underline{V}} = -\dfrac{b}{\underline{V}^2} < 0 \Rightarrow b > 0
\end{aligned}\right\} \begin{aligned}&\text{for fluid}\\&\text{to be}\\&\text{stable}\end{aligned}$$

[Note: a, $b > 0$ by problem statement.]

and

$$\dfrac{\partial^2 S}{\partial \underline{U}\,\partial \underline{V}} = \dfrac{\partial}{\partial \underline{U}}\bigg|_V\left(\dfrac{\partial \underline{S}}{\partial \underline{V}}\right)_U = \dfrac{\partial}{\partial \underline{U}}\bigg|_V \dfrac{b}{\underline{V}} \equiv 0$$

Thus, the stability criteria yield

$$a = \underbrace{\left(\dfrac{\partial \underline{U}}{\partial T}\right)_V}_{\substack{\text{from}\\\text{Eqn. (2)}}} = C_V > 0 \text{ since } a \text{ and } b \text{ are positive constants}$$

and

$$b = -\dfrac{\underline{V}^2}{T}\left(\dfrac{\partial P}{\partial \underline{V}}\right)_T > 0 \Rightarrow \left(\dfrac{\partial P}{\partial \underline{V}}\right)_T < 0$$

Thus, fluid is always stable and does not have a first order phase transition.

5.8 At limit of stability $(\partial P/\partial \underline{V})_T = 0$ for the van der Waals equation:

$$\left(P + \dfrac{a}{\underline{V}^2}\right)(\underline{V} - b) = RT$$

So that at limit of stability

$$\left(\dfrac{\partial P}{\partial \underline{V}}\right)_T = 0 = \dfrac{-RT}{\underline{V}-b} + \dfrac{2a}{\underline{V}^3} = 0 \text{ ; or}$$

$$\dfrac{2a}{\underline{V}^3} = \dfrac{RT}{(\underline{V}-b)^2} = \dfrac{1}{\underline{V}-b}\left(\dfrac{RT}{\underline{V}-b}\right) = \dfrac{1}{\underline{V}-b}\left(P + \dfrac{a}{\underline{V}^2}\right)$$

Thus $P = a(\underline{V} - 2b)/\underline{V}^3$; or using

$$a = 3P_C V_C^2 \text{ and } b = \frac{V_C}{3} \quad \Rightarrow \quad P_r = \frac{3V_r - 2}{V_r^3}$$

To obtain the envelope, we compute P_r for various values of V_r

V_r	10	2	1	0.8	0.7
P_r	0.028	0.5	1.0	0.781	0.0343

Notice, that the critical point $(V_r = 1, \ P_r = 1)$ is the upper limit of metastability (i.e., $P_r \leq 1$), as well as the limit of single phase stability.

5.9 T and P will be taken as the independent variables at a second order phase transition

Then $\qquad\qquad\qquad\qquad \underline{G}^I = \underline{G}^{II}; \ \underline{S}^I = \underline{S}^{II}$, since $\underline{S} = -\left(\dfrac{\partial \underline{G}}{\partial T}\right)_P$

and

$$\underline{V}^I = \underline{V}^{II}, \text{ where } \underline{V} = \left(\frac{\partial \underline{G}}{\partial P}\right)_T$$

and, of course, $T^I = T^{II}$ and $P^I = P^{II}$.

From $\underline{S}^I = \underline{S}^{II}$ we have that along the 2nd order phase transition curve that $d\underline{S}^I = d\underline{S}^{II}$ or

$$\left(\frac{\partial \underline{S}^I}{\partial T}\right)_P dT + \left(\frac{\partial \underline{S}^I}{\partial P}\right)_T dP = \left(\frac{\partial \underline{S}^{II}}{\partial T}\right)_P dT + \left(\frac{\partial \underline{S}^{II}}{\partial P}\right)_T dP$$

$$\Rightarrow \frac{C_P^I}{T} dT - \left(\frac{\partial \underline{V}^I}{\partial T}\right)_P dP = \frac{C_P^{II}}{T} dT - \left(\frac{\partial \underline{V}^{II}}{\partial T}\right)_P dP$$

Thus

$$\left(\frac{\partial P}{\partial T}\right)_{\substack{\text{along} \\ \text{transition} \\ \text{curve}}} = \frac{C_P^I - C_P^{II}}{T\left\{\left(\partial \underline{V}^I / \partial T\right)_P - \left(\partial \underline{V}^{II} / \partial T\right)_P\right\}} \qquad\qquad (1)$$

Similarly, equating $d\underline{V}^I = d\underline{V}^{II}$ yields

$$\left(\frac{\partial \underline{V}^I}{\partial T}\right)_P dT + \left(\frac{\partial \underline{V}^I}{\partial P}\right)_T dP = \left(\frac{\partial \underline{V}^{II}}{\partial T}\right)_P dT + \left(\frac{\partial \underline{V}^{II}}{\partial P}\right)_T dP$$

Thus

$$\left(\frac{dP}{dT}\right)_{\substack{\text{along} \\ \text{transition} \\ \text{curve}}} = \frac{-\left\{\left(\partial \underline{V}^I / \partial T\right)_P - \left(\partial \underline{V}^{II} / \partial T\right)_P\right\}}{\left(\partial \underline{V}^I / \partial P\right)_T - \left(\partial \underline{V}^{II} / \partial P\right)_T} \qquad\qquad (2a)$$

However, since $\underline{V}^I = \underline{V}^{II}$, we can divide numerator and denominator by $\underline{V}$ and obtain

$$\left(\frac{\partial P}{\partial T}\right)_{\substack{\text{along} \\ \text{transition} \\ \text{curve}}} = \frac{\underline{a}^{\mathrm{I}} - \underline{a}^{\mathrm{II}}}{\underline{k}_T^{\mathrm{I}} - \underline{k}_T^{\mathrm{II}}} \tag{2b}$$

Note: The Clausius-Clapeyron equation is

$$T\left(\frac{\partial P}{\partial T}\right)_{\substack{\text{along} \\ \text{transition} \\ \text{curve}}} = \frac{\underline{H}^{\mathrm{I}} - \underline{H}^{\mathrm{II}}}{\underline{V}^{\mathrm{I}} - \underline{V}^{\mathrm{II}}} \tag{3}$$

However, this form is indeterminate for a 2nd order phase transition. Applying L'Hopital's rule to eqn. (3) taking derivatives of numerator and denominator with respect to T at constant P

$$T\left(\frac{\partial P}{\partial T}\right)_{\substack{\text{along} \\ \text{transition} \\ \text{curve}}} = \frac{C_P^{\mathrm{I}} - C_P^{\mathrm{II}}}{\left(\partial \underline{V}^{\mathrm{I}}/\partial T\right) - \left(\partial \underline{V}^{\mathrm{II}}/\partial T\right)} \text{ which is eqn. (1)!}$$

Similarly, applying L'Hopital's rule, but now taking derivatives with respect to P at constant T.

$$T\left(\frac{\partial P}{\partial T}\right)_{\substack{\text{along} \\ \text{transition} \\ \text{curve}}} = \frac{\left(\partial \underline{H}^{\mathrm{I}}/\partial P\right)_T - \left(\partial \underline{H}^{\mathrm{II}}/\partial P\right)_T}{\left(\partial \underline{V}^{\mathrm{I}}/\partial P\right)_T - \left(\partial \underline{V}^{\mathrm{II}}/\partial P\right)_T}$$

$$= \frac{\left[\underline{V}^{\mathrm{I}} - T\left(\partial \underline{V}^{\mathrm{I}}/\partial T\right)_P - \underline{V}^{\mathrm{II}} + T\left(\partial \underline{V}^{\mathrm{II}}/\partial T\right)_P\right]}{\left(\partial \underline{V}^{\mathrm{I}}/\partial P\right)_T - \left(\partial \underline{V}^{\mathrm{II}}/\partial P\right)_T}$$

but $\underline{V}^{\mathrm{I}} = \underline{V}^{\mathrm{II}}$ so that

$$\Rightarrow T\left(\frac{\partial P}{\partial T}\right)_{\substack{\text{along} \\ \text{transition} \\ \text{curve}}} = -T\frac{\left(\partial \underline{V}^{\mathrm{I}}/\partial T\right)_P - \left(\partial \underline{V}^{\mathrm{II}}/\partial T\right)_P}{\left(\partial \underline{V}^{\mathrm{I}}/\partial P\right)_T - \left(\partial \underline{V}^{\mathrm{II}}/\partial P\right)_T}$$

which is eqn. (2a)!

5.10 (a) $\left(\dfrac{dP}{dT}\right)_{\substack{\text{along} \\ \text{transition} \\ \text{curve}}} = \dfrac{\Delta H}{T\Delta V} \quad \Rightarrow \quad \dfrac{dP}{d\ln T} = \dfrac{\hat{H}_{\mathrm{L}} - \hat{H}_{\mathrm{S}}}{\hat{V}_{\mathrm{L}} - \hat{V}_{\mathrm{S}}} = \dfrac{335 \times 10^5 \ \mathrm{J/kg}}{-0.000093 \ \mathrm{m^3/kg}}$

$$= -3.61 \times 10^3 \ \mathrm{J/m^3}$$

$$\frac{dP}{d\ln T} = -3.61 \times 10^9 \ \mathrm{J/m^3} = -3.61 \times 10^9 \ \mathrm{Pa} \Rightarrow P_2 - P_1 = -3.61 \times 10^9 \ln\frac{T_2}{T_1}$$

$$\text{or } T_2 = T_1 \exp\left\{\frac{-2.985 \times 10^{-10}}{\mathrm{Pa}}(P_2 - P_1)\right\}$$

(b) $\left.\dfrac{dP}{dT}\right|_{\substack{\text{along} \\ \text{transition} \\ \text{curve}}} = \dfrac{\Delta \underline{H}}{T\Delta \underline{V}} \quad \text{but} \quad \Delta \underline{V} \approx \underline{V}^{\mathrm{V}} \sim \dfrac{RT}{P}$

$$\frac{dP}{dT} = \frac{\Delta \underline{H} P}{RT^2} \; ; \quad \frac{d \ln P}{dT} = \frac{\Delta \underline{H}}{RT^2}$$

If we assume that $\Delta \underline{H}$ is constant, then

$$\ln \frac{P_2}{P_1} = -\frac{\Delta \underline{H}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \Rightarrow T_2 = \left[\frac{1}{T_1} - \frac{R}{\Delta \underline{H}} \ln \frac{P_2}{P_1} \right]^{-1}$$

(c) Denver: $P_2 = 8.46 \times 10^5 \text{ Pa}$

$$T_2^{\text{F}} = 273.15 \exp \left\{ -2.985 \times 10^{-10} \left(8.46 \times 10^4 - 1.013 \times 10^5 \right) \right\}$$

$$= 273.15 \text{ K} = 0°C \text{ (freezing point essentially unchanged)}$$

$$T_2^{\text{B}} = \left[\frac{1}{373.15} - \frac{8.314 \times 10^3}{2.255 \times 10^6 \times 18} \ln \frac{8.46 \times 10^4}{1.013 \times 10^5} \right]^{-1} = 368.08 \text{ K} = 94.9°C$$

5.11 This problem involves the application of the Clausius-Clapeyron equation. We will assume that the heats of fusion, sublimation and vaporization are all constant. Thus we will use $\ln\dfrac{P_2}{P_1} = -\dfrac{\Delta \underline{H}}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$ in all cases. Now $\Delta \underline{H}^{\mathrm{vap}} = \Delta \underline{H}^{\mathrm{sub}} - \Delta \underline{H}^{\mathrm{fus}}$. To calculate $\Delta \underline{H}^{\mathrm{sub}}$ we will use the following sublimation data:

State 1: Triple point; $T = 112.9°\mathrm{C} = 386.05\,\mathrm{K}$; $P = 1.157\times10^4\,\mathrm{Pa}$
State 2: $T = 105.4°\mathrm{C} = 378.55\,\mathrm{K}$; $P = 8.00\times10^3\,\mathrm{Pa}$

$$\Rightarrow \ln\left(\frac{1.157\times10^4}{8.00\times10^3}\right) = 0.369 = -\frac{\Delta \underline{H}^{\mathrm{sub}}}{R}\left(\frac{1}{386.05} - \frac{1}{378.55}\right)$$

$$\Rightarrow \Delta \underline{H}^{\mathrm{sub}} = 5.980\times10^4\ \mathrm{J/mol}$$

$$\Delta \underline{H}^{\mathrm{fus}} = 1.527\times10^4\ \mathrm{J/mol} \Rightarrow \Delta \underline{H}^{\mathrm{vap}} = (5.980 - 1.527)\times10^4$$

$$= 4.453\times10^4\ \mathrm{J/mol}$$

and $\Delta \underline{H}^{\mathrm{vap}}/R = 5356\,\mathrm{K}$. To find the normal boiling temperature we again use Clausius-Clapeyron equation.

$$\ln\left(\frac{1.013\times10^5}{1.157\times10^4}\right) = \frac{-4.453\times10^4}{8.314}\left(\frac{1}{T_2} - \frac{1}{386.05}\right) \qquad \begin{array}{l}\text{State 1 = T.\,P.}\\ \text{State 2 = N.\,B.\,P.}\end{array}$$

$$\Rightarrow T_2 = 457.7\,\mathrm{K} = 184.5°\mathrm{C}$$

Experimental value $= 183°\mathrm{C}$; difference due to assumption that $\Delta \underline{H}^{\mathrm{vap}}$ is a constant.

5.12 (a) At equilibrium $P^{\mathrm{sat}}(\mathrm{ice}) = P^{\mathrm{sat}}(\mathrm{water})$

Equating the $\ln P^{\mathrm{sat}}$'s gives

$$28.8962 - \frac{614.01}{T} = 26.3026 - \frac{5432.8}{T} \qquad \Rightarrow \qquad T = 273.1°\mathrm{C}$$

and

$$\ln P^{\mathrm{sat}}(\mathrm{ice}) = 28.8962 - \frac{6140.1}{273.1} = 6.4096 \Rightarrow P^{\mathrm{sat}} = 607.7\,\mathrm{Pa}$$

(b) $\ln P = A - \dfrac{B}{T}$ and $\dfrac{d\ln P}{dT} = \dfrac{\Delta \underline{H}}{RT^2}$ also

$$\frac{d\ln P}{dT} = +\frac{B}{T^2} \Rightarrow \Delta \underline{H} = B\cdot R$$

Thus

$$\left.\frac{\Delta \underline{H}}{R}\right|_{\mathrm{ice}\rightarrow\mathrm{vapor}} = 6140.1 \text{ and } \Delta \underline{H}^{\mathrm{sub}} = 5.105\times10^4\ \mathrm{J/mol}$$

$$\left.\frac{\Delta \underline{H}}{R}\right|_{\mathrm{water}\rightarrow\mathrm{vapor}} = 5432.8 \text{ and } \Delta \underline{H}^{\mathrm{sub}} = 4.517\times10^4\ \mathrm{J/mol}$$

$$\Delta \underline{H}^{\mathrm{fus}} = \Delta \underline{H}|_{\mathrm{ice}\rightarrow\mathrm{water}} = \Delta \underline{H}^{\mathrm{sub}} - \Delta \underline{H}^{\mathrm{vap}} = 5.880\times10^3\ \mathrm{J/mol}$$

5.13 (Also available as a Mathcad worksheet. The Mathcad solution includes graphs.)

(a) Use the Clausius-Clapeyron equation

$$\frac{\Delta \underline{H}^{\text{vap}}}{R} = \frac{\ln(P_2/P_1)}{1/T_1 - 1/T_2}$$

Plotting $\ln P$ vs. $\dfrac{1}{T}$ and graphically taking slope, I find $\Delta \underline{H}^{\text{vap}} \sim 42700 \text{ J/mol}$.

(b) The vapor pressure is low enough that the ideal gas approximation should be valid—thus

$$\frac{d \ln P^{\text{vap}}}{dT} = \frac{\Delta \ln P^{\text{vap}}}{\Delta T} = \frac{\Delta \underline{H}^{\text{vap}}}{RT^2}$$

either graphically or analytically, we find

$$\Delta \underline{H}^{\text{vap}} \sim 313,600 \text{ J/mol}$$

5.14 (a) Start with Eqn. (5.4-6)

$$f = P \exp\left\{ \frac{1}{RT} \int_0^P \left(\underline{V} - \frac{RT}{P} \right) dP \right\} \Rightarrow \ln\frac{f}{P} = \int_0^P \left(\frac{P\underline{V}}{RT} - 1 \right) dP$$

but $\dfrac{1}{P} dP = \dfrac{d(P\underline{V})}{P\underline{V}} - \dfrac{d\underline{V}}{\underline{V}} = \dfrac{dZ}{Z} - \dfrac{d\underline{V}}{\underline{V}}$ so

$$\ln\frac{f}{P} = \int_{Z=1}^Z (Z-1)\frac{dZ}{Z} - \int_{\underline{V}=\infty}^{\underline{V}} \left(\frac{P\underline{V}}{RT} - 1 \right)\frac{d\underline{V}}{\underline{V}} = (Z-1) - \ln\frac{Z}{1} - \int_{\underline{V}=\infty}^{\underline{V}} \left(\frac{P}{RT} - \frac{1}{\underline{V}} \right)d\underline{V}$$

or

$$\ln\frac{f}{P} = (Z-1) - \ln Z + \frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}} \left(\frac{RT}{\underline{V}} - P \right)d\underline{V} \qquad \text{(Eqn. 5.4-8)}$$

(b) $Z = 1 + \dfrac{B(T)}{\underline{V}}$ and $P = \dfrac{RT}{\underline{V}}\left(1 + \dfrac{B}{\underline{V}} \right)$

$$\ln\frac{f}{P} = \frac{B}{\underline{V}} - \ln\left(1 + \frac{B}{\underline{V}} \right) + \frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}} \left[\left(\frac{RT}{\underline{V}} - \frac{RT}{\underline{V}} - \frac{RT}{\underline{V}}\cdot\frac{B}{\underline{V}} \right) \right]d\underline{V}$$

$$= \frac{B}{\underline{V}} - \ln Z + B\int_{\underline{V}=\infty}^{\underline{V}} \frac{1}{\underline{V}^2}d\underline{V} = \frac{ZB}{\underline{V}} - \ln Z$$

(c)   vdW e.o.s.

$$P = \frac{RT}{\underline{V} - b} - \frac{a}{\underline{V}^2}; \ Z^{vdW} = \frac{P\underline{V}}{RT} = \frac{\underline{V}}{\underline{V} - b} - \frac{a}{\underline{V}^2 RT}$$

$$\int_{\underline{V}=\infty}^{\underline{V}} \left(\frac{RT}{\underline{V}} - P \right) d\underline{V} = \int_{\underline{V}=\infty}^{\underline{V}} \left(\frac{RT}{\underline{V}} - \frac{RT}{\underline{V} - b} + \frac{a}{\underline{V}^2} \right) d\underline{V} = RT \ln \frac{\underline{V}}{\underline{V} - b} - \frac{a}{\underline{V}} \Big|_{\underline{V}=\infty}^{\underline{V}}$$

$$= RT \ln \frac{\underline{V}}{\underline{V} - b} - \frac{a}{\underline{V}} \Big|$$

so

$$\ln \frac{f^{vdW}}{P} = \ln \frac{\underline{V}}{\underline{V} - b} - \frac{a}{RT\underline{V}} + (Z - 1) - \ln Z$$

$$= \ln Z - \ln \left(Z - \frac{Pb}{RT} \right) - \frac{a}{RT} \cdot \frac{RT}{P\underline{V}} \cdot \frac{P}{RT} + (Z - 1) - \ln Z$$

$$= (Z - 1) - \frac{A}{Z} - \ln(Z - B)$$

where $A = \dfrac{aP}{(RT)^2}$ and $B = \dfrac{Pb}{RT}$.

(d) Peng-Robinson equation of state. Start with

$$\int_{\underline{V}=\infty}^{\underline{V}} \left(\frac{RT}{\underline{V}} - P \right) d\underline{V} = \int_{\underline{V}=\infty}^{\underline{V}} \left[\frac{RT}{\underline{V}} - \frac{RT}{\underline{V} - b} + \frac{a}{\underline{V}(\underline{V} + b) + b(\underline{V} - b)} \right] d\underline{V}$$

$$= RT \ln \frac{\underline{V}}{\underline{V} - b} - \frac{a}{2\sqrt{2}b} \ln \left[\frac{\underline{V} + (1 + \sqrt{2})b}{\underline{V} + (1 - \sqrt{2})b} \right]$$

$$= RT \ln \frac{Z}{Z - B} - \frac{a}{2\sqrt{2}b} \ln \left[\frac{\underline{V} + (1 + \sqrt{2})b}{\underline{V} + (1 - \sqrt{2})b} \right]$$

[See solution to Problem 4.2 for integral]. Therefore

$$\ln \frac{f^{PR}}{P} = (Z - 1) - \ln Z + \ln \frac{Z}{Z - B} - \frac{a}{2\sqrt{2}bRT} \ln \left[\frac{\underline{V} + (1 + \sqrt{2})b}{\underline{V} + (1 - \sqrt{2})b} \right]$$

$$= (Z - 1) - \ln(Z - B) - \frac{a}{2\sqrt{2}bRT} \ln \frac{\underline{V} + (1 + \sqrt{2})b}{\underline{V} + (1 - \sqrt{2})b}$$

5.15 (a) $f_{H_2S}^{liq} = f_{H_2S}^{vap}$; $f^{vap} = P(f/P)$, where the fugacity coefficient, f/P will be gotten from corresponding states.

$$P_{C, H_2S} = 89.42 \text{ bar} \Rightarrow P_r = \frac{20}{89.42} = 0.2237$$

$$T_{C, H_2S} = 373.2 \text{ K} \Rightarrow T_r = \frac{25.5 + 273.15}{373.2} = 0.8002$$

$$Z_{C, H_2S} = 0.284, \text{ which is reasonably close to } 0.27$$

From Fig. 5.4-1, $\dfrac{f}{P} = 0.765$, $f_{H_2S} = 20 \times 0.765 = 15.3$ bar .

(b) For a liquid, from Eqn. (5.4-18)

$$f = P^{vap}\left(\frac{f}{P}\right)_{sat} \exp\left[\int_{P^{vap}}^{P} \frac{V}{RT} dP\right]$$

Since $P^{vap} = 6.455 \times 10^3$ Pa at the temperature of interest, we will assume that $(f/P)_{sat} \sim 1$. Also, we will consider the liquid to be incompressible. Thus

$$\int_{P^{vap}}^{P} \frac{V}{RT} dP = \frac{V}{RT} \int_{P^{vap}}^{P} dP = \frac{V(P - P^{vap})}{RT}$$

and

$$f_{H_2S} = P^{vap} \exp\left[\frac{V(P - P^{vap})}{RT}\right] = 6455 \exp\left[\frac{0.018(P - 6455)}{8.314 \times 10^3 \times 310.6}\right] Pa$$

so that

Pressure, Pa	f_{H_2S}, Pa	Reported
$P = 1.0 \times 10^7$	6,921	6,925
5.0×10^7	9,146	9,175
1.0×10^8	12,960	12,967

5.16 (also available as a Mathcad worksheet)

(a) There are (at least) two ways to solve this problem. One way is to start from

$$f = P \exp\left\{\frac{1}{RT}\int_{0}^{P}\left(V - \frac{RT}{P}\right)dP\right\}$$

or

$$RT \ln \frac{f}{P} = \int_{0}^{P}\left(V - \frac{RT}{P}\right)dP$$

$$\frac{RT}{P} = \frac{8.314 \times 10^{-6} \text{ MPa} \cdot \text{m}^3/\text{mol K} \times (273.15 + 400)\text{K}}{P(\text{MPa}) \times 18.01 \text{ g/mol} \times 10^{-3} \text{ kg/g}} = \frac{0.310748}{P} \text{ m}^3/\text{kg}$$

From Steam Tables $T = 400°C$

P MPa	$\hat{V}$ m³/kg	$\hat{V} - RT/P$
0.01	31.063	−0.0118
0.05	6.029	−0.00596
0.10	3.103	−0.00448
0.2	1.5493	−0.00444
0.3	1.0315	−0.00433
0.4	0.7726	−0.00427
0.5	0.6173	−0.00420
0.6	0.5137	−0.00421
0.8	0.3843	−0.00413
1.0	0.3066	−0.00415
1.2	0.2548	−0.00416
1.4	0.2178	−0.00416
1.6	0.19005	−0.00417
1.8	0.16847	−0.00417
2.0	0.15120	−0.00417

By numerical integration of this data we find that

$$RT \ln \frac{f}{P} \sim -0.0084 \ \text{MPa} \cdot \text{m}^3/\text{kg}$$

$$\Rightarrow \ln \frac{f}{P} = \frac{-0.0084 \ \text{MPa} \cdot \text{m}^3/\text{kg}}{0.310748 \ \text{MPa} \cdot \text{m}^3/\text{kg}} = -0.027032$$

so $f/P = 0.97333$ and $f = 1.947 \ \text{MPa}$. A second way to use the steam tables is to assume that steam at $400°C$ and 0.01 MPa is an ideal gas. From the steam tables, at these conditions, we have

$$\hat{H} = 3279.6 \ \text{kJ/kg}; \ \hat{S} = 9.6077 \ \text{kJ/kg K}$$

$$\Rightarrow \hat{G} = \hat{H} - T\hat{S} = 3279.6 - 673.15 \times 9.6077 = -3187.8 \ \text{kJ/kg}$$

$$= -57412.7 \ \text{kJ/kmol} = \underline{G}(400°C, \ 0.01 \ \text{MPa}) = \underline{G}^{IG}(400°C, \ 0.01 \ \text{MPa})$$

Also

$$\underline{G}^{IG}(T = 400°C, \ 2 \ \text{MPa}) - \underline{G}^{IG}(T = 400°C, \ 0.01 \ \text{MPa}) = \int\limits_{P=0.01 \, \text{MPa}}^{2 \, \text{MPa}} \underline{V}^{IG} dP$$

$$\underline{G}^{IG}(T = 400°C, \ 2 \ \text{MPa}) = -57412.7 \ \text{kJ/kmol} + \int\limits_{0.01}^{2 \, \text{MPa}} \frac{RT}{P} dP$$

$$= -57412.7 + 8.314 \ln 200 = -27760.3 \ \text{kJ/kmol}$$

Also, from steam tables

$$\underline{G}(T = 400°C, \ 2 \ \text{MPa}) = (3247.6 - 673.15 \times 7.1271) \times 18.01$$

$$= -27915.63 \ \text{kJ/kmol}$$

$$\frac{f}{P} = \exp\left(\frac{\underline{G} - \underline{G}^{IG}}{RT}\right) = \exp\left(\frac{-27915.63 + 27760.3}{8.314 \times 673.15}\right)$$

$$= 0.9726$$

$$f = 0.9726 \times 2 \ \text{MPa} = 1.945 \ \text{MPa}$$

(b) Corresponding states $\left(T_C = 647.3 \text{ K}, \ P_C = 22.048 \text{ MPa}, \ w = 0.344\right)$

$$T_r = \frac{400 + 273.15}{647.3} = 1.04\,; \quad P_r = \frac{2}{22.048} = 0.0907$$

From corresponding states chart (actually from Table in Hougen, Watson and Rogatz, Vol. II, p. 601) we have

$$\frac{f}{P} = 0.983 \Rightarrow f = 1.966 \text{ MPa}$$

(c) Using the program PR1 we find

$$f = 19.40 \text{ bar} = 1.940 \text{ MPa}$$

Comment: The steam table results are probably the most accurate, and the corresponding states results the least accurate. Note that with the availability of the computer program PR1, the P-R e.o.s. is the easiest to use. The results would be even more accurate if the PRSV equation was used.

5.17 (a) $\dfrac{P\underline{V}}{RT} = 1 + \dfrac{B}{\underline{V}} + \dfrac{C}{\underline{V}^2} + \cdots\,; \ \Rightarrow \underline{V} = \dfrac{RT}{P} + \dfrac{BRT}{\underline{V}P} + \dfrac{CRT}{\underline{V}^2 P} + \cdots$

Thus

$$\frac{P\underline{V}}{RT} = 1 + \frac{B}{RT/P + BRT/\underline{V}P + CRT/\underline{V}^2 P + \cdots}$$

$$+ \frac{C}{RT/P + BRT/\underline{V}P + CRT/\underline{V}^2 P + \cdots} + \cdots$$

$$= 1 + \frac{B(P/RT)}{1 + B\{RT/P + \cdots\}^{-1} + C\{RT/P + \cdots\}^{-2} + \cdots} + \frac{C(P/RT)^2}{1 + 2B/\underline{V} + \cdots}$$

Now keeping terms of order 1, B, B^2 and C only yields

$$\frac{P\underline{V}}{RT} = 1 + B\left(\frac{P}{RT}\right)\left(1 - B\frac{P}{RT} + \cdots\right) + C\left(\frac{P}{RT}\right)^2$$

$$= 1 + \frac{BP}{RT} + \left(C - B^2\right)\left(\frac{P}{RT}\right)^2 + \cdots$$

(b) $\underline{V} = \dfrac{RT}{P} + B + \left(C - B^2\right)\left(\dfrac{P}{RT}\right) + \cdots$ and $\underline{V}^{\text{IG}} = \dfrac{RT}{P}$. Therefore

$$\underline{V} - \underline{V}^{\text{IG}} = B + \left(C - B^2\right)\left(\frac{P}{RT}\right) + \cdots \text{ and}$$

$$\frac{f}{P} = \exp\left\{\frac{1}{RT}\int_0^P \left[B + \left(C - B^2\right)\frac{P}{RT} + \cdots\right] dP\right\}$$

or

$$\frac{f}{P} = \exp\left\{\frac{BP}{RT} + \frac{\left(C - B^2\right)}{2}\left(\frac{P}{RT}\right)^2 + \cdots\right\}$$

We will consider a number of alternatives for using the virial coefficient data. The first is to start with Eqn. (5.4-6a)

$$\frac{f}{P} = \exp\left\{\frac{1}{RT}\int_0^P\left(\underline{V} - \frac{RT}{P}\right)dP\right\} = \exp\left\{\frac{1}{RT}\int_0^P\left(\underline{V} - \underline{V}^{IG}\right)dP\right\} \qquad (1)$$

thus we need to evaluate the integral $1/RT\int_0^P\left(\underline{V} - \underline{V}^{IG}\right)dP$. Since the truncated virial equation $P/RT = 1/\underline{V} + B/\underline{V}^2 + C/\underline{V}^3$ can not easily be solved for $\underline{V}$ as a function of T and P, the following procedure will be used:

i) Choose values of $\underline{V}$ and compute

$$P = \frac{RT}{\underline{V}}\left(1 + \frac{B}{\underline{V}} + \frac{C}{\underline{V}^2}\right) \quad \text{and} \quad P^{IG} = \frac{RT}{\underline{V}}$$

ii) Plot P and P^{IG} as a function of $\underline{V}$

iii) Use these two plots to obtain $\underline{V}^{IG}$ and $\underline{V}$ (real gas) at the same value of P, also compute $\underline{V}(T,P) - \underline{V}^{IG}(T,P)$

iv) Finally, use a numerical or graphical integration scheme to get f/P as a function of P

Same representative values of $\underline{V} - \underline{V}^{IG}$ are given below

$P\left(10^6\,\text{Pa}\right)$	1	2	3	4	5	6	7	8
$-\left(\underline{V} - \underline{V}^{IG}\right)$ m^3/kmol	0.187	0.180	0.187	0.223	0.206	0.211	0.201	0.180

$P\left(10^6\,\text{Pa}\right)$	9	10	11	12	13	14	15
$-\left(\underline{V} - \underline{V}^{IG}\right)$ m^3/kmol	0.1573	0.1384	0.1215	0.1069	0.0944	0.0834	0.0739

Using the data and performing the integration we obtain

$P\left(10^6\,\text{Pa}\right)$	1	3	5	7	9	10	11	13	15
f/P		0.939	0.822	0.703	0.602	0.527	0.499	0.475	0.439	0.412

An alternative is to note that $dP = \left(\frac{\partial P}{\partial \underline{V}}\right)_T d\underline{V}$ and, with

$$P = \frac{RT}{\underline{V}}\left(1 + \frac{B}{\underline{V}} + \frac{C}{\underline{V}^2}\right), \text{ that } \left(\frac{\partial P}{\partial \underline{V}}\right)_T = \left(-\frac{1}{\underline{V}^2} - \frac{2B}{\underline{V}^3} - \frac{3C}{\underline{V}^4}\right)RT$$

and

$$\frac{1}{RT}\int_0^P \left(\underline{V} - \underline{V}^{IG}\right) dP = \frac{1}{RT}\int_{\underline{V}(0)}^{\underline{V}(P)} \underline{V}\left(\frac{\P P}{\P \underline{V}}\right)_T d\underline{V} - \frac{1}{RT}\int_0^P \frac{RT}{P} dP$$

$$= \lim_{P_0 \to 0}\left[-\int_{\underline{V}(P_0)}^{\underline{V}(P)}\left(\frac{1}{\underline{V}} + \frac{2B}{\underline{V}^2} + \frac{3C}{\underline{V}^3}\right)d\underline{V} - \int_{P_0}^P \frac{dP}{P}\right]$$

$$= \lim_{P_0 \to 0}\left[-\ln P\underline{V} + \ln P_0\underline{V}(P_0) + 2B\left(\frac{1}{\underline{V}(P)} - \frac{1}{\underline{V}(P_0)}\right) + \frac{3C}{2}\left(\frac{1}{\underline{V}^2(P)} - \frac{1}{\underline{V}^2(P_0)}\right)\right]$$

$$= -\ln P\underline{V} + \ln RT + \frac{2B}{\underline{V}} + \frac{3C}{2\underline{V}^2}$$

[Note: $\lim_{P_0 \to 0} \underline{V}(P_0) = \infty$]

Thus

$$\frac{f}{P} = \exp\left\{\ln\frac{RT}{P\underline{V}} + \frac{2B}{\underline{V}} + \frac{3C}{2\underline{V}^2}\right\} = \frac{RT}{P\underline{V}}\exp\left\{\frac{2B}{\underline{V}} + \frac{3C}{2\underline{V}^2}\right\}$$

but $P\underline{V}/RT = 1 + B/\underline{V} + C/\underline{V}^2$ and

$$\frac{f}{P} = \frac{\exp\left\{2B/\underline{V} + 3C/2\underline{V}^2\right\}}{1 + B/\underline{V} + C/\underline{V}^2} = \frac{\exp\left\{-0.3326/\underline{V} + 0.01938/\underline{V}^2\right\}}{1 - 0.1663/\underline{V} + 0.012921/\underline{V}^2} \qquad (2)$$

for $\underline{V}$ in m^3/kmol.

The use of this equation leads to results that are somewhat more accurate than the graphical integration scheme. Still another possibility is to use the results of part (a) which yields

$$\frac{f}{P} = \exp\left\{-0.00619 P - 1.0207 \times 10^{-5} P^2\right\} \text{ for } P \text{ in bar} \qquad (3)$$

The results of using this equation are listed below.

Finally we can also compute (f/P) using corresponding states (Figure 5.4-1). For methyl fluoride $T_C = 317.7$ K and $P_C = 5.875$ MPa (note Z_C is unknown is $\underline{V}_C$ has not been measured). Thus, $T_r = (273.15 + 50)/317.7 = 1.017$, and for each pressure P_r can be computed, and f/P found from Fig. 5.4-1.

The results for each of the calculations are given below:

P (bar)	10	30	50	70	100	130	150
eqn. (1) f/P	0.939	0.822	0.703	0.602	0.499	0.439	0.412
eqn. (2) f/P	0.939	0.822	0.710	0.607	0.503	0.442	0.416
eqn. (3) f/P	0.939	0.823	0.715	0.617	0.486	0.376	0.314
Corresponding states f/P	0.96	0.85	0.72	0.60	0.47	0.39	0.345

Note that at low pressure, all the results for f/P are similar. At high pressures, however, the results differ. Equation (3) is approximate, and probably the least accurate. Equation (2) should be the most accurate, except that there is a question as to how accurate it is to use an equation of state with only the second and third virial coefficients for pressures as high as 150 bar.

5.18 (a) Assume the vapor phase is ideal, and that $\Delta \underline{H}^{\text{vap}}$ is approximately constant (or an average $\Delta \underline{H}^{\text{vap}}$ can be used).

$$\ln \frac{P_2}{P_1} = -\frac{\Delta \underline{H}^{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{1}$$

$$\Rightarrow \ln\left(\frac{2.026}{1.013}\right) = \frac{-\Delta \underline{H}^{\text{vap}}}{R}\left(\frac{1}{222.0 + 273.15} - \frac{1}{178.0 + 273.15}\right)$$

$$\Rightarrow \frac{\Delta \underline{H}^{\text{vap}}}{R} = 3.52 \times 10^3 / \text{K} \qquad \Delta \underline{H}^{\text{vap}} = 2.93 \times 10^4 \text{ J/mol}$$

(b) $\Delta \underline{H}^{\text{vap}}(T) = \underline{H}(\text{sat. vap},T) - \underline{H}(\text{sat. liq}, T)$

$$= \left[\underline{H}(\text{sat. vap, } T) - \underline{H}^{\text{IG}}(T)\right] - \left[\underline{H}(\text{sat. liq., } T) - \underline{H}^{\text{IG}}(T)\right]$$

$$\Rightarrow \Delta \underline{H}^{\text{vap}}(T) = T_C\left[\left(\frac{\underline{H} - \underline{H}^{\text{IG}}}{T_C}\right)_{\text{sat. vap, } T} - \left(\frac{\underline{H} - \underline{H}^{\text{IG}}}{T}\right)_{\text{sat. liq., } T}\right]$$

(c) $T_r = \dfrac{T}{T_C} = \dfrac{200 + 273.15}{283.1 + 273.15} = 0.851$

$$\left(\frac{\underline{H}^{\text{IG}} - \underline{H}}{T_C}\right)_{\substack{\text{sat. vap} \\ T_r = 0.851}} = 5.06 \text{ J/mol K} \quad \text{and} \quad \left(\frac{\underline{H}^{\text{IG}} - \underline{H}}{T_C}\right)_{\substack{\text{sat. liq.} \\ T_r = 0.851}} = 44.69 \text{ J/mol K}$$

$$\Delta \underline{H}^{\text{vap}}(T) = 556.45 \text{ K}[44.69 - 5.06] = 2.205 \times 10^4 \text{ J/mol}$$

(d) The reason for the discrepancy is probably not the inaccuracy of corresponding states (since $Z_C = 0.272$ which is close to 0.27) but rather the assumption of an ideal vapor phase in the Clausius-Clapeyron equation. We correct for gas-phase nonideality below.

$$\text{at } T = 178°\text{C}, \ T_r = 0.811, \ Z = 0.82$$
$$T = 222°\text{C}, \ T_r = 0.890, \ Z = 0.71$$

The average value of the compressibility is

$$\overline{Z} = \frac{1}{2}(0.82 + 0.71) = 0.765$$

We now replace eqn. 1 with

$$\ln \frac{P_2}{P_1} = \frac{-\Delta \underline{H}^{\text{vap}}}{ZR}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \Rightarrow \Delta \underline{H}^{\text{vap}} = 0.765 \times \left(2.93 \times 10^4 \text{ J/mol}\right)$$

$$= 2.24 \times 10^4 \text{ J/mol}$$

which is in much better agreement with the result of part (c). A better way to proceed would be to compute the compressibility as a function of temperature, i.e., find $Z = Z(T, P)$ and then integrate

$$\frac{dP}{dT} = \frac{\Delta \underline{H}^{\text{vap}} P}{Z(T, P)RT^2}$$

rather than use an average value of Z, i.e. $\overline{Z}$.

5.19 Basis: vessel volume $1\,\text{m}^3$ (cancels out of problem)

x = fraction of vessel filled with liquid water

$$N = \text{total number of moles of water} = \frac{x}{\underline{V}^{\text{L}}} + \frac{(1-x)}{\underline{V}^{\text{V}}} \quad (\text{per } 1\,\text{m}^3 \text{ of vessel})$$

1) Total number of moles same at all conditions
2) x is the same at initial loading and at critial point

State 1—low pressure $\underline{V}^{\text{V}} \gg \underline{V}^{\text{L}}$

$$\Rightarrow N_1 = \frac{x}{\underline{V}^{\text{L}}} + \frac{(1-x)}{\underline{V}^{\text{V}}} \approx \frac{x}{\underline{V}^{\text{L}}}$$

State 2—Critical point $\underline{V}^{\text{V}} = \underline{V}^{\text{L}} = \underline{V}_C \Rightarrow N_2 = \frac{1-x}{\underline{V}_C} + \frac{x}{\underline{V}_C} = \frac{1}{\underline{V}_C}$ but

$$N_1 = N_2 \Rightarrow \frac{x}{\underline{V}^{\text{L}}} = \frac{1}{\underline{V}_C} \quad \text{or} \quad x = \frac{\underline{V}^{\text{L}}}{\underline{V}_C}$$

(a) Using steam tables

$$\underline{V}^{\text{L}}(25°\text{C}) = 0.001003\ \text{m}^3/\text{kg}\,;\ \underline{V}_C = 0.003155\ \text{m}^3/\text{kg}$$

$$x = \frac{0.001003}{0.003155} = 0.3179$$

$\Rightarrow$ Initial fill should contain 31.79% of volume with liquid (which was reported in the Chemical and Engineering News article).

(b) Peng-Robinson equation of state

$$\underline{V}_{\text{L}}(25°\text{C}) = 0.2125 \times 10^{-4}\ \text{m}^3/\text{mol}$$

and the P-R equation of state predicts $Z_C = 0.3074$ (solution to Problem **4.11b**) so

$$\underline{V}_C = \frac{Z_C R T_C}{P_C} = \frac{0.3074 \times 8.314 \times 10^{-6}\ \text{MPa}\ \text{m}^3/\text{mol K} \times 647.3\ \text{K}}{22.048\ \text{MPa}}$$

$$= 0.75033 \times 10^{-4}\ \text{m}^3/\text{mol} \Rightarrow x = 0.2832$$

or an initial fill of 28.32% of volume with liquid.

5.20 (a) One theory for why ice skating is possible is because ice melts due to the pressure put upon it under the ice skates, and then refreezes when skate leaves and the pressure is released. Skate actually moves over a film of water on the sheet of ice. To find the lowest temperature we use the Clapeyron equation to calculate the change in freezing point as a result of the applied pressure. Properties of ice:

$$r = 0.90\ \text{g/cc} \Rightarrow \underline{V}^S = 1.11\ \text{cc/g}$$

$$\Delta\hat{H}^{\text{fus}} = \Delta\hat{H}^{\text{sub}} - \Delta\hat{H}^{\text{vap}} = 2834.8 - 2501.3 = 333.5\ \text{J/g} \quad (\text{at } 0.01°\text{C})$$

(Appendix III)

$$\left(\frac{\partial P}{\partial T}\right)_{sat} = \frac{\Delta \hat{H}}{T\Delta \hat{V}} \Rightarrow \frac{\partial P}{\partial T} = \frac{333.5 \text{ J/g}}{273.15 \text{ K} \times (1-1.11) \text{ cc/g}}$$

$$= -1.110 \text{ J/cc K} = -111.4 \text{ bar/K}$$

$$\text{or } \left(\frac{\partial T}{\partial P}\right) \sim -0.0090 \text{ K/bar} \Rightarrow \Delta T = -0.009 \text{ K/bar } (\Delta P)$$

Assume 70 kg person on 0.6 cm^2 skate area (well sharpened)

$$\Delta P = \frac{70}{0.6} = 116.7 \text{ kg/cm}^2 \times 0.9807 \text{ bar/kg/cm}^2 = 114.4 \text{ bar}$$

$$\Rightarrow \Delta T = -1.03°C$$

assuming skate makes complete contact with ice. If the surface is irregular (as it is) maybe contact only over 10% of area. In this case $\Delta T = -9.3°C$. My observation in Minnesota was that it was possible to skate down to ~$-20°C$ (5% contact area??). Of course, the thermodynamic model for this process may be incorrect. Other possibilities include the melting of ice as a result of friction, or by heat transfer from the skater's foot to the ice. I believe the thermodynamic theory to be the a reasonable explanation of the phenomena.

(b) Since $\Delta \hat{H}^{fus} > 0$ and $\Delta \hat{V}^{fus} > 0$ for CO_2 and most other materials, freezing point will be elevated not depressed. Liquid film can not form and ice skating is impossible.

(c) More difficult to quantify. Similar to (a) for freezing point depression, which on release of pressure causes refreezing and formation of snowball; but in this case there is also considerable heat transfer from the hands to the surface of the snowball that causes melting.

5.21 (also available as a Mathcad worksheet)

5.21

From Eq. 5.7-4 $\quad \Delta T = \Delta P \cdot \Delta V \cdot T / \Delta H \qquad bar := 10^5 \cdot Pa$

Water

$$\Delta T := \frac{1000 \cdot bar \cdot \left(-0.0906 \cdot 10^{-6} \cdot \frac{m^3}{g}\right) \cdot 273.1 \cdot K}{333.8 \cdot \frac{joule}{g}} \qquad \Delta T = {}^{-}7.412 \cdot K$$

Acetic acid

$$\Delta T := \frac{1000 \cdot bar \cdot \left(0.01595 \cdot 10^{-6} \cdot \frac{m^3}{g}\right) \cdot 289.8 \cdot K}{187 \cdot \frac{joule}{g}} \qquad \Delta T = 2.472 \cdot K$$

Tin

$$\Delta T := \frac{1000 \cdot bar \cdot \left(0.00389 \cdot 10^{-6} \cdot \frac{m^3}{g}\right) \cdot 505.0 \cdot K}{58.6 \cdot \frac{joule}{g}} \qquad \Delta T = 3.352 \cdot K$$

Bismuth

$$\Delta T := \frac{1000 \cdot bar \cdot \left(-0.00342 \cdot 10^{-6} \cdot \frac{m^3}{g}\right) \cdot 544 \cdot K}{52.7 \cdot \frac{joule}{g}} \qquad \Delta T = {}^{-}3.53 \cdot K$$

5.22 (also available as a Mathcad worksheet)

5.22

$$i := 0 .. 10$$

$$R := 8.314$$

$$\Delta H(T, a, b, c) := R \cdot \left[c \cdot (T)^2 + b \cdot T - a \right]$$

Ag(s) $\qquad Tmax := 1234 \qquad Tmin := 298 \qquad a := {}^{-}14710 \quad b := {}^{-}0.328 \quad c := 0$

$$Y_i := \frac{Tmax - Tmin}{10} \cdot (i) + Tmin$$

T, K	ΔHm, J/mol
Y_i	$\Delta H(Y_i, a, b, c)$
298	$1.215 \cdot 10^5$
391.6	$1.212 \cdot 10^5$
485.2	$1.21 \cdot 10^5$
578.8	$1.207 \cdot 10^5$
672.4	$1.205 \cdot 10^5$
766	$1.202 \cdot 10^5$
859.6	$1.2 \cdot 10^5$
953.2	$1.197 \cdot 10^5$
$1.047 \cdot 10^3$	$1.194 \cdot 10^5$
$1.14 \cdot 10^3$	$1.192 \cdot 10^5$
$1.234 \cdot 10^3$	$1.189 \cdot 10^5$

Ag(l) $\quad$ Tmax $:= 2485$ $\quad$ Tmin $:= 1234$ $\quad$ a $:= -14260$ $\quad$ b $:= -0.458$ $\quad$ c $:= 0$

$$Y_i := \frac{Tmax - Tmin}{10} \cdot (i) + Tmin$$

	T, K	ΔHsub, J/mol
	Y_i	$\Delta H\left(Y_i, a, b, c\right)$
	$1.234 \cdot 10^3$	$1.139 \cdot 10^5$
	$1.359 \cdot 10^3$	$1.134 \cdot 10^5$
	$1.484 \cdot 10^3$	$1.129 \cdot 10^5$
	$1.609 \cdot 10^3$	$1.124 \cdot 10^5$
	$1.734 \cdot 10^3$	$1.12 \cdot 10^5$
	$1.86 \cdot 10^3$	$1.115 \cdot 10^5$
	$1.985 \cdot 10^3$	$1.11 \cdot 10^5$
	$2.11 \cdot 10^3$	$1.105 \cdot 10^5$
	$2.235 \cdot 10^3$	$1.1 \cdot 10^5$
	$2.36 \cdot 10^3$	$1.096 \cdot 10^5$
	$2.485 \cdot 10^3$	$1.091 \cdot 10^5$

BeO(s) $\quad$ Tmax $:= 2800$ $\quad$ Tmin $:= 298$ $\quad$ a $:= -34230$ $\quad$ b $:= -0.869$ $\quad$ c $:= 0$

$$Y_i := \frac{Tmax - Tmin}{10} \cdot (i) + Tmin$$

	T, K	ΔHm, J/mol
	Y_i	$\Delta H\left(Y_i, a, b, c\right)$
	298	$2.824 \cdot 10^5$
	548.2	$2.806 \cdot 10^5$
	798.4	$2.788 \cdot 10^5$
	$1.049 \cdot 10^3$	$2.77 \cdot 10^5$
	$1.299 \cdot 10^3$	$2.752 \cdot 10^5$
	$1.549 \cdot 10^3$	$2.734 \cdot 10^5$
	$1.799 \cdot 10^3$	$2.716 \cdot 10^5$
	$2.049 \cdot 10^3$	$2.698 \cdot 10^5$
	$2.3 \cdot 10^3$	$2.68 \cdot 10^5$
	$2.55 \cdot 10^3$	$2.662 \cdot 10^5$
	$2.8 \cdot 10^3$	$2.644 \cdot 10^5$

Ge(s) $Tmax := 1210$ $Tmin := 298$ $a := -20150$ $b := -0.395$ $c := 0$

$$Y_i := \frac{Tmax - Tmin}{10} \cdot (i) + Tmin$$

T, K   ΔHm, J/mol

Y_i	$\Delta H(Y_i, a, b, c)$
298	$1.665 \cdot 10^5$
389.2	$1.662 \cdot 10^5$
480.4	$1.659 \cdot 10^5$
571.6	$1.656 \cdot 10^5$
662.8	$1.654 \cdot 10^5$
754	$1.651 \cdot 10^5$
845.2	$1.648 \cdot 10^5$
936.4	$1.645 \cdot 10^5$
$1.028 \cdot 10^3$	$1.642 \cdot 10^5$
$1.119 \cdot 10^3$	$1.639 \cdot 10^5$
$1.21 \cdot 10^3$	$1.636 \cdot 10^5$

Mg(s) $Tmax := 924$ $Tmin := 298$ $a := -7780$ $b := -0.371$ $c := 0$

$$Y_i := \frac{Tmax - Tmin}{10} \cdot (i) + Tmin$$

T, K   DHm, J/mol

Y_i	$\Delta H(Y_i, a, b, c)$
298	$6.376 \cdot 10^4$
360.6	$6.357 \cdot 10^4$
423.2	$6.338 \cdot 10^4$
485.8	$6.318 \cdot 10^4$
548.4	$6.299 \cdot 10^4$
611	$6.28 \cdot 10^4$
673.6	$6.261 \cdot 10^4$
736.2	$6.241 \cdot 10^4$
798.8	$6.222 \cdot 10^4$
861.4	$6.203 \cdot 10^4$
924	$6.183 \cdot 10^4$

Mg(l)   Tmax := 1380   Tmin := 924   a := - 7750   b := - 0.612   c := 0

$$Y_i := \frac{Tmax - Tmin}{10} \cdot (i) + Tmin$$

T, K   DHm, J/mol

Y_i $\Delta H(Y_i, a, b, c)$

Y_i	$\Delta H(Y_i, a, b, c)$
924	$5.973 \cdot 10^4$
969.6	$5.95 \cdot 10^4$
$1.015 \cdot 10^3$	$5.927 \cdot 10^4$
$1.061 \cdot 10^3$	$5.904 \cdot 10^4$
$1.106 \cdot 10^3$	$5.88 \cdot 10^4$
$1.152 \cdot 10^3$	$5.857 \cdot 10^4$
$1.198 \cdot 10^3$	$5.834 \cdot 10^4$
$1.243 \cdot 10^3$	$5.811 \cdot 10^4$
$1.289 \cdot 10^3$	$5.788 \cdot 10^4$
$1.334 \cdot 10^3$	$5.764 \cdot 10^4$
$1.38 \cdot 10^3$	$5.741 \cdot 10^4$

NaCl(s)
        Tmax := 1074   Tmin := 298   a := - 12440   b := - 0.391   c := - 0.46 \cdot 10^{-3}

$$Y_i := \frac{Tmax - Tmin}{10} \cdot (i) + Tmin$$

T, K   DHm, J/mol

Y_i $\Delta H(Y_i, a, b, c)$

Y_i	$\Delta H(Y_i, a, b, c)$
298	$1.021 \cdot 10^5$
375.6	$1.017 \cdot 10^5$
453.2	$1.012 \cdot 10^5$
530.8	$1.006 \cdot 10^5$
608.4	$1 \cdot 10^5$
686	$9.94 \cdot 10^4$
763.6	$9.871 \cdot 10^4$
841.2	$9.799 \cdot 10^4$
918.8	$9.721 \cdot 10^4$
996.4	$9.639 \cdot 10^4$
$1.074 \cdot 10^3$	$9.552 \cdot 10^4$

Si(s)

$$Tmax := 1683 \qquad Tmin := 1200 \qquad a := -18000 \qquad b := -0.444 \qquad c := 0$$

$$Y_i := \frac{Tmax - Tmin}{10} \cdot (i) + Tmin$$

T, K	DHm, J/mol
Y_i	$\Delta H(Y_i, a, b, c)$
$1.2 \cdot 10^3$	$1.452 \cdot 10^5$
$1.248 \cdot 10^3$	$1.45 \cdot 10^5$
$1.297 \cdot 10^3$	$1.449 \cdot 10^5$
$1.345 \cdot 10^3$	$1.447 \cdot 10^5$
$1.393 \cdot 10^3$	$1.445 \cdot 10^5$
$1.442 \cdot 10^3$	$1.443 \cdot 10^5$
$1.49 \cdot 10^3$	$1.442 \cdot 10^5$
$1.538 \cdot 10^3$	$1.44 \cdot 10^5$
$1.586 \cdot 10^3$	$1.438 \cdot 10^5$
$1.635 \cdot 10^3$	$1.436 \cdot 10^5$
$1.683 \cdot 10^3$	$1.434 \cdot 10^5$

5.23 (also available as a Mathcad worksheet)

5.23

The metal tin undergoes a transition from a gray phase to a white phase at 286 K at ambient pressure. Given that the enthalpy change of this transition is 2090 kJ/mole and that the volume change of this transition is -4.35 cm3/mole, compute the temperature at which this transition occurs at 100 bar.

From Eq. 5.7-4 $\qquad \Delta T = \Delta P^* \Delta V^* T / \Delta H \qquad bar := 10^5 \cdot Pa$

$$\Delta T := \frac{99 \cdot bar \cdot \left(-4.35 \cdot 10^{-6} \cdot \frac{m^3}{mole}\right) \cdot 286 \cdot K}{2090000 \cdot \frac{joule}{mole}} \qquad \Delta T = -5.893 \bullet 10^{-3} \; \bullet K$$

5.24 For the solid-liquid transition

$$\left(\frac{\partial P}{\partial T}\right)_{eq} = \frac{\Delta \underline{H}^f}{T \Delta \underline{V}} \Rightarrow \left(\frac{\partial P}{\partial \ln T}\right)_{eq} = \frac{\Delta \underline{H}^f}{\Delta \underline{V}} = \frac{127 \; J/g}{0.1317 \; cc/g} = 964.3 \; J/cc$$

$$\left(\frac{\partial P}{\partial \ln T}\right)_{eq} = 964.3 \; J/cc = 964.3 \times 10^6 \; J/m^3 = 9643 \; bar = 9.643 \times 10^8 \; Pa$$

$$\Rightarrow P_2 = P_1 + 9643 \times \ln \frac{T_2}{T_1}$$

$$\Rightarrow T^{TP} = T_1 \exp\left\{\frac{P^{TP} - P_1}{9.643 \times 10^8 \text{ Pa}}\right\} = 278.7 \exp\left\{\frac{P^{TP} - 10^5 \text{ Pa}}{9.643 \times 10^8 \text{ Pa}}\right\} \qquad (1)$$

For the solid-vapor transition, assuming an ideal vapor phase

$$\ln\frac{P_2}{P_1} = -\frac{\Delta \underline{H}^{sub}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\Rightarrow -\frac{\Delta \underline{H}^{sub}}{R} = \frac{\ln(P_2/P_1)}{1/T_2 - 1/T_1} = \frac{\ln(26.67/13.33)}{3.696 \times 10^{-3} - 3.822 \times 10^{-3}} = -5513 \text{ K}$$

$$\Rightarrow \ln\frac{P_2}{P_1} = -5513\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

and

$$T^{TP} = \left[\frac{1}{T_1} - 0.1814 \times 10^{-3} \ln\frac{P^{TP}}{P_1}\right]^{-1} = \frac{1000}{3.696 - 0.1814\ln\left(P^{TP}/26.67\right)} \qquad (2)$$

Solving Eqns. (1) and (2) simultaneously gives

$$P^{TP} = 0.483 \text{ bar} = 4.83 \text{ kPa} \quad \text{and} \quad T^{TP} = 278.7 \text{ K}$$

[The melting temperature of benzene ~ triple point temperature $= 553°C = 278.7 \text{ K}$, which agrees exactly with our prediction].

5.25 First, at 298.15 K, lets relate the Gibbs free energy at any pressure to the value given at 1 bar.

$$\underline{G}_{dia}(298.15, P) = \underline{G}_{dia}(298, P = 1 \text{ bar}) + \left(\frac{(P-1)\text{bar} \times 3510\frac{\text{kg}}{\text{m}^3} \times 1000\frac{\text{g}}{\text{kg}} \times \frac{1 \text{ mol}}{12 \text{ g}}}{8.314 \times 10^{-5}\frac{\text{bar m}^3}{\text{mol K}} \times 298.15\text{K}}\right)$$

$$\underline{G}_g(29815, P) = \underline{G}_g(298, P = 1 \text{ bar}) + \left(\frac{(P-1)\text{bar} \times 2220\frac{\text{kg}}{\text{m}^3} \times 1000\frac{\text{g}}{\text{kg}} \times \frac{1 \text{ mol}}{12 \text{ g}}}{8.314 \times 10^{-5}\frac{\text{bar m}^3}{\text{mol K}} \times 298.15\text{K}}\right)$$

Note that

$$\underline{V}_{dia} = \frac{1}{3510}\frac{\text{m}^3}{\text{kg}} \times \frac{1}{1000}\frac{\text{kg}}{\text{g}} \times 12\frac{\text{g}}{\text{mol}} = 3.4188 \times 10^{-6}\frac{\text{m}^3}{\text{mol}}$$

$$\underline{V}_g = \frac{1}{2220}\frac{\text{m}^3}{\text{kg}} \times \frac{1}{1000}\frac{\text{kg}}{\text{g}} \times 12\frac{\text{g}}{\text{mol}} = 5.4054 \times 10^{-6}\frac{\text{m}^3}{\text{mol}}$$

Therefore

$$\underline{G}_{dia}(298.15, P) - \underline{G}_g(29815, P) = \underline{G}_{dia}(298, P = 1 \text{ bar}) - \underline{G}_g(298, P = 1 \text{ bar})$$

$$+ \left(\frac{(P-1)\text{bar} \times (3.4188 - 5.4054) \times 10^{-6} \dfrac{\text{m}^3}{\text{mol}}}{8.314 \times 10^{-5} \dfrac{\text{bar m}^3}{\text{mol K}} \times 298.15 \text{ K}} \right)$$

at equilibrium at 298.15 K we have

$$0 = 2900 - 0 - (P-1) \times 8.0143 \times 10^{-5}$$

$$P = 1 + \frac{2900}{8.0143 \times 10^{-5}} = 36185 \times 10^6 \text{ bar} = 36.185 \text{ Mbar}$$

To find the transition pressure at other temperatures we use the Clapeyron equation

$$\left(\frac{\partial P}{\partial T} \right)_{sat} = \frac{\Delta S}{\Delta V} = \frac{(2.377 - 5.740)\dfrac{\text{J}}{\text{mol K}}}{(3.4188 - 5.4054) \times 10^{-6} \dfrac{\text{m}^3}{\text{mol}}} \times 1 \frac{\text{Pa m}^3}{\text{J}}$$

$$= 1.6928 \times 10^6 \frac{\text{Pa}}{\text{K}} = 16.928 \frac{\text{bar}}{\text{K}}$$

which indicates that for every degree K increase about 298.15 K we need to increase the pressure by 16.928 bar. However, this is a small percentage increase compared to the 36.185 MPa pressure required at 298.15 K. So the transition is essentially (within engineering accuracy) only very weakly dependent on pressure.

5.26 Mass balance: $M_f = M_i$

Energy balance: $U_f = U_i$

Equilibrium criterion: $\overline{G}^S = \overline{G}^L = \overline{G}^V$; also $S = \text{maximum}$
We will assume the vapor phase is an ideal gas.
Properties of the triple point (a convenient reference state):

$$\hat{U}(\text{liquid}, T = 0°\text{C}, \text{triple point}) = 0 \qquad \text{(reference state)}$$

$$\hat{U}(\text{solid}, T = 0°\text{C}) = \underset{\text{since } \Delta \hat{V} \cong 0}{-\Delta \hat{H}(\text{solid} \rightarrow \text{vapor})} = -335 \text{ J/g}$$

$$\hat{U}(\text{vapor}, T = 0°\text{C}) = \Delta \hat{H}^{\text{vap}} - RT$$

$$= 2530 \text{ J/g} - 8.314 \times 273.15 \text{ J/mol} \times \frac{1 \text{ mol}}{18 \text{ g}}$$

$$= 2403.8 \text{ J/g}$$

Energy content of original system:

$$\hat{U}(\text{liquid}, T = -10°\text{C}) = 0 + 4.22 \text{ J/g}°\text{C} \times (-10°\text{C}) = -42.2 \text{ J/g}$$

$$\hat{U}(\text{solid}, T = -10°\text{C}) = -335 \text{ J/g} + 2.1 \text{ J/g}°\text{C} \times (-10°\text{C}) = -356 \text{ J/g}$$

$$\hat{U}(\text{vapor}, T = -10°\text{C}) = 2403.8 \text{ J/g} + C_V(-10°\text{C}) \qquad \text{where } C_V \sim C_P - R$$

$$= 2403.8 + \left(2.03 - \frac{8.314}{18} \right)(-10°\text{C}) = 2388.1 \text{ J/g}$$

Also, initial specific volume of vapor phase

$$\underline{V}^V = \frac{RT}{P} = \frac{8.314 \text{ Pa} \cdot \text{m}^3/\text{mol K} \times 263.15 \text{ K}}{287.6 \text{ Pa}} = 7609 \text{ m}^3/\text{mol}$$

Ratio of mass initially present in vapor to mass in liquid

$$= \frac{M^{\mathrm{V}}}{M^{\mathrm{L}}} = \frac{\underline{V}^{\mathrm{L}}}{\underline{V}^{\mathrm{V}}} = \frac{1.8 \times 10^{-5} \ \mathrm{m^3/mol}}{7.609 \ \mathrm{m^3/mol}} = 2.37 \times 10^{-6}$$

$\Rightarrow$ Negligible mass of system initially present in gas phase!

Since the initial system is a subcooled liquid + vapor, the following possibilities exist for the equilibrium state.

(1) *All* the liquid freezes and some vapor remains (i.e., a solid-vapor system at equilibrium). The energy released (heat of fusion) would then go to heat the system—Since 335 J/g are released, and $C_{\mathrm{P}} \sim 4.22 \ \mathrm{J/g^{\circ}C}$, too much energy is released for only the solid and vapor to be present.

(2) *Some* of the liquid vaporizes and some freezes, so that a solid-liquid-vapor mixture is present. Thus, the system is at the triple point at equilibrium. [The energy released in solidification of the water goes to heat the system up to $0\,^{\circ}\mathrm{C}$, the triple point temperature.]

We will consider this second possibility here; as a first guess, the small amount of vapor will not be included in the calculations.

Let x = fraction of liquid that solidified

M^{L} = initial mass of liquid in the system

Energy balance

$$M^{\mathrm{L}}\hat{U}^{\mathrm{L}}(-10^{\circ}\,\mathrm{C}) = (1-x)M^{\mathrm{L}}\hat{U}^{\mathrm{L}}(0^{\circ}\,\mathrm{C}) + xM^{\mathrm{L}}\hat{U}^{\mathrm{S}}(0^{\circ}\,\mathrm{C})$$

$$-42.2 \ \mathrm{J} = (1-x)(0) + x(-335)$$

$$\Rightarrow x = 0.126 \ \text{fraction that is solid}$$

$$1 - x = 0.874 \ \text{fraction that is liquid}$$

Now lets go back and determine the amount of vapor in the system

$$\text{triple point pressure} = 0.611 \ \mathrm{kPa} = 611 \ \mathrm{Pa}$$
$$\uparrow \text{Steam tables}$$

As a first approximation, assume that the vapor still occupies about 1/2 of the total volume—this is reasonable, since we expect little volume change of the condensed phase due either to freezing or thermal expansion.

$$\frac{M^{\mathrm{V}}}{M} = \frac{\left(1.8 \times 10^{-5} \ \mathrm{m^3/mol}\right) \times 611 \ \mathrm{Pa}}{8.314 \ \mathrm{Pa \cdot m^3/mol \ K} \times 273.15 \ \mathrm{K}} = 4.84 \times 10^{-6}$$

If we now include this amount of vapor in the energy balance, it makes only an insignificant change in the computed solid and liquid fractions. $\Rightarrow$ We will neglect the presence of the vapor. To compute the entropy change, we notice that if we started with 1 gram of liquid, the net change in the system would be

1 g liquid $(-10^{\circ}\,\mathrm{C})$ 0.874 g liquid $(0^{\circ}\,\mathrm{C})$

$+$ $\rightarrow 0.126$ g solid $(0^{\circ}\,\mathrm{C})$

2.37×10^{-6} g vapor $(-10^{\circ}\mathrm{C}, \ 287.6 \ \mathrm{Pa})$ 4.84×10^{-6} vapor $(0^{\circ}\,\mathrm{C}, \ 611 \ \mathrm{Pa})$

Entropy changes
1 g liquid $(-10^{\circ}\mathrm{C}) \rightarrow$ 1 g liquid $(0^{\circ}\mathrm{C})$

$$\Delta S = C_P \ln\frac{T_f}{T_i} = 4.22 \text{ J/gK} \ln\frac{273.15}{263.15} = 0.1574 \text{ J/gK}$$

0.126 g liquid (0°C) → 0.126 g solid (0°C)

$$\Delta\hat{G} = 0 = \Delta\hat{H} - T\Delta\hat{S}$$

$$\Delta\hat{S} = \frac{\Delta\hat{H}}{T} \text{ and } \Delta S = M\frac{\Delta\hat{H}}{T}$$

$$\Delta S = \frac{-335 \text{ J/g}}{273.15 \text{ K}} \times 0.126 \text{ g} = -0.1545 \text{ J/K}$$

$(4.84 - 2.37)\times 10^{-6} = 2.47\times 10^{-6}$ g liquid (0°C) → 2.47×10^{-6} g vapor (0°C)

$$\Delta S = 2.47\times 10^{-6}\frac{\Delta\hat{H}^{vap}}{T} = 2.47\times 10^{-6}\times\frac{2530}{273.16} = 0.229\times 10^{-4} \text{ J/K}$$

⇒ vapor makes a negligible contribution in computing ΔS

$$\Delta S = 0.1574 - 0.1545 = 0.0029 \text{ J/K} \text{ for each gram of water present.}$$

5.27 Gibbs Phase Rule (Eqn. 5.6-1) $F = 3 - P$
  (a) Only solids can have many as 3 phases present. These can only exist at a single point of T and P as there are no degrees of freedom.
  If only 2 solid phases, $F = 1 \Rightarrow$ a single degree of freedom. Can fix either T or P.
  If only one solid phase present, then $F = 2$, both T and P can vary independently.
  (b) If a liquid is also present

Liquid alone	$F = 3 - 1 = 2$	T and P independently variable
Liquid + 1 solid	$F = 3 - 2 = 1$	Can vary T or P, the other follows
Liquid + 2 solids	$F = 0$	Only a single point

  (c) Same as (b), with vapor replacing liquid in discussion above.
  (d) If liquid and vapor are already present, then $P = 2$
  ⇒ 1 degree of freedom if no solid is present (i.e., either T or P can be fixed, not both)
  If liquid and vapor and solid are present, $P = 3$
  ⇒ $F = 0$ Triple point is a unique point on phase diagram.

5.28 Criterion for equilibrium at constant T and V as that $A =$ minimum. However, from Problem **5.4** this implies $\underline{G}^V = \underline{G}^L$ (not $\underline{A}^V = \underline{A}^L$!)

Now $\underline{G} = \underline{A} + P\underline{V}$ and $P = -(\partial A/\partial\underline{V})_T$. Thus, at equilibrium

$$\underline{G}^V = \underline{A}^V - \left(\frac{\partial\underline{A}^V}{\partial\underline{V}}\right)_T \underline{V}^V = \underline{G}^L = \underline{A}^L - \left(\frac{\partial\underline{A}^L}{\partial\underline{V}^L}\right)_T \underline{V}^L \qquad (1)$$

Also at equilibrium $P^V = P^L \Rightarrow \left(\frac{\partial\underline{A}^V}{\partial\underline{V}^V}\right)_T = \left(\frac{\partial\underline{A}^L}{\partial\underline{V}^L}\right)_T$

⇒ Pressures are equal when derivatives of $\underline{A}$ with respect to $\underline{V}$ are equal. The derivative of $\underline{A}$ with respect to $\underline{V}$ is the tangent to the curve in the $\underline{A} - \underline{V}$ plane. Thus both curves must have a common tangent if equilibrium is to occur, and the slope of this tangent line is the negative of the equilibrium

pressure. Now must prove that the points of intersection of the tangent line and $\underline{A}$ curve are points at which $\underline{G}^{V} = \underline{G}^{L}$. From the figure we have $\underline{A}^{V} = \underline{A}^{L} + (\partial \underline{A}/\partial \underline{V})_{T}(\underline{V}^{V} - \underline{V}^{L})$ but this is exactly what is required by Eqn. (1) for $\underline{G}^{V} = \underline{G}^{L}$! So we have indeed identified the equilibrium state.

$$\left(\frac{\partial \underline{A}}{\partial \underline{V}}\right)\left(\underline{V}^{V} - \underline{V}^{L}\right)$$
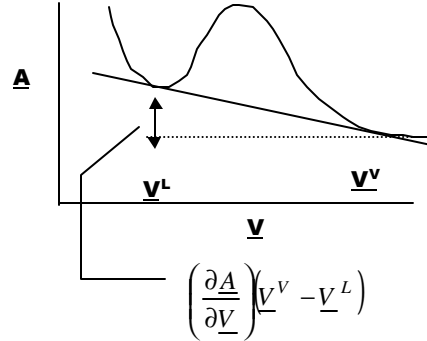
5.29 (a) From the equilibrium criteria we have $T^{V} = T^{L}$, $P^{V} = P^{L}$ and

$$\underline{G}^{V} = \underline{G}^{L} \Rightarrow \int_{\underline{V}^{V}, T}^{\underline{V}^{L}, T} \underline{V} dP = 0 \text{ or } \int_{\underline{V}^{L}}^{\underline{V}^{V}} \underline{V}\left(\frac{\partial P}{\partial \underline{V}}\right)_{T} dV = 0$$

(b) For the van der Waals equation we have

$$P_{r} = \frac{8T_{r}}{3V_{r} - 1} - \frac{3}{V_{r}^{3}} \tag{1}$$

and

$$\left(\frac{\partial P_{r}}{\partial V_{r}}\right) = \frac{6}{V_{r}^{3}} - \frac{24T_{r}}{(3V_{r} - 1)^{2}} = 6\left\{\frac{1}{V_{r}^{3}} - \frac{4T_{r}}{(3V_{r} - 1)^{2}}\right\}$$

Thus

$$\int_{V_{r}^{L}}^{V_{r}^{V}} V_{r}\left(\frac{\partial P_{r}}{\partial V_{r}}\right) dV_{r} = 0 = \int_{V_{r}^{L}}^{V_{r}^{V}} \left(\frac{1}{V_{r}^{2}} - \frac{4T_{r}V_{r}}{(3V_{r} - 1)^{2}}\right) dV_{r}$$

$$0 = -\frac{1}{V_{r}}\Big|_{V_{r}^{L}}^{V_{r}^{V}} - \frac{4T_{r}}{9}\left[\ln(3V_{r} - 1) - (3V_{r} - 1)^{-1}\right]_{V_{r}^{L}}^{V_{r}^{V}}$$

and

$$\ln\frac{\left(3V_{r}^{L} - 1\right)}{\left(3V_{r}^{V} - 1\right)} + \left(3V_{r}^{V} - 1\right)^{-1} - \left(3V_{r}^{L} - 1\right)^{-1} + \frac{9}{4T_{r}V_{r}^{L}}\left(1 - \frac{V_{r}^{L}}{V_{r}^{V}}\right) = 0 \tag{2}$$

Another equation arises from the fact that $P^{V} = P^{L} \Rightarrow P_{r}^{V} = P_{r}^{L}$ so that, using Eqn. (1)

$$\frac{8T_r}{3V_r^{\mathrm{V}}-1} - \frac{3}{\left(V_r^{\mathrm{V}}\right)^2} = \frac{8T_r}{3V_r^{\mathrm{L}}-1} - \frac{3}{\left(V_r^{\mathrm{L}}\right)^2} \ ,$$

or, solving for the reduced temperature

$$T_r = \frac{3}{8}\frac{\left\{\left(1/V_r^{\mathrm{V}}\right)^2 - \left(1/V_r^{\mathrm{L}}\right)^2\right\}}{\left\{\left(1/3V_r^{\mathrm{V}}-1\right)-\left(1/3V_r^{\mathrm{L}}-1\right)\right\}} \tag{3}$$

This is an independent equation between T_r, V_r^{V} and V_r^{L}. Using Eqn. (3) in Eqn. (2) gives'

$$\ln\left\{\frac{\left(3V_r^{\mathrm{L}}-1\right)}{\left(3V_r^{\mathrm{V}}-1\right)}\right\} + \left(3V_r^{\mathrm{V}}-1\right)^{-1} - \left(3V_r^{\mathrm{L}}-1\right)$$

$$+\frac{6V_r^{\mathrm{V}}V_r^{\mathrm{L}}}{V_r^{\mathrm{V}}+V_r^{\mathrm{L}}}\left\{\frac{1}{3V_r^{\mathrm{V}}-1} - \frac{1}{3V_r^{\mathrm{L}}-1}\right\} = 0 \tag{4}$$

(c) Procedure used in solution

i) Guess (or choose) a value of V_r^{V}, compute V_r^{L} which satisfies Eqn. (4).

ii) Use V_r^{V} and V_r^{L} so obtained to compute T_r from Eqn. (3).

iii) Use V_r and T_r and Eqn. (1) to get $P_r = P_r^{\mathrm{vap}}$. [Note: This calculation was done on a digital computer.] Results are at end of problem solution.

(d) The Clausius-Clapeyron equation can be written as

$$\left.\frac{dP}{dT}\right|_{\substack{\text{coexistance}\\\text{curve}}} = \frac{\Delta\underline{H}}{T\Delta\underline{V}} = \frac{P_C}{T_C}\frac{dP_r^{\mathrm{vap}}}{dT_r} = \frac{\Delta\underline{H}^{\mathrm{vap}}}{T\Delta\underline{V}}$$

or

$$\frac{dP_r^{\mathrm{vap}}}{dT_r} = \frac{\Delta\underline{H}^{\mathrm{vap}}}{T_r\Delta\underline{V}}\frac{1}{P_C} = \frac{\Delta\underline{H}^{\mathrm{vap}}}{T_r\Delta\underline{V}}\frac{3\underline{V}_C^2}{a} = \frac{9b}{a}\frac{\Delta\underline{H}^{\mathrm{vap}}}{T_r\Delta\underline{V}_r}$$

Since $a = 3P_C\underline{V}_C^2$; $\underline{V}_C = 3b$. Now $9b/a$ has units of $(\text{energy})^{-1}$, so define a reduced heat of vaporization, $\Delta H_r^{\mathrm{vap}}$, to be $9b/a\,\Delta\underline{H}^{\mathrm{vap}}$. Thus

$$\Delta\underline{H}_r^{\mathrm{vap}} = T_r\Delta V_r\frac{dP_r^{\mathrm{vap}}}{dT}$$

Thus $\Delta H_r^{\mathrm{vap}}$ can be computed by taking derivatives of results of part (c). (This was done graphically). The results are as shown below.

$\underline{V}_r^{\mathrm{V}}$	$\underline{V}_r^{\mathrm{L}}$	P_r^{vap}	T_r	$\overline{T}_r$	$\Delta H_r^{\mathrm{vap}}$
3×10^3	0.3690	2.617×10^{-4}	0.2948		
				0.3124	9.1
1×10^3	0.3745	8.772×10^{-4}	0.3300		
				0.3341	8.69
8×10^2	0.3758	1.123×10^{-3}	0.3382		
				0.3477	8.69
5×10^2	0.3789	1.894×10^{-3}	0.3571		
				0.3686	8.51

3×10^2	0.3829	33503×10^{-3}	0.3802			
				0.3986	8.77	
1.5×10^2	0.3896	7.299×10^{-3}	0.4171			
				0.4297	8.87	
100	0.3947	0.01153	0.4423			
				0.4522	8.70	
75	0.3985	0.01597	0.4621			
				0.4704	8.52	
60	0.4020	0.02056	0.4787			
				0.4859	8.54	
50	0.4052	0.02527	0.4931			
				0.5025	8.62	
40	0.4095	0.03254	0.5119			
				0.5251	8.53	
30	0.4158	0.04505	0.5383			
				0.5591	8.85	
20	0.4268	0.07112	0.5799			
				0.5964	8.01	
15	0.4365	0.09810	0.6129			
				0.6389	7.81	
10	0.4538	0.1534	0.6649			
				0.6807	7.51	
8	0.4658	0.1954	0.6965			
				0.7184	7.33	
6	0.4849	0.2650	0.7402			
				0.7550	6.97	
5	0.4998	0.3198	0.7697			
				0.7885	6.64	
4	0.5226	0.3996	0.8072			
				0.8323	5.86	
3	0.5596	0.5240	0.8573			
				0.8922	4.89	
2	0.6410	0.7332	0.9270			
				0.9354	3.94	
1.8	0.6710	0.7899	0.9437			
				0.9567	3.22	
1.5	0.7364	0.8830	0.9697			
				0.9849	1.43	
1.0	1.0	1.0	1.0			

Results are plotted below.
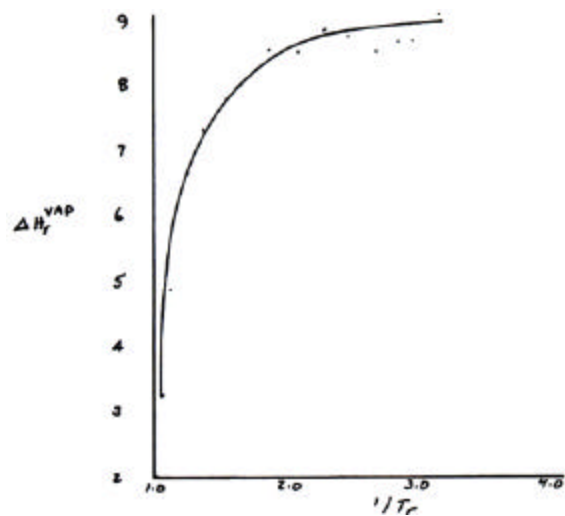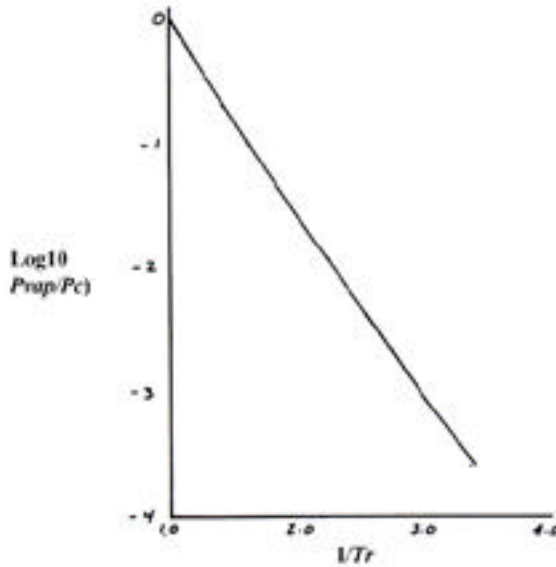
The reduced vapor pressure and heat of vaporization for the van der Waals fluid.

5.30 (a) Restricted form of Gibbs Phase Rule: $F = 3 - P$

$\Rightarrow P$ must be 3 or less

$\Rightarrow$ quaternary point can not exist in a 1-component fluid.

(b) 2 phases $\Rightarrow F = 3 - 2 = 1$ degree of freedom.

Thus, if any property of *one* of the phases is specified, this is sufficient to fix all of the thermodynamic properties of both phases! However, if only the total molar volume of the two-phase system (or some other two-phase property), i.e., $\underline{V} = x^I \underline{V}^I(T,P) + x^{II} \underline{V}^{II}(T,P)$, this is not sufficient to solve for x^I, $\underline{V}^I$ and $\underline{V}^{II}$. That is, many choices of T and P can yield the same value of the total molar volume by varying the mass distribution between the two phases.

Consider now the situation in which the total molar volume and total molar enthalpy is specified. In this case we have

$$1 = x^I + x^{II}$$

$$\underline{V} = x^I \underline{V}^I(T,P) + x^{II} \underline{V}^{II}(T,P)$$

$$\text{and } \underline{H} = x^I \underline{H}^I(T,P) + x^{II} \underline{H}^{II}(T,P)$$

The unknowns here are x^I, x^{II} and either T or P (note that since the system has only one degree of freedom, either T or P, but not both are independent variables). Thus, given equation of state information (relating $\underline{V}$ and $\underline{H}$ to T and P, and the two-phase coexistance curve), the equations above provide 3 equations to be solved for the 3 unknowns.

5.31 (a) $d\underline{S} = \left(\dfrac{\partial \underline{S}}{\partial T}\right)_P dT + \left(\dfrac{\partial \underline{S}}{\partial P}\right)_T dP$. Thus

$$\left(\frac{\partial \underline{S}}{\partial T}\right)_{\substack{\text{sat} \\ \text{curve}}} = \left(\frac{\partial \underline{S}}{\partial T}\right)_P + \left(\frac{\partial \underline{S}}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_{\substack{\text{sat} \\ \text{curve}}}$$

but

$$\left(\frac{\partial \underline{S}}{\partial T}\right)_P = \frac{C_P}{T} \; ; \; \left(\frac{\partial P}{\partial T}\right)_{\substack{\text{sat} \\ \text{curve}}} = \frac{\Delta \underline{H}^{\text{vap}}}{T \Delta \underline{V}^{\text{vap}}}$$

and, by the Maxwell relations

$$\left(\frac{\partial \underline{S}}{\partial P}\right)_T = -\left(\frac{\partial \underline{V}}{\partial T}\right)_P = -\underline{V}\alpha$$

Thus

$$C_{\text{sat}} = T\left(\frac{\partial \underline{S}}{\partial T}\right)_{\substack{\text{sat} \\ \text{curve}}} = C_P - \alpha \underline{V} \frac{\Delta \underline{H}^{\text{vap}}}{\Delta \underline{V}^{\text{vap}}} = C_P - \left(\frac{\partial \underline{V}}{\partial T}\right)_P \frac{\Delta \underline{H}^{\text{vap}}}{\Delta \underline{V}^{\text{vap}}}$$

and

$$C_{\text{sat}}^i = C_P^i - \alpha^i \underline{V}^i \frac{\Delta \underline{H}^{\text{vap}}}{\Delta \underline{V}^{\text{vap}}} = C_P^i - \left(\frac{\partial \underline{V}}{\partial T}\right)_P^i \frac{\Delta \underline{H}^{\text{vap}}}{\Delta \underline{V}^{\text{vap}}} \; ;$$

where i denotes the phase.

(b) For the liquid

$$\Delta \underline{V}^{\text{vap}} \gg \underline{V}^{\text{L}} , \text{ and } \alpha^i \sim 0 \Rightarrow C_{\text{sat}}^{\text{L}} \sim C_P^{\text{L}}$$

For the vapor we will use $C_P \sim [\underline{H}(T_2) - \underline{H}(T_1)]/(T_2 - T_1)$ and $(\partial \underline{V}/\partial T)_P \sim [\underline{V}(T_2) - \underline{V}(T_1)]/(T_2 - T_1)$ and

$$C_{\text{sat}}^{\text{V}} = C_P^{\text{V}} - \alpha^{\text{V}} \underline{V}^{\text{V}} \frac{\Delta \underline{H}^{\text{vap}}}{\Delta \underline{V}^{\text{vap}}}$$

[C_P and $(\partial \underline{V}/\partial T)_P$ will be evaluated using finite differences above and steam tables. In each case T_1 will be taken as the saturation temperature, and T_2 to be the next higher temperature in the steam tables.]

Thus, at $100\,°C$ (0.1 MPa)

$$C_P^{\text{V}} = \frac{2776.4 - 2676.1}{50} = 2.006 \text{ kJ/kg K} ;$$

$$\left(\frac{d\underline{V}}{dT}\right)_P = \frac{1.9364 - 1.6958}{50} = 0.00481 \text{ m}^3/\text{kg K}$$

at $370\,°C$ (21.0 MPa) $C_P^{\text{V}} = 14.6$ kJ/kg K and

$\left(\dfrac{d\underline{V}}{dT}\right)_P = 0.000141$ m^3/kg K. Thus, at $100\,°C$

$$C_{\text{sat}}^{\text{V}} = 2.006 \text{ kJ/kg K} - 0.00481 \text{ m}^3/\text{kg K} \times \frac{2257.0 \text{ kJ/kg}}{1.6719 \text{ m}^3/\text{kg}}$$

$$= -4.488 \text{ kJ/kg K}$$

at $370\,°C$

$$C_{sat}^V = 14.6 \text{ kJ/kg K} - 0.000141 \text{ m}^3/\text{kg K} \times \frac{441.6 \text{ kJ/kg}}{0.0027 \text{ m}^3/\text{kg}}$$

$$= -8.359 \text{ kJ/kg K}$$

5.32 (a) Multiply out the terms, and this is easily proved.

(b) $S_{UN} = \dfrac{\partial^2 S}{\partial N \partial U} = \left.\dfrac{\partial}{\partial N}\right|_{U,V}\left(\dfrac{1}{T}\right) = -\dfrac{1}{T^2}\left(\dfrac{\partial T}{\partial N}\right)_{U,V} = \left(\dfrac{\partial^2 S}{\partial U \partial N}\right)$

$= \left.\dfrac{\partial}{\partial U}\right|_{N,V}\left(\dfrac{\partial S}{\partial N}\right)_{U,V}$

but $dS = \dfrac{1}{T}dU + \dfrac{P}{T}dV - \dfrac{G}{T}dN \Rightarrow \left(\dfrac{\partial S}{\partial N}\right)_{U,V} = -\dfrac{G}{T}$ so that

$$\dfrac{\partial^2 S}{\partial U \partial N} = \dfrac{\partial}{\partial U}\left(-\dfrac{G}{T}\right)_{V,N} = -\dfrac{1}{T}\left(\dfrac{\partial \underline{G}}{\partial U}\right)_{N,V} - \dfrac{G}{T^2}\left(\dfrac{\partial T}{\partial U}\right)_{V,N}$$

$$= -\dfrac{1}{TN}\left(\dfrac{\partial \underline{G}}{\partial \underline{U}}\right)_{\underline{V}} + \dfrac{G}{NT^2}\left(\dfrac{\partial T}{\partial \underline{U}}\right)_{\underline{V}} = -\dfrac{1}{TN}\left(\dfrac{\partial \underline{G}}{\partial T}\right)_{\underline{V}}\left(\dfrac{\partial T}{\partial \underline{U}}\right)_{\underline{V}} + \dfrac{G}{NT^2 C_v}$$

Now $d\underline{G} = \underline{V}dP - \underline{S}dT$; thus

$$\left(\dfrac{\partial \underline{G}}{\partial T}\right)_{\underline{V}} = \underline{V}\left(\dfrac{\partial P}{\partial T}\right)_{\underline{V}} - \underline{S}$$

and

$$S_{UN} = -\dfrac{1}{C_V NT}\left\{\underline{V}\left(\dfrac{\partial P}{\partial T}\right)_{\underline{V}} - \underline{S}\right\} + \dfrac{G}{NT^2 C_V} = \dfrac{-\underline{V}}{NC_v T}\left(\dfrac{\partial P}{\partial T}\right)_{\underline{V}} + \dfrac{G + T\underline{S}}{NT^2 C_V}$$

but $\underline{G} + T\underline{S} = \underline{H}$. Thus

$$S_{UN} = -\dfrac{1}{T^2}\left(\dfrac{\partial T}{\partial N}\right)_{U,V} = -\dfrac{\underline{V}}{NC_V T}\left(\dfrac{\partial P}{\partial T}\right)_{\underline{V}} + \dfrac{\underline{H}}{NT^2 C_V}$$

(c) $S_{VN} = \dfrac{\partial}{\partial N}\dfrac{\partial S}{\partial V} = \dfrac{\partial}{\partial N}\left(\dfrac{P}{T}\right)_{U,V} = \dfrac{1}{T}\left(\dfrac{\partial P}{\partial N}\right)_{U,V} - \dfrac{P}{T^2}\left(\dfrac{\partial T}{\partial N}\right)_{U,V}$

$= \dfrac{\partial}{\partial V}\dfrac{\partial S}{\partial N} = -\left(\dfrac{\partial (\underline{G}/T)}{\partial V}\right)_{U,N} = -\dfrac{1}{T}\left(\dfrac{\partial \underline{G}}{\partial V}\right)_{U,N} + \dfrac{G}{T^2}\left(\dfrac{\partial T}{\partial V}\right)_{U,N}$

$= -\dfrac{1}{NT}\left(\dfrac{\partial \underline{G}}{\partial \underline{V}}\right)_{\underline{U}} + \dfrac{G}{NT^2}\left(\dfrac{\partial T}{\partial \underline{V}}\right)_{\underline{U}} = -\dfrac{1}{NT}\left(\dfrac{\partial \underline{G}}{\partial T}\right)_{\underline{U}}\left(\dfrac{\partial T}{\partial \underline{V}}\right)_{\underline{U}} + \dfrac{G}{NT^2}\left(\dfrac{\partial T}{\partial \underline{V}}\right)_{\underline{U}}$

$= \left(\dfrac{\partial T}{\partial \underline{V}}\right)_{\underline{U}}\dfrac{1}{NT^2}\left[G - T\left(\dfrac{\partial \underline{G}}{\partial T}\right)_{\underline{U}}\right]$

but

$$dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P \right] dV \Rightarrow \left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P \right]$$

Also

$$\left(\frac{\partial \underline{G}}{\partial T}\right)_U = \frac{\partial(\underline{G},\, \underline{U})}{\partial(T,\, \underline{U})} = \frac{\partial(\underline{G},\, \underline{U})}{\partial(T,\, \underline{V})} \cdot \frac{\partial(T,\, \underline{V})}{\partial(T,\, \underline{U})}$$

$$= \frac{(\partial \underline{G}/\partial T)_{\underline{V}}(\partial \underline{U}/\partial \underline{V})_T - (\partial \underline{G}/\partial \underline{V})_T(\partial \underline{U}/\partial T)_{\underline{V}}}{(\partial \underline{U}/\partial \underline{V})_T}$$

$$= \left(\frac{\partial \underline{G}}{\partial T}\right)_{\underline{V}} - \frac{C_V(\partial \underline{G}/\partial \underline{V})_T}{(\partial \underline{U}/\partial \underline{V})_T};$$

$$d\underline{G} = \underline{V}dP - \underline{S}dT\;;\; \left(\frac{\partial \underline{G}}{\partial T}\right)_{\underline{V}} = \underline{V}\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - \underline{S}\;\text{ and }\;\left(\frac{\partial \underline{G}}{\partial \underline{V}}\right)_T = \underline{V}\left(\frac{\partial P}{\partial \underline{V}}\right)_T$$

Thus,

$$\left(\frac{\partial \underline{G}}{\partial T}\right)_U = \underline{V}\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - \underline{S} - \frac{C_V \underline{V}(\partial P/\partial \underline{V})_T}{T(\partial P/\partial T)_{\underline{V}} - P}$$

$$\underline{G} - T\left(\frac{\partial \underline{G}}{\partial T}\right)_U = \underline{H} - T\underline{S} - \underline{V}T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} + T\underline{S} + \frac{C_V T\underline{V}(\partial P/\partial \underline{V})_T}{T(\partial P/\partial T)_{\underline{V}} - P}$$

$$\left\{ T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P \right\}\left\{ \underline{G} - T\left(\frac{\partial \underline{G}}{\partial T}\right)_U \right\}$$

$$= \left\{ \underline{H} - \underline{V}T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} \right\}\left\{ T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P \right\} + C_V T\underline{V}\left(\frac{\partial P}{\partial \underline{V}}\right)_T$$

so that, finally,

$$S_{VN} = \frac{1}{T}\left(\frac{\partial P}{\partial N}\right)_{U,V} - \frac{P}{T^2}\left(\frac{\partial T}{\partial N}\right)_{U,V}$$

$$= -\frac{1}{NC_V T^2}\left\{ \underline{H} - \underline{V}T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} \right\}\left\{ T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P \right\} - \frac{\underline{V}}{NT}\left(\frac{\partial P}{\partial \underline{V}}\right)_T$$

(d) $\;\; S_{NN} = \left(\frac{\partial^2 S}{\partial N^2}\right)_{U,V} = \left.\frac{\partial}{\partial N}\right|_{U,V}\left\{ -\frac{G}{T} \right\} = -\frac{1}{T}\left(\frac{\partial \underline{G}}{\partial N}\right)_{U,V} + \frac{G}{T^2}\left(\frac{\partial T}{\partial N}\right)_{U,V}$

$$\overset{\text{eqn.}}{\underset{\text{A4-10}}{=}} -\frac{1}{TN}\left\{ \left(\frac{\partial \underline{G}}{\partial N}\right)_{U,V} - \underline{G} \right\} + \frac{G}{NT^2}\left(\frac{\partial T}{\partial N}\right)_{U,V}$$

Now

$$dG = VdP - SdT + \underline{G}dN \Rightarrow \left(\frac{\partial G}{\partial N}\right)_{U,V} = V\left(\frac{\partial P}{\partial N}\right)_{U,V} - S\left(\frac{\partial T}{\partial N}\right)_{U,V} + \underline{G}$$

$$\Rightarrow S_{NN} = -\frac{V}{TN}\left(\frac{\partial P}{\partial N}\right)_{U,V} + \frac{S}{TN}\left(\frac{\partial T}{\partial N}\right)_{U,V} + \frac{G}{T^2 N}\left(\frac{\partial T}{\partial N}\right)_{U,V}$$

$$= -\frac{V}{TN}\left(\frac{\partial P}{\partial N}\right)_{U,V} + \frac{H}{T^2 N}\left(\frac{\partial T}{\partial N}\right)_{U,V} = -\frac{\underline{V}}{T}\left(\frac{\partial P}{\partial N}\right)_{U,V} + \frac{\underline{H}}{T}\left(\frac{\partial T}{\partial N}\right)_{U,V}$$

but from above

$$\frac{1}{T^2}\left(\frac{\partial T}{\partial N}\right)_{U,V} = \frac{\underline{V}}{NC_V T}\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - \frac{H}{NT^2 C_V}$$

and, from equating the two expressions for S_{VN}

$$\frac{1}{T}\left(\frac{\partial P}{\partial N}\right)_{U,V} = \frac{-\underline{H}(\partial P/\partial T)_V}{NC_V T} + \frac{\underline{V}}{NC_V}\left(\frac{\partial P}{\partial T}\right)_{\underline{V}}^2 - \frac{\underline{V}}{NT}\left(\frac{\partial P}{\partial \underline{V}}\right)_T$$

Putting these expressions together yields

$$S_{NN} = \frac{2\underline{HV}}{NC_V T}\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - \frac{\underline{H}^2}{NC_V T^2} - \frac{\underline{V}^2(\partial P/\partial T)_{\underline{V}}^2}{NC_V} + \frac{\underline{V}^2}{NT}\left(\frac{\partial P}{\partial \underline{V}}\right)_T$$

(e) It is now simple algebra to combine the expressions above, and those in Sec. 5.2, and show that

$$\theta_3 = \frac{S_{UU}S_{NN} - S_{UN}^2}{S_{UU}} - \frac{(S_{UU}S_{VN} - S_{UV}S_{UN})^2}{S_{UU}(S_{UU}S_{VV} - S_{VN}^2)}$$

is exactly zero!!

5.33 (Mathcad worksheets in the Mathcad Utilities Directory are also available to do these calculations) Students in my thermodynamics courses have produced thermodynamics diagrams for many fluids using the program PR1 and following the methods in illustrations of Chapters 4 and 5. The following figures are examples of some of these diagrams. It should be noted that all of these diagrams are in qualitative, but not quantitative agreement with thermodynamic diagrams generated using more accurate equations of state. In particular, liquid densities are not predicted very accurately from the Peng-Robinson e.o.s. so that the location of the two-phase dome is somewhat shifted as are the other thermodynamic properties. Diagrams for other substances will be found in the file named "Other figs"

Thermodynamic properties of nitrogen by Tom Petti
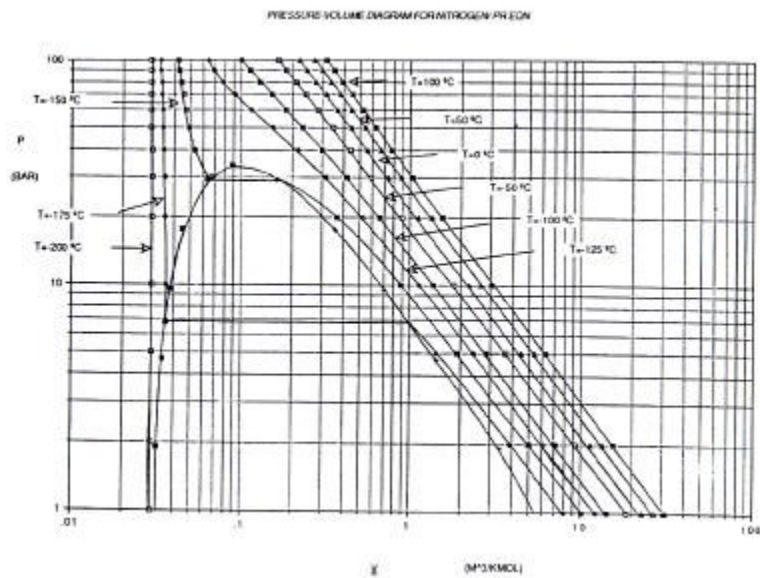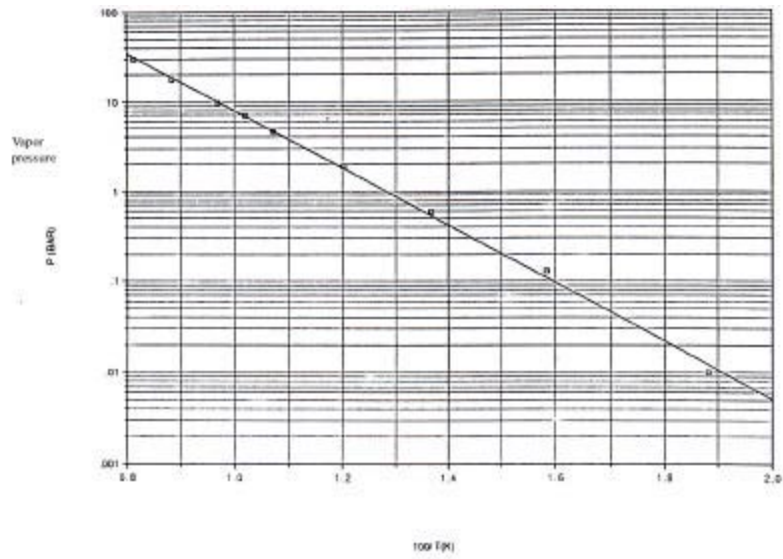
Pressure-volume diagram for nitrogen Peng-Robinson eos.

PRESSURE-ENTHALPY DIAGRAM FOR NITROGEN/ PR EQN
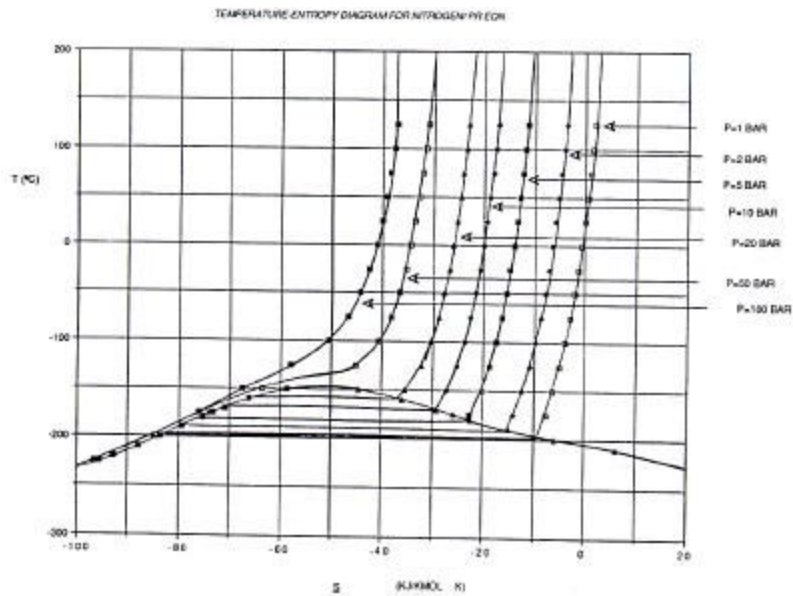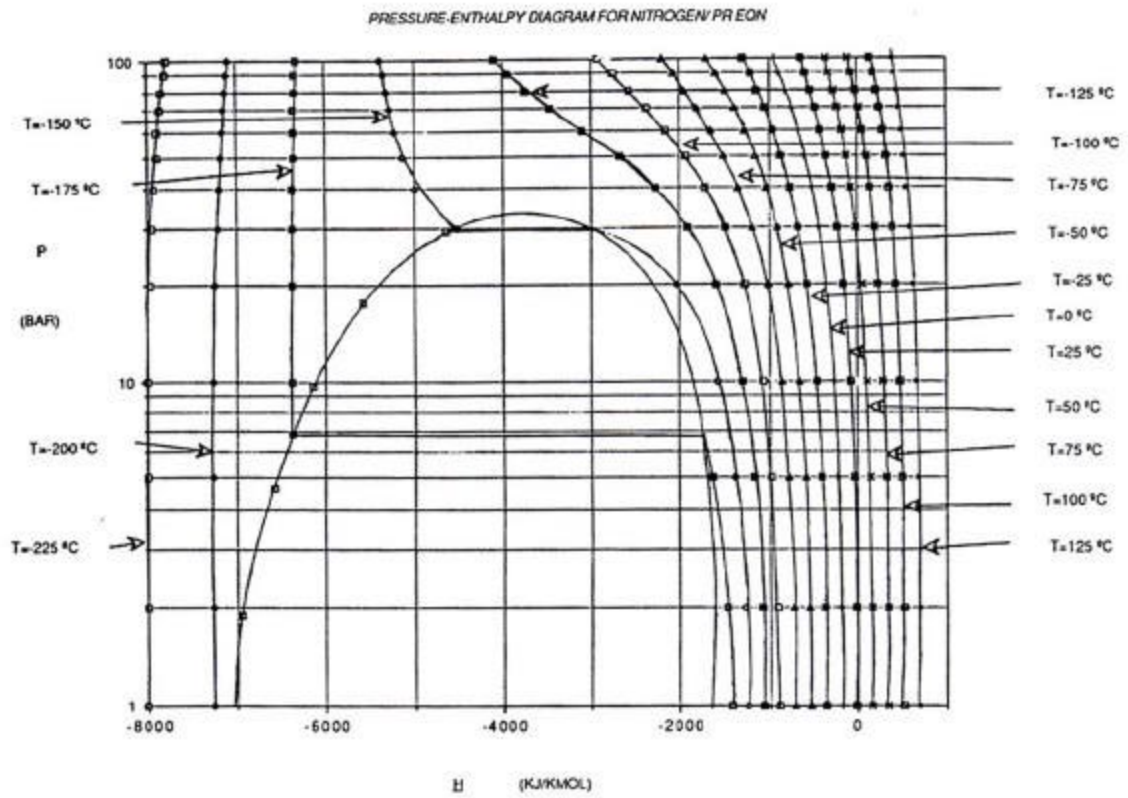
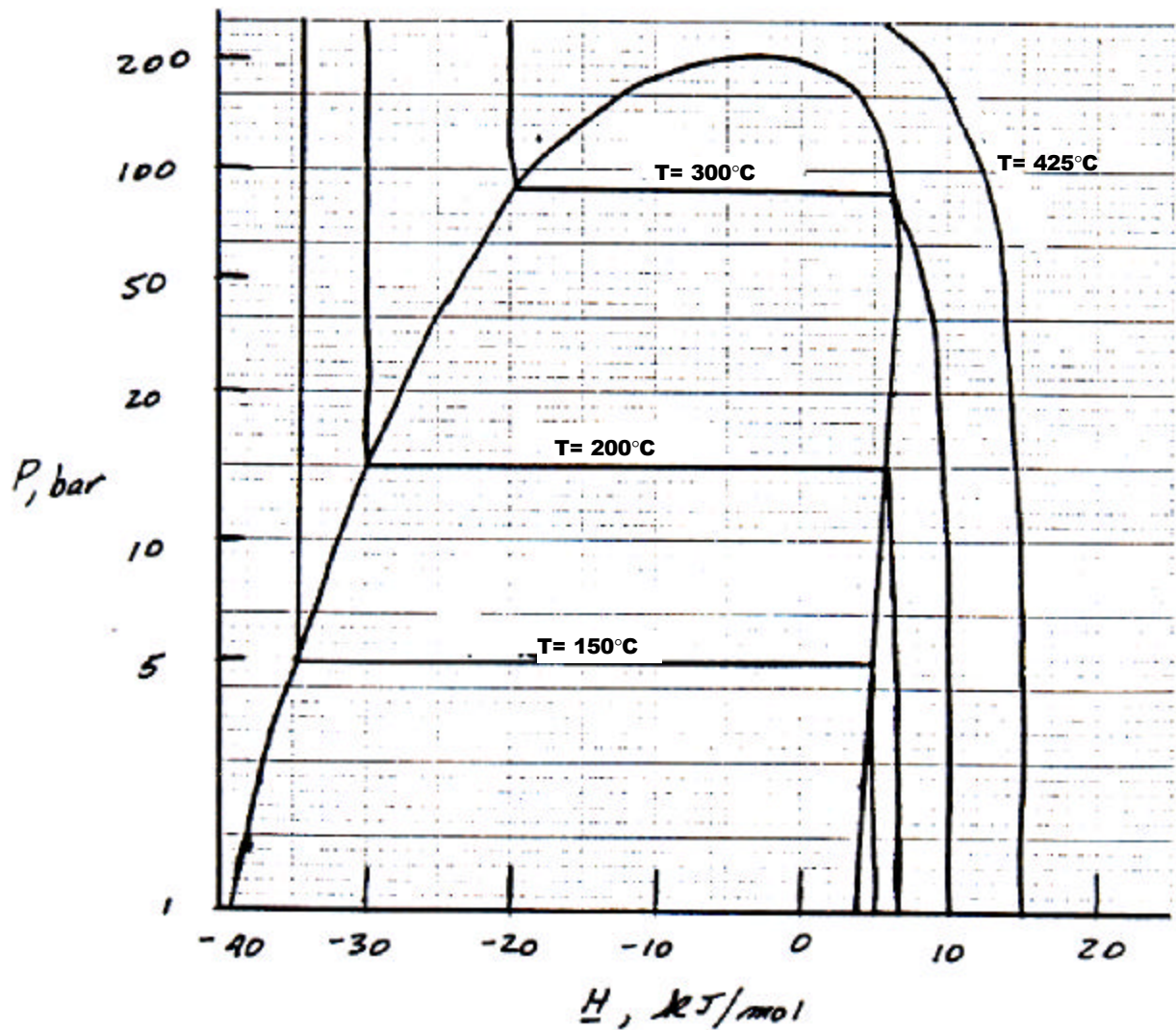**5.34** Thermodynamic properties of water (steam) by Allen Donn.
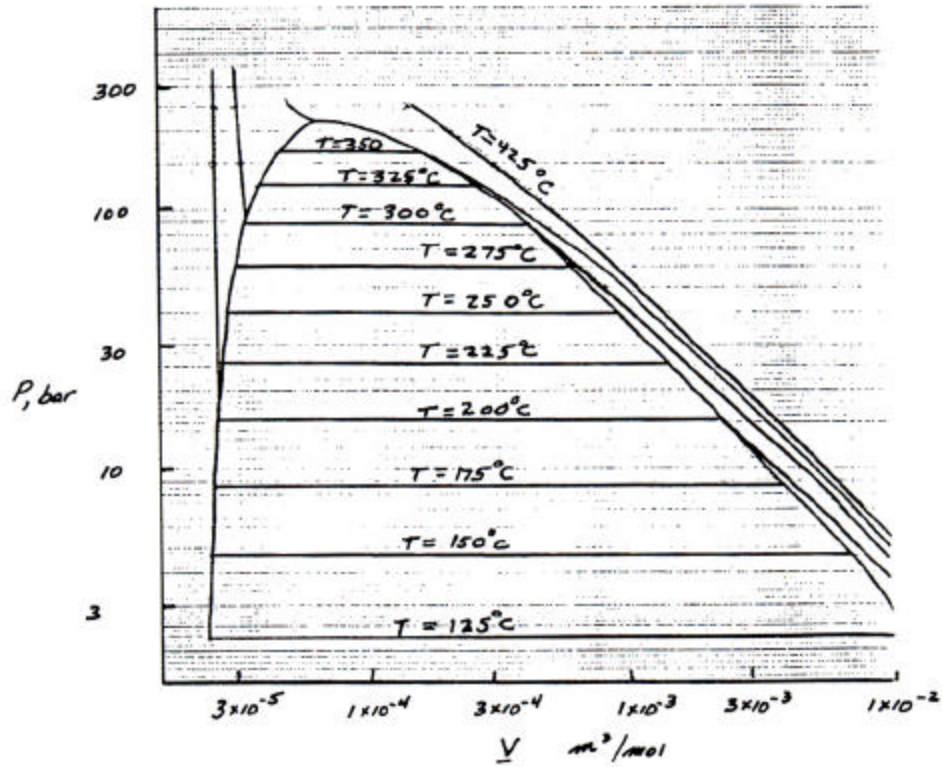
Pressure-volume diagram of steam computed with the Peng-Robinson equation of state
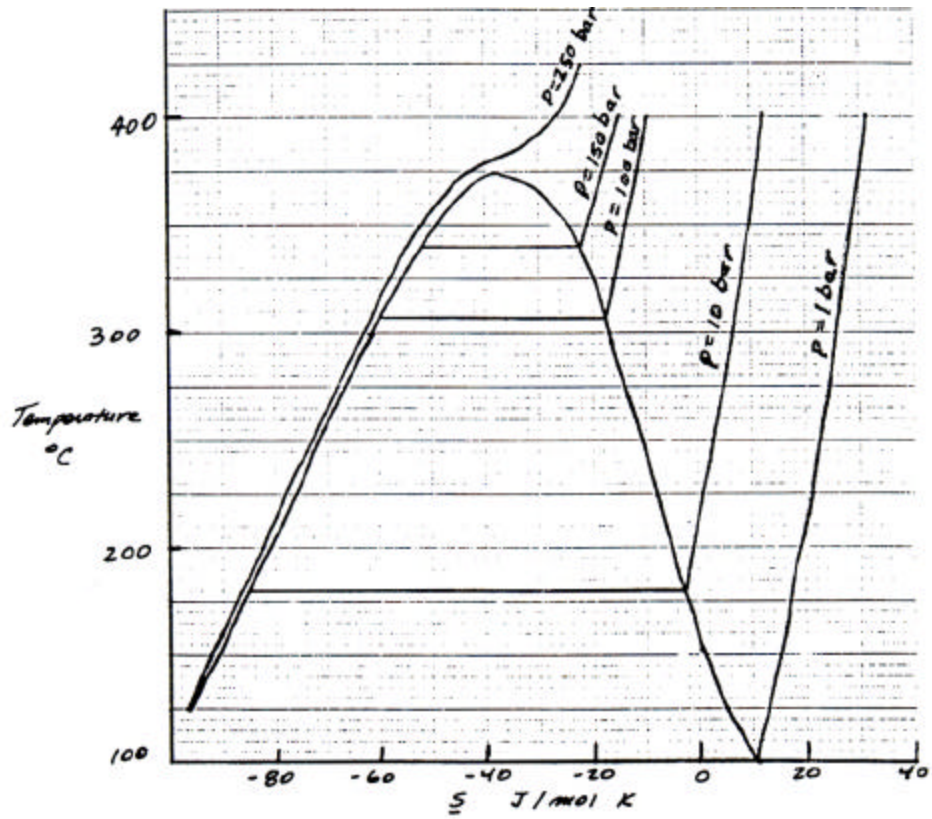
Temperature-entropy diagram of steam computed with the Peng-Robinson equation of state.

Pressure-enthalpy diagram of steam computed with the Peng-Robinson equation of state.

5.35(a) This would be a difficult problem if it were not for the availability of the program PR1. Using this program, the critical properties and the heat capacity data in the text, and the $T = 273.15\,\text{K}$, $P = 1$ bar reference state (which cancels out of the problem) we find for ethylene

$$85 \text{ bar and } 25^{\circ}\text{C} = 298.15\,\text{K}$$
$$\underline{H} = -6388 \text{ J/mol}$$
$$\underline{S} = -52.79 \text{ J/mol K}$$

By trial and error, using guessed values of T until we obtain $P^{\text{vap}} = 10$ bar , we obtain

$$T = 221.35\,\text{K}; \ \underline{S}^{\text{V}} = -29.44 \text{ J/mol K}; \ \underline{V}^{\text{V}} = 0.1536 \times 10^{-2} \text{ m}^3/\text{mol};$$
$$\underline{S}^{\text{L}} = -78.71 \text{ J/mol K}; \ \underline{V}^{\text{L}} = 0.5454 \times 10^{-4} \text{ m}^3/\text{mol}.$$

Now considering the fluid initially in the tank that will be in the tank finally as the system we have

$$N_i = N_f \text{ and } \underline{S}_i = \underline{S}_f$$

(b) Now there can not be only vapor in the tank (entropy too high) or only liquid (entropy too low), so there must be two phase mixture. Let $x^L =$ mass (or mole) fraction of liquid. Thus:

$$x^L \underline{S}^L + (1 - x^L)\underline{S}^V = \underline{S}_i = -52.79 \text{ J/mol K}$$

$$x^L(-78.71) + (1 - x^L)(-29.44) = -52.79$$

$$x^L = \frac{-52.79 + 29.44}{-78.71 + 29.44} = 0.474; \; x^V = 0.526$$

Thus, 47.4 wt % of fluid in tank is liquid, and 52.6% is vapor. Based on 1 mole in tank we have

$$\underline{V} = 0.474 \times 0.5454 \times 10^{-4} + 0.526 \times 0.1536 \times 10^{-2} = 8.338 \times 10^{-4} \text{ m}^3/\text{mol}$$

$$\text{volume \% liquid} = \frac{0.474 \times 0.5454 \times 10^{-4}}{8.338 \times 10^{-4}} \times 100 = 3.1\%$$

$$\text{volume \% vapor} = 96.9\%$$

5.36   (also available as a Mathcad worksheet)

$$\left(\frac{\partial P}{\partial T}\right)_{\text{sat}} = \frac{\Delta \underline{H}}{T\Delta \underline{V}}$$

Assume $\underline{V}^{\text{V}} \gg \underline{V}^{\text{L}} \Rightarrow \Delta \underline{V} \sim \underline{V}^{\text{V}} = \dfrac{ZRT}{P}$,

$$\left(\frac{\partial P}{\partial T}\right)_{\text{sat}} = \frac{\Delta \underline{H}}{ZRT^2/P} \Rightarrow \left(\frac{\partial \ln P}{\partial T}\right)_{\text{sat}} = \frac{\Delta \underline{H}}{ZRT^2}$$

but

$$\left(\frac{\partial \ln P}{\partial T}\right)_{\text{sat}} = \frac{\partial}{\partial T}\left(43.552 - \frac{5622.7}{T} - 4.70504\ln T\right)$$

$$= +\frac{5622.7}{T^2} - \frac{4.70504}{T} = \frac{1}{T^2}(5622.7 - 4.70504T)$$

Thus

$$\frac{\Delta \underline{H}}{ZRT^2} = \frac{1}{T^2}(5622.7 - 4.70504T)$$

or

$$\Delta \underline{H} = ZR(5622.7 - 4.70504T) = 31{,}602 \ \ \text{J/mol at } 75°C$$

$$Z = \frac{31{,}602}{8.314 \times (5622.7 - 4.70504\times(273.15+75))} = 0.9539$$

but

$$\frac{P\underline{V}}{RT} = 1 + \frac{B}{\underline{V}} = Z = 0.9539$$

so

$$\frac{B}{\underline{V}} = 0.9539 - 1 = -0.04607 \ ; \ \ B = -0.04607\underline{V}$$

Then $\underline{V} = 0.9539\, RT/P$. To find P use

$$\ln P^{\text{vap}} = 43.552 - \frac{5622.7}{(273.15+75)} - 4.70504\ln(273.15+75)$$

$$P^{\text{vap}} = 0.8736 \text{ bar}$$

$$\underline{V} = \frac{0.9539 \times 8.314 \times 10^{-5} \times (273.15+75)}{0.8736} = 3.1606\times10^{-2} \ \ \text{m}^3/\text{mol}$$

and

$$B = -1.456\times10^{-3} \ \ \text{m}^3/\text{mol}$$

5.37

We start with Eqn. (5.7-4), the Clapeyron equation

$$\left(\frac{\P P^{\text{sat}}}{\P T}\right)_{\underline{G}^{\text{I}}=\underline{G}^{\text{II}}} = \frac{\Delta\underline{H}}{T\Delta\underline{V}}$$

[Note: Error in problem statement of 1st printing. Disregard comment that the volume change on fusion is zero.]

From the problem statement $\Delta\underline{H} = 48.702 \text{ kJ/mol}$, but no data on $\Delta\underline{V}$ is given. Also $P^{\text{sat}} = 1.013$ bar at $T = 18.5°\text{C} = 291.65 \text{ K}$. Based on other hydrocarbons, we can guess that

$$\Delta\underline{V}^{\text{fus}} \sim 1 \text{ to } 2\times10^{-4} \text{ m}^3/\text{kg}$$

We will use this as an estimate and determine the effect on T_m. Also, the molecular weight of hexadecane is 226.45. Thus

$$\frac{dP}{d\ln T} = \frac{48.702 \text{ kJ/mol}\times1000 \text{ J/kJ}}{\boldsymbol{d}\times10^{-4} \text{ m}^3/\text{kg}\times226.54 \text{ g/mol}\times1 \text{ kg/1000 g}}$$

$$= \frac{214.98}{\boldsymbol{d}}\times10^7 \text{ J/m}^3$$

[where $\boldsymbol{d}$ is 1 or 2]

$$= \frac{214.98\times10^7}{\boldsymbol{d}} \text{ J/m}^3\times10^{-2} \text{ bar}\cdot\text{m}^3/\text{kJ}\times10^{-3} \text{ kJ/J} = \frac{214.98\times10^2}{\boldsymbol{d}} \text{ bar}$$

$$dP = \frac{21498}{\boldsymbol{d}}d\ln T \Rightarrow (P - 1.013 \text{ bar}) = \frac{21498}{\boldsymbol{d}}\ln\frac{T_2}{291.65 \text{ K}}$$

$$T_2 = 291.65\exp\left[\frac{(200 - 1.013)\times\boldsymbol{d}}{21498}\right] = \begin{cases} 294.36 & \text{if } \boldsymbol{d} = 1 \\ 297.10 & \text{if } \boldsymbol{d} = 2 \end{cases}$$

So the freezing point is raised between 2.7 and 5.5 K, depending on the (unknown) value of $\Delta\underline{V}^{\text{fus}}$.

5.38 (also available as a Mathcad worksheet)

This is a one-component adiabatic flash process. I will assume that only vapor + liquid are present, and then show that this is indeed the case.

There are two ways to solve this problem. One is to calculate all the thermodynamic properties, and the second is to use the steam tables. Both methods will be considered here

(1) Calculating all thermodynamic properties, and assuming the vapor phase is ideal.

energy balance: $10.\ \hat{U}^{\text{L}}(T = 95°\text{C}) = (10 - x)\hat{U}^{\text{L}}(T) + x\hat{U}^{\text{V}}(T)$

equilibrium requirements: $T^{\text{L}} = T^{\text{V}}$; $P^{\text{L}} = P^{\text{V}}$; and $\underline{G}^{\text{L}} = \underline{G}^{\text{V}} \Rightarrow P = P^{\text{vap}}$

Also, using data supplied earlier,

$$P^{\text{vap}} = \exp\left(14.790 - \frac{5432.8}{T}\right)$$

and by the ideal gas law

$$P = \frac{N^V RT}{V^V} = \frac{x/18 \text{ mol} \times 8.314 \times 10^{-5} \ (\text{bar} \cdot \text{m}^3/\text{mol K})T}{\underbrace{1 \times 10^{-3} - (10-x)/10^6}_{\substack{\text{volume taken up} \\ \text{by liquid}}}}$$

Equating P and P^{vap} we have

$$\frac{x/18 \times 8.314 \times 10^{-5}T}{1 \times 10^{-3} - (10-x)/10^6} = \exp\!\left(14.790 - \frac{5432.8}{T}\right) = \frac{x}{18} \cdot \frac{83.14T}{1000 - (10-x)}$$

Also we have for the internal energies

$\hat{U}^L(T = 0°C) = 0$ reference state

$\hat{U}^L(T = 95°C) = 95°C \times 4.184 \ \text{J/g}°C = 397.48 \ \text{J/g}$

$\hat{U}^L(T) = (T - 273.15) \times 4.184$ [assuming $C_v = \text{constant}$]

$\hat{U}^V(T = 0°C) = \Delta\hat{H}^{\text{vap}} - RT = 2260 - \dfrac{8.314 \times 273.15}{18} = 2133.83 \ \text{J/g}$

$\hat{U}^V(T) = 2133.83 + (T - 273.15) \times 2.09$

so that

$$10 \times 397.48 = (10-x) \times 4.184 \times (T - 273.15) + x[2133.83 + (T - 273.15) \times 2.09]$$

I find that the solution to these equations is

$$T = 352.68 \ \text{K} \quad \text{and} \quad P = 0.5411 \ \text{bar}$$
$$x = 0.3289 \ \text{g}$$

This is so far above the melting point of water, that the presence of an ice phase is impossible.

(2) Using the steam tables
energy balance:

$$10 \cdot \hat{U}^L(T = 95°C) = 10 \times 397.88 = \underbrace{(10-x)\hat{U}^L(T) - x\hat{U}^V(T)}_{\text{both at saturation}}$$

also $P = P^{\text{sat}}(T)$ and

$$V = 0.001 \ \text{m}^3 = (10-x)\hat{V}^L(T) + x\hat{V}^V(T)$$

Procedure

i) Guess T, get $P^{\text{sat}}(T)$, $\hat{V}^L(T)$, $\hat{V}^V(T)$, $\hat{U}^L(T)$ and $\hat{U}^V(T)$ from steam tables

ii) See if Eqns. (1) and (2) are satisfied by using Eqn. (2) to get x, and then seeing if Eqn. (1) is satisfied.

For example, guess $T = 80°C$:

$\hat{V}^L = 1.029 \times 10^{-6} \ \text{m}^3/\text{g}$ $\hat{U}^L = 334.86 \ \text{J/g}$

$\hat{V}^V = 3.407 \times 10^{-3} \ \text{m}^3/\text{g}$ $\hat{U}^V = 2482.2 \ \text{J/g}$

$P = 47.39 \ \text{kPa}$

$$\Rightarrow x(\text{eqn. (2)}) = 0.29058; \ x(\text{eqn. (1)}) = 0.29348$$

by iteration and interpolation

$$T = 79.4°\text{C}, \quad P = 0.4739 \text{ bar} \quad \text{and} \quad x = 0.29 \text{ grams}.$$

Difference between this solution and the previous one is due to the inaccuracies of the approximate vapor pressure equation in Part 1, and the assumption of constant heat capacities.

5.39 All the P-V data for this problem was obtained with a simple basic language program written for this problem. Calculations were done for n-butane as a representative fluid. The van der Waals loop region is shown on the diagram. What is interesting is that, in addition to the van der Waals loop, there is much structure in the P-V plot. Much of it occurs in the region of $b > \underline{V}$ and $\underline{V} < 0$, so that it has no relevance to our calculations. In the region $\underline{V} > b$ there is only the van der Waals loop behavior at low reduced temperatures, and the hyperbolic behavior $(P\underline{V} = RT)$ at very high temperatures. The main point is that the cubic equations we use exhibit quite complicated P-$\underline{V}$ behavior, but only relatively simple behavior in the region of interest to us, which is $\underline{V} > b$.
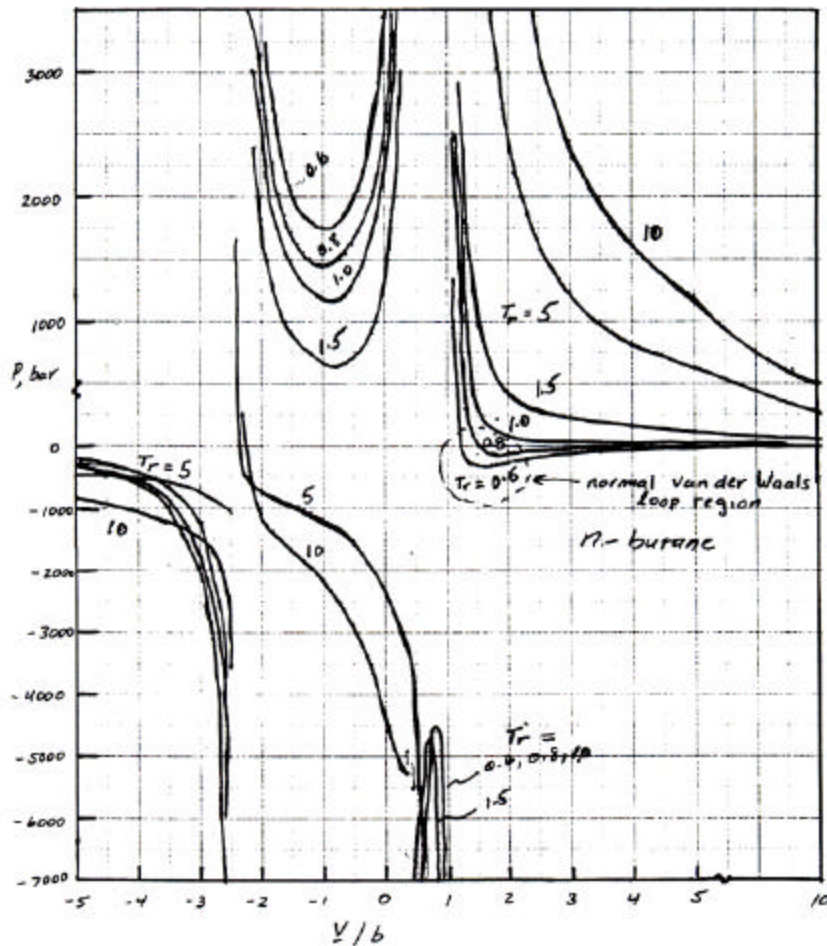
P-$\underline{V}$ diagram for n-butane calculated with the Peng-Robinson equation of state for realizable ($\underline{V} > b$) and physically unrealizable ($\underline{V} < b$) regions.

5.40 Let T_E = the equilibrium transition temperature when both solid phases are stable.

$$d\underline{G} = \underline{V}dP - \underline{S}dT$$

Also $dH = TdS + VdP$ so at constant pressure

$$\left(\frac{\P\underline{S}}{\P T}\right)_P = \frac{1}{T}\left(\frac{\P\underline{H}}{\P T}\right)_P = \frac{C_p}{T}$$

$\Rightarrow$ phase with higher heat capacity will have a higher entropy since the entropy of both phases are zero at 0 K.
Then, again at constant pressure

$$\left(\frac{\P\underline{G}}{\P T}\right)_P = -\underline{S}$$

Since both phases have the same Gibbs free energy at the temperature, T, this implies that the substance with the larger entropy (which arises from larger heat capacity) will have the lower Gibbs free energy, and therefore be the stable phase.

5.41 $\dfrac{P\underline{V}}{RT} = 1 + \dfrac{B(T)}{\underline{V}}$; $P = \dfrac{RT}{\underline{V}} + \dfrac{B(T)RT}{\underline{V}^2}$

$\left(\dfrac{\P P}{\P\underline{V}}\right)_T = -\dfrac{RT}{\underline{V}^2}$; $\dfrac{-2B(T)RT}{\underline{V}^3} < 0$

$\dfrac{2B(T)}{\underline{V}^3} > -\dfrac{1}{\underline{V}^2}$; $B(T) > -\dfrac{\underline{V}^3}{\underline{V}^2 2} = -\dfrac{\underline{V}}{2}$; $B(T) > -\dfrac{\underline{V}}{2}$

Back to virial eq.

$\dfrac{P\underline{V}^2}{RT} - \underline{V} - B(T) = 0$; $\underline{V} = \dfrac{+1 \pm \sqrt{1 + (4PB/RT)}}{2P/RT}$

$\underline{V} = \dfrac{RT}{2P} \pm \dfrac{RT}{2P}\sqrt{1 + \dfrac{4PB}{RT}}$

$B > -\dfrac{1}{2}\left[\dfrac{RT}{2P}\right]\left[1 \pm \sqrt{1 + \dfrac{4PB}{RT}}\right]$

$\dfrac{B}{1 \pm \sqrt{1 + (4PB/RT)}} > -\dfrac{RT}{4P}$ fluid will be stable

In fact, $B(T) > -\dfrac{\underline{V}}{2}$ is sufficient since $|B(T)| \ll \underline{V}$ in all conditions where second virial coefficient is used.

Approximation $B(T) > -\dfrac{\underline{V}}{2} \Rightarrow B(T) \gtrsim -\dfrac{RT}{2P}$ for stability.

5.42 Easy way

$$\frac{dU}{dt} = \dot{Q} - P\frac{dV}{dt} \; ; \; \frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{S}_{gen}$$

System of constant entropy $\dot{Q} = -T\dot{S}_{gen}$

Also constant pressure

$$\frac{dU}{dt} = -T\dot{S}_{gen} - P\frac{dV}{dt} = -T\dot{S}_{gen} - \frac{d}{dt}(PV)$$

$$\frac{dU}{dt} + \frac{d}{dt}(PV) = \frac{d}{dt}(U + PV) = \frac{dH}{dt} = -T\dot{S}_{gen} \leq 0$$

$\Rightarrow H = $ maximum at equilibrium

$$dH = 0$$

$$d^2H \geq 0 \Rightarrow$$

$$dH = TdS + VdP$$

$$d^2H = \left(\frac{\partial T}{\partial S}\right)_P (dS)^2 + \left(\frac{\partial T}{\partial P}\right)_S dSdP + \left(\frac{\partial V}{\partial S}\right)_P dPdS + \left(\frac{\partial V}{\partial P}\right)_S (dP)^2$$

$$d^2H = \left(\frac{\partial T}{\partial S}\right)_P (\partial S)^2 \geq 0 \Rightarrow \left(\frac{\partial T}{\partial S}\right)_P \geq 0$$

$$\left(\frac{\partial T}{\partial S}\right)_P = \frac{T}{C_P} \geq 0 \Rightarrow C_P > 0$$

More theoretically correct way

Equilibrium criterion for a closed system at constant entropy and pressure.

$$\frac{dU}{dt} = \dot{Q} - P\frac{dV}{dt} \; ; \; \frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{S}_{gen}$$

$$\dot{Q} = T\frac{dS}{dt} - T\dot{S}_{gen}$$

$$\frac{dU}{dt} = T\frac{dS}{dt} - P\frac{dV}{dt} - T\dot{S}_{gen}$$

Constant entropy $\frac{dS}{dt} = 0$; constant pressure $P\frac{dV}{dt} = \frac{d}{dt}(PV)$

$$\Rightarrow \frac{dU}{dt} = -\frac{d}{dt}(PV) - T\dot{S}_{gen} \; ; \; \frac{d}{dt}(U + PV) = -T\dot{S}_{gen}$$

$$\frac{dH}{dt} = -T\dot{S}_{gen} \leq 0 \Rightarrow \frac{dH}{dt} \leq 0 \Rightarrow H = \text{minimum stability}$$

$$d^2H > 0 \text{ but } dH = TdS + VdP + \underline{G}_i dN$$

$$d^2H = \left(H_{SS}^{I} + H_{SS}^{II}\right)\left(dS^{I}\right)^2 + \left(H_{NN}^{I} + H_{NN}^{II}\right)\left(dN^{I}\right)^2$$

$$+ 2\left(H_{SN}^{I} + H_{SN}^{II}\right)dS^{I}dN^{I} > 0$$

$$= \frac{N^{I} + N^{II}}{N^{I}N^{II}}\left[N^{I}H_{SS}^{I}\left(dS^{I}\right)^2 + 2N^{I}H_{SN}^{I}dS^{I}dN^{I} + N^{I}H_{NN}^{I}\left(dN^{I}\right)^2\right] > 0$$

Making a transformation of variables

$$dx_1 = dS^{I} + \frac{H_{SN}}{H_{NN}}dN \; ; \; dx_2 = dN^{I}$$

$$q_1 = NH_{SS} \; ; \; q_2 = \frac{\left(NH_{SS}NH_{NN} - N^2 H_{SN}^2\right)}{NH_{SS}}$$

As a check

$$q_1 dx_1^2 + q_2 dx_2^2$$

$$= NH_{SS}\left(dS^I + \frac{H_{SN}}{H_{SS}}\, dN^I\right)^2 + \frac{NH_{SS}NH_{NN} - N^2 H_{SN}^2}{NH_{SS}} dN^{I2}$$

$$= NH_{SS}\,dS^{I2} + 2\,NH_{SS} \cdot \frac{H_{SN}}{H_{SS}}\, dS^I dN^I + NH_{SS} \cdot \frac{H_{SN}^2}{H_{SS}^2}\, dN^{I2}$$

$$+\, NH_{NN}\, dN^{I2} - \frac{NH_{SN}^2}{H_{SS}}\, dN^{I2}$$

which is correct so

$$q_1 dx_1^2 + q_2 dx_2^2 \geq 0 \Rightarrow q_1 > 0, \; q_2 > 0$$

$$q_1 = NH_{SS} = N\left(\frac{\partial^2 H}{\partial^2 S}\right)_P = N\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial S}\right)_P = N\left(\frac{\partial T}{\partial S}\right)_P > 0$$

but $$d\underline{S} = \frac{C_P}{T}dT - \left(\frac{\partial \underline{V}}{\partial T}\right)_P \; ; \; \left(\frac{\partial \underline{S}}{\partial T}\right)_P = \frac{C_P}{T} \Rightarrow \left(\frac{\partial S}{\partial T}\right)_P = \frac{NC_P}{T}$$

$$\Rightarrow N\frac{T}{NC_P} > 0 \; ; \; N > 0, \; T > 0 \Rightarrow C_P > 0$$

Second criterion

$$\frac{NH_{SS}NH_{NN} - N^2 H_{SN}^2}{NH_{SS}} \; ; \; H_{NN} = \left(\frac{\partial^2 H}{\partial N^2}\right)_{S,P} = \frac{\partial}{\partial N}(G)\Big|_{S,P} = \left(\frac{\partial G}{\partial N}\right)_{S,P}$$

$$H_{SN} = \frac{\partial}{\partial N}\Big|_{S,P}\left(\frac{\partial H}{\partial S}\right)_{P,N} = \frac{\partial}{\partial N}(T)_{S,P} = \left(\frac{\partial T}{\partial N}\right)_{S,P}$$

$$NH_{NN} - N\frac{H_{SN}^2}{H_{SS}} = N\left(\frac{\partial G}{\partial N}\right)_{S,P} - N\frac{(\partial T/\partial N)_{S,P}^2}{(\partial T/\partial S)_{P,N}} = ?$$

5.43 (also available as a Mathcad worksheet)

5.43 ISENTHALPIC CLAUSIUS EQUATION OF STATE CALCULATION

$$Cp_0 := 20.97 \qquad bb_0 := 4.28 \cdot 10^{-5} \qquad bb_1 := 1.35 \cdot 10^{-7} \qquad b(T) := bb_0 + bb_1 \cdot T$$

$$R := 8.314 \cdot 10^{-5}$$

Input initial temperature and pressure of calculation $\quad Ti := 120 + 273.15 \quad Pi := 50 \quad$ **bar**

Input final pressure $\quad Pf := 10 \quad$ **bar**

Initial state calculations $\qquad T := Ti \qquad P := Pi \qquad Vi := \frac{(R \cdot Ti)}{Pi} + b(Ti)$

$$Zi := \frac{(Pi \cdot Vi)}{R \cdot Ti} \qquad Zi = 1.1467$$

$$DELHin := \left[R \cdot T \cdot (Zi - 1) - \frac{\left(R \cdot Ti^2 \cdot bb_1\right)}{Vi - b(Ti)}\right] \cdot 10^5$$

$$DELHin = 214$$

Guess for final state $\qquad T := 0.8 \cdot Ti \qquad P := Pf$

Residual enthalpy (DELHF) $\qquad V(T,P) := \frac{(R \cdot T)}{P} + b(T) \qquad Z(T,P) := \frac{(P \cdot V(T,P))}{R \cdot T}$

$$\text{DELHF}(T, P) := \left[R \cdot T \cdot (Z(T, P) - 1) - \frac{\left(R \cdot T^2 \cdot bb_1 \right)}{V(T, P) - b(T)} \right] \cdot 10^5$$

Ideal gas properties changes relative to the initial state $\text{DELHIG}(T, P) := Cp_0 \cdot (T - Ti)$

Solve for the exit temperature

Given $\text{DELHF}(T, P) + \text{DELHIG}(T, P) - \text{DELHin} = 0$ $T := \text{find}(T)$ $T = 401.314$

$\delta H := \text{DELHF}(T, P) + \text{DELHIG}(T, P) - \text{DELHin}$ $HF := \text{DELHF}(T, P) + \text{DELHIG}(T, P)$

SUMMARY OF RESULTS

	FEED	**EXIT**
Temperature, K	Ti = 393.15	T = 401.314
Pressure, bar	Pi = 50	P = 10
Compressibility	Zi = 1.1467	Z(T, P) = 1.0291
Enthalpy (relative to the feed)	0	HF = 214

$$\delta H = -3.1264 \cdot 10^{-13}$$

Symbolic determination of enthalpy departure function for the   File: 5-43 symbolic
Clausius equation of state

$$b(T, bb) := bb_0 + bb_1 \cdot T$$

$$P(T, V, R, bb) := \frac{(R \cdot T)}{V - b(T, bb)}$$

$$\frac{d}{dT} P(T, V, R, bb) \rightarrow \frac{R}{\left(V - bb_0 - bb_1 \cdot T \right)} + R \cdot \frac{T}{\left(V - bb_0 - bb_1 \cdot T \right)^2} \cdot bb_1$$

$$\text{der}(T, V, R, bb) := \frac{d}{dT} P(T, V, R, bb)$$

$$\text{Int}(T, V, R, bb) := T \cdot \text{der}(T, V, R, bb) - P(T, V, R, bb)$$

$$\text{Int}(T, V, R, bb) \rightarrow T \cdot \left[\frac{R}{\left(V - bb_0 - bb_1 \cdot T \right)} + R \cdot \frac{T}{\left(V - bb_0 - bb_1 \cdot T \right)^2} \cdot bb_1 \right] - R \cdot \frac{T}{\left(V - bb_0 - bb_1 \cdot T \right)}$$

Upon simplification $$R \cdot T^2 \cdot \frac{bb_1}{\left(V - bb_0 - bb_1 \cdot T \right)^2}$$

$$DelH(T, V, R, bb) := \int_{10^{15}}^{V} Int(T, S, R, bb) \, dS$$

MATHCAD has trouble with an infinite lower limit, so use a very large number instead

$$DelH(T, V, R, bb) \rightarrow -R \cdot T^2 \cdot \frac{bb_1}{(V - bb_0 - bb_1 \cdot T)} - R \cdot T^2 \cdot \frac{bb_1}{(-1000000000000000 + bb_0 + bb_1 \cdot T)}$$

This term can be neglected, would be zero if an infinite lower limit could be used

$$DelH(T, V, R, bb) := -R \cdot T^2 \cdot \frac{bb_1}{(V - bb_0 - bb_1 \cdot T)}$$

Final result

5.44 Clausius EOS: $P = \dfrac{RT}{V - b(T)}$

Condition for stability is $\left(\dfrac{\partial P}{\partial V} \right)_T < 0$

For the Clausius equation

$$\left(\frac{\partial P}{\partial \underline{V}} \right)_T = -\frac{RT}{(\underline{V} - b)^2} \quad \text{Since } R > 0, \ T > 0 \text{ and } (\underline{V} - b)^2 > 0.$$

Then $\left(\dfrac{\partial P}{\partial \underline{V}} \right)_T$ must be negative or

$\left(\dfrac{\partial P}{\partial \underline{V}} \right)_T < 0 \Rightarrow$ Single phase is stable at all conditions.

5.45 See solution to Problem 5.41. If fluid is unstable, then a vapor-liquid phase transition can occur.

5.46 Redlich-Kwong equation of state

$$\ln \frac{f}{P} = \frac{1}{RT} \int_{\underline{V}=\infty}^{\underline{V}=ZRT/P} \left(\frac{RT}{\underline{V}} - P \right) d\underline{V} - \ln Z + (Z - 1)$$

$$\int\left(\frac{RT}{\underline{V}} - P\right)d\underline{V} = \int\limits_{\underline{V}=\infty}^{\underline{V}}\left(\frac{RT}{\underline{V}} - \frac{RT}{\underline{V}-b} + \frac{a(T)}{\underline{V}(\underline{V}+b)}\right)d\underline{V}$$

$$= RT\ln\frac{\underline{V}}{\underline{V}\to\infty} - RT\ln\frac{\underline{V}-b}{(\underline{V}-b)_{\underline{V}\to\infty}} + a(T)\int\limits_{\underline{V}=\infty}^{\underline{V}}\frac{d\underline{V}}{\underline{V}(\underline{V}+b)}$$

$$= RT\ln\frac{\underline{V}}{\underline{V}-b} + a\left(-\frac{1}{b}\right)\ln\left(\frac{\underline{V}+b}{\underline{V}}\right) = RT\ln\frac{Z}{Z-B} - \frac{a}{b}\ln\left(\frac{Z+B}{Z}\right)$$

$$\ln\frac{f}{P} = \ln\frac{Z}{Z-B} - \frac{a}{bRT}\ln\left(\frac{Z+B}{Z}\right) - \ln Z + (Z-1)$$

$$= -\ln(Z-B) - \frac{a}{bRT}\ln\left(\frac{Z+B}{Z}\right) + (Z-1)$$

$$= (Z-1) - \ln(Z-B) - \frac{a}{bRT}\ln\left(\frac{Z+Pb/RT}{Z}\right)$$

$$A = \frac{aP}{RT^2}; \quad B = \frac{bP}{RT}$$

$$\ln\frac{f}{P} = (Z-1) - \ln(Z-B) - \frac{A}{B}\ln\left(\frac{Z+B}{Z}\right)$$

Using the same analysis for the Soave-Redlich-Kwong equation of state leads to
the following

$$\ln\frac{f}{P} = (Z-1) - \ln\left(Z - \frac{Pb}{RT}\right) - \frac{a(T)}{RTb}\ln\left[\frac{Z+(Pb/RT)}{Z}\right]$$

$$= (Z-1) - \ln(Z-B) - \frac{a(T)}{RTb}\ln\left[\frac{Z+B}{Z}\right]$$

5.47 (also available as a Mathcad worksheet)
See Mathcad for the graphs.

Problem 5.47

$$P(V, T, R, a, b) := \frac{R\cdot T}{V-b} - \frac{a}{T^{0.5}\cdot V\cdot(V+b)}$$

$$\int\left(\frac{R\cdot T}{V} - P(V, T, R, a, b)\right)dV \to R\cdot T\cdot\ln(V) - 1.\cdot\ln(V - 1.\cdot b)\cdot R\cdot T + \frac{a}{\left(\sqrt{T}\cdot b\right)}\cdot\ln(V) - 1.\cdot\frac{a}{\left(\sqrt{T}\cdot b\right)}\cdot\ln(V+b)$$

$$Tc := 126.2\cdot K \qquad Pc := 3.396\cdot10^6\cdot Pa \qquad R := 8.314\cdot\frac{Pa\cdot m^3}{mole\cdot K} \qquad a := 0.42748\cdot\frac{R^2\cdot Tc^{2.5}}{Pc} \qquad b := 0.08664\cdot\frac{R\cdot Tc}{Pc}$$

$$T := 110\cdot K$$

$$i := 0.. 100 \qquad V_0 := 1.5\cdot b \qquad V_{i+1} := V_i\cdot1.001^i \qquad V_0 = 4.015\bullet10^{-5}\ \bullet m^3\bullet mole^{-1}$$

$$P_i := \frac{R\cdot T}{V_i - b} - \frac{a}{T^{0.5}\cdot V_i\cdot(V_i + b)} \qquad\qquad Z_i := \frac{P_i\cdot V_i}{R\cdot T} \qquad\qquad V_{100} = 5.655\bullet10^{-3}\ \bullet m^3\bullet mole^{-1}$$

$$fop_i := \ln\left(\frac{V_i}{V_i - b}\right) - \ln\left(Z_i\right) + Z_i - 1 + \frac{a}{T^{1.5}\cdot R\cdot b}\cdot\ln\left(\frac{V_i}{V_i + b}\right)$$
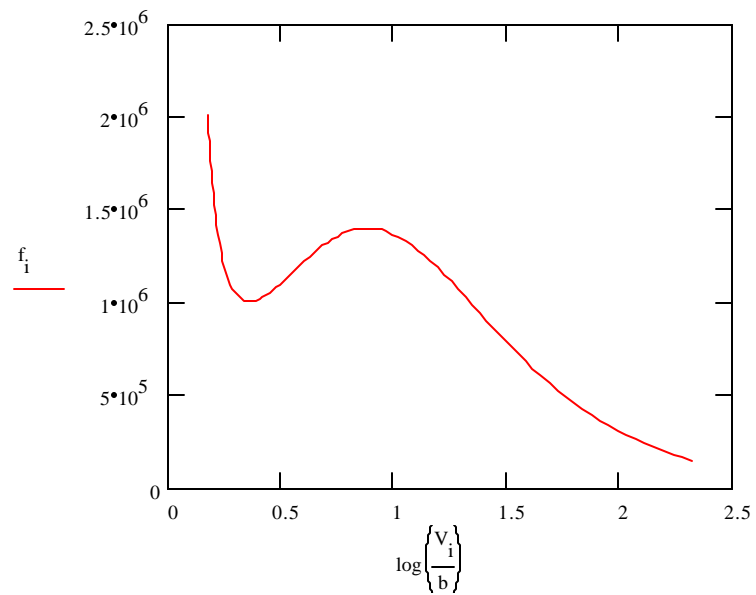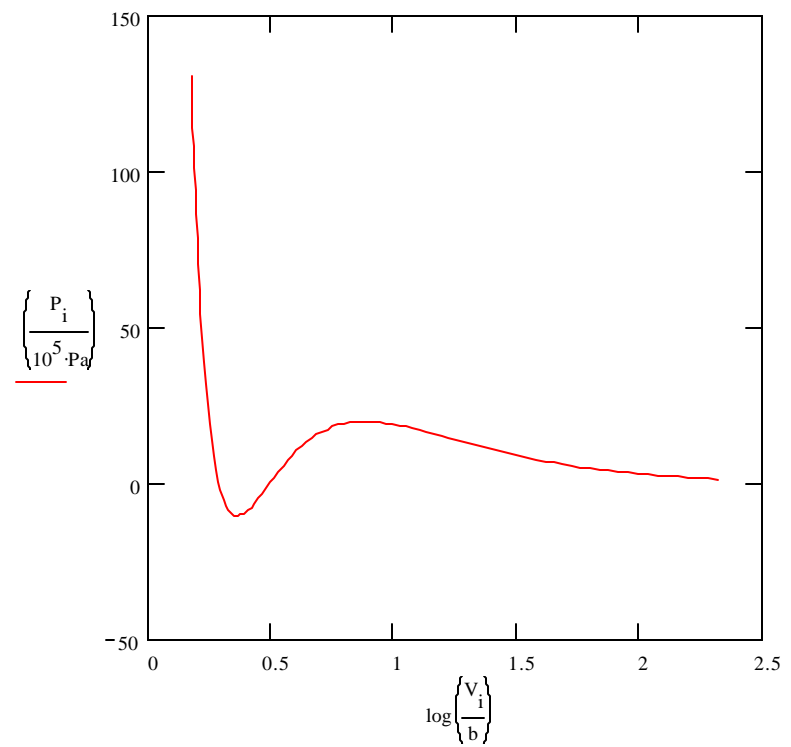
$f_i := P_i \cdot \exp\left(fop_i\right)$

$T := 150 \cdot K$

$i := 0 .. 100$ $\qquad$ $V_0 := 1.5 \cdot b$ $\qquad$ $V_{i+1} := V_i \cdot 1.001^i$ $\qquad$ $V_0 = 4.015 \cdot 10^{-5} \cdot m^3 \cdot mole^{-1}$
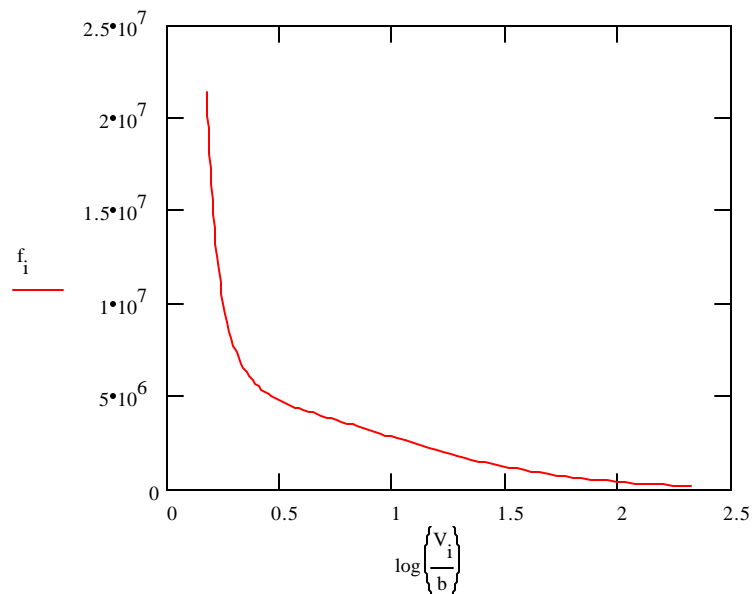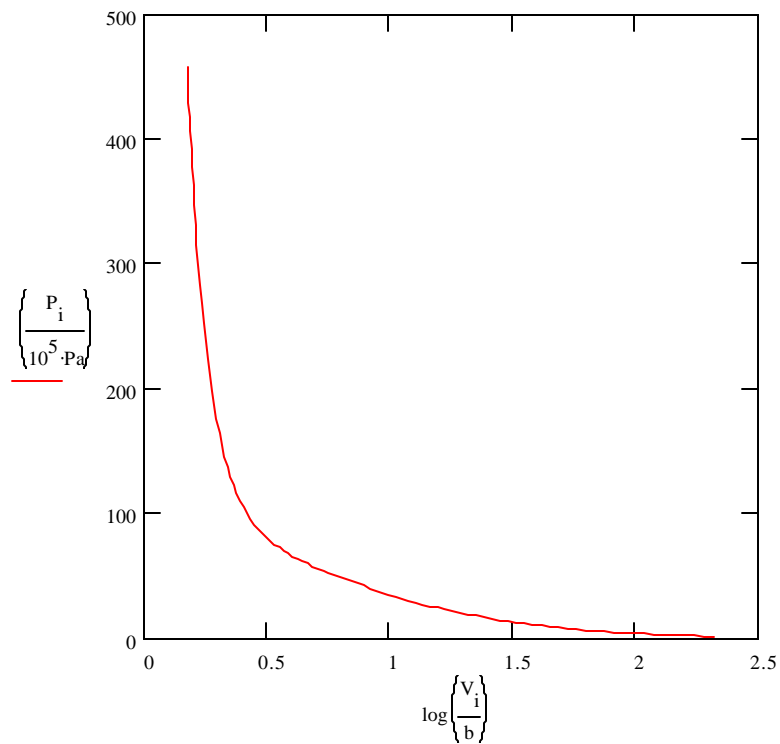
$$P_i := \frac{R \cdot T}{V_i - b} - \frac{a}{T^{0.5} \cdot V_i \cdot (V_i + b)} \qquad Z_i := \frac{P_i \cdot V_i}{R \cdot T} \qquad V_{100} = 5.655 \cdot 10^{-3} \cdot m^3 \cdot mole^{-1}$$

$$fop_i := \ln\left(\frac{V_i}{V_i - b}\right) - \ln\left(Z_i\right) + Z_i - 1 + \frac{a}{T^{1.5} \cdot R \cdot b} \cdot \ln\left(\frac{V_i}{V_i + b}\right)$$

$$f_i := P_i \cdot \exp\left(fop_i\right)$$

5.48   (also available as a Mathcad worksheet)

Problem 5.48

a) If ethanol is an ideal gas, the $f = P$, so that the fugacity of ethanol is 505 kPa

b) Starting from eqn. 5.48 we have that

$\ln (f/P) = (B/V) - \ln Z + (Z-1)$ $mol := 1$

$P := 505000 \cdot Pa$ $T := (273.15 + 126) \cdot K$ $R := 8.314 \cdot \dfrac{(Pa \cdot m^3)}{mol \cdot K}$ $B := -523 \cdot 10^{-6} \cdot \dfrac{m^3}{mol}$

$V := \dfrac{(R \cdot T)}{P}$ $V = 6.571 \cdot 10^{-3} \ \cdot m^3$

Given $\dfrac{(P \cdot V)}{R \cdot T} = 1 + \dfrac{B}{V}$ $V := find(V)$ $V = 5.998 \cdot 10^{-3} \ \cdot m^3$

$Z := \dfrac{(P \cdot V)}{R \cdot T}$ $Z = 0.913$

$fsat := P \cdot exp\left[\dfrac{B}{V} - \ln(Z) + (Z - 1)\right]$ $fsat = 4.592 \cdot 10^5 \ \cdot Pa$

5.49   (also available as a Mathcad worksheet)

Problem 5.49

The density of ethanol is 0.789 g/cc at 20 C which we will also use at 126 C, and its molecul weight is 46.07. Therefore its liquid molar volume is

$kPa := 10^3 \cdot Pa$ $MPa := 10^6 \cdot Pa$

$Vl := \dfrac{\left(46.07 \cdot 10^{-3} \cdot \dfrac{kg}{mol}\right)}{0.789 \cdot 10^3 \cdot \dfrac{kg}{m^3}}$ $Vl = 5.839 \cdot 10^{-5} \ \cdot m^3$

a)
$f := fsat \cdot exp\left[\dfrac{((25 \cdot MPa - 505 \cdot kPa) \cdot Vl)}{R \cdot T}\right]$ $f = 7.066 \cdot 10^5 \ \cdot Pa$

b)

$VV(p) := Vl \cdot \left[1 + 1.09 \cdot 10^{-6} \cdot kPa^{-1} \cdot (101.3 \cdot kPa - p)\right]$ $VV(25 \cdot MPa) = 5.681 \cdot 10^{-5} \ \cdot m^3$

$f := fsat \cdot exp\left[\dfrac{1}{R \cdot T} \cdot \int_{505 \cdot kPa}^{25 \cdot MPa} VV(p) dp\right]$ $f = 7.024 \cdot 10^5 \ \cdot Pa$

5.50 (also available as a Mathcad worksheet)

5.50 FUGACITY CALCULATION USING SRK EQUATION

Read in properties for Pentane $\quad$ Tc $:= 469.6 \quad$ Pc $:= 33.74 \quad$ om $:= 0.251$

kappa calculation $\qquad$ kap $:= 0.480 + 1.574 \cdot \text{om} - 0.176 \cdot \text{om} \cdot \text{om}$

S-R-K Constants: $\qquad$ R $:= 0.00008314 \qquad$ b $:= 0.08664 \cdot \dfrac{R \cdot Tc}{Pc} \qquad$ ac $:= 0.42748 \cdot \dfrac{R^2 \cdot Tc^2}{Pc}$

Note that these are being defined as a function of temperature.

$$\text{alf}(T) := 1 \cdot \left[1 + \text{kap} \cdot \left(1 - \sqrt{\frac{T}{Tc}} \right) \right]^2 \qquad a(T) := ac \cdot \text{alf}(T)$$

$$CA(T, P) := \frac{a(T) \cdot P}{(R \cdot T)^2} \qquad CB(T, P) := \frac{P \cdot b}{R \cdot T} \qquad Da(T) := \frac{d}{dT} a(T)$$

$$Z(T, P) := \begin{vmatrix} A \leftarrow CA(T, P) \\ B \leftarrow CB(T, P) \\ V \leftarrow \begin{bmatrix} -A \cdot B \\ A - B^2 - B \\ -1 \\ 1 \end{bmatrix} \\ ZZ \leftarrow \text{polyroots}(V) \\ \text{for } i \in 0..2 \\ \quad \left(ZZ_i \leftarrow 0 \right) \text{ if } \left(\text{Im}\left(ZZ_i \right) \neq 0 \right) \\ ZZ \leftarrow \text{sort}(ZZ) \\ ZZ_0 \leftarrow ZZ_2 \text{ if } \left(\left| ZZ_0 \right| < 10^{-5} \right) \\ ZZ_2 \leftarrow ZZ_0 \text{ if } \left(\left| ZZ_2 \right| < 10^{-5} \right) \\ ZZ \end{vmatrix}$$

Vector of coefficients in the SRK equation in the form
0=-A*B+(A-B^2-B)*Z-*Z^2+Z^3

Solution to the cubic

Set any imaginary roots to zero
Sort the roots

Set the value of any imaginary roots to value of the real root

Enter temperature T, and pressure P.

$\quad$ T $:= 100 \quad$ **C** $\qquad$ T $:= 273.15 + T \quad$ **K** $\qquad$ P $:= 50$

Fugacity expressions [actually ln(f/P)] for the liquid fl and vapor fv

$$fl(T, P) := \left(Z(T, P)_0 - 1 \right) - \ln\left(Z(T, P)_0 - CB(T, P) \right) - \frac{CA(T, P)}{CB(T, P)} \cdot \ln\left(\frac{Z(T, P)_0 + CB(T, P)}{Z(T, P)_0} \right)$$

$$fv(T, P) := \left(Z(T, P)_2 - 1 \right) - \ln\left(Z(T, P)_2 - CB(T, P) \right) - \frac{CA(T, P)}{CB(T, P)} \cdot \ln\left(\frac{Z(T, P)_2 + CB(T, P)}{Z(T, P)_2} \right)$$

Fugacity			**Fugacity coefficient**	

$fugl := P \cdot exp(fl(T, P))$ $fugl = 6.49272$ $fl(T, P) = {}^-2.04134$ $phil := \dfrac{fugl}{P}$ $phil = 0.12985$

$fugv := P \cdot exp(fv(T, P))$ $fugv = 6.49272$ $fv(T, P) = {}^-2.04134$ $phiv := \dfrac{fugv}{P}$ $phiv = 0.12985$

SUMMARY OF RESULTS

$T = 373.15$ **K**   **Vapor pressure, bar** $P = 50$

	LIQUID	**VAPOR**
Compressibility	$Z(T, P)_0 = 0.23249$	$Z(T, P)_2 = 0.23249$
Fugacity coefficient	$phil = 0.12985$	$phiv = 0.12985$
Fugacity, bar	$fugl = 6.49272$	$fugv = 6.49272$

Read in properties for Benzene $Tc := 562.1$ $Pc := 48.94$ $om := 0.212$

 kappa calculation $kap := 0.480 + 1.574 \cdot om - 0.176 \cdot om \cdot om$

S-R-K Constants: $R := 0.00008314$ $b := 0.08664 \cdot \dfrac{R \cdot Tc}{Pc}$ $ac := 0.42748 \cdot \dfrac{R^2 \cdot Tc^2}{Pc}$

Note that these are being defined as a function of temperature.

$$alf(T) := 1 \cdot \left[1 + kap \cdot \left(1 - \sqrt{\dfrac{T}{Tc}} \right) \right]^2$$ $a(T) := ac \cdot alf(T)$

$$CA(T, P) := \dfrac{a(T) \cdot P}{(R \cdot T)^2} \qquad CB(T, P) := \dfrac{P \cdot b}{R \cdot T} \qquad Da(T) := \dfrac{d}{dT} a(T)$$

$$Z(T,P) := \begin{vmatrix} A \leftarrow CA(T,P) \\[4pt] B \leftarrow CB(T,P) \\[4pt] V \leftarrow \begin{bmatrix} -A \cdot B \\ A - B^2 - B \\ -1 \\ 1 \end{bmatrix} \\[4pt] ZZ \leftarrow polyroots(V) \\[4pt] \text{for } i \in 0..2 \\[4pt] \quad \left(ZZ_i \leftarrow 0\right) \text{ if } \left(Im\!\left(ZZ_i\right) \neq 0\right) \\[4pt] ZZ \leftarrow sort(ZZ) \\[4pt] ZZ_0 \leftarrow ZZ_2 \text{ if } \left(\left| ZZ_0 \right| < 10^{-5}\right) \\[4pt] ZZ_2 \leftarrow ZZ_0 \text{ if } \left(\left| ZZ_2 \right| < 10^{-5}\right) \\[4pt] ZZ \end{vmatrix}$$

Vector of coefficients in the SRK equation in the form
0=-A*B+(A-B^2-B)*Z-*Z^2+Z^3

Solution to the cubic

Set any imaginary roots to zero
Sort the roots

Set the value of any imaginary roots to value of the real root

Enter temperature T, and pressure P.

$T := 100 \quad \mathbf{C} \qquad T := 273.15 + T \quad \mathbf{K} \qquad P := 50$

Fugacity expressions [actually ln(f/P)] for the liquid fl and vapor fv

$$fl(T,P) := \left(Z(T,P)_0 - 1\right) - \ln\!\left(Z(T,P)_0 - CB(T,P)\right) - \frac{CA(T,P)}{CB(T,P)} \cdot \ln\!\left(\frac{Z(T,P)_0 + CB(T,P)}{Z(T,P)_0}\right)$$

$$fv(T,P) := \left(Z(T,P)_2 - 1\right) - \ln\!\left(Z(T,P)_2 - CB(T,P)\right) - \frac{CA(T,P)}{CB(T,P)} \cdot \ln\!\left(\frac{Z(T,P)_2 + CB(T,P)}{Z(T,P)_2}\right)$$

Fugacity   **Fugacity coefficient**

$fugl := P \cdot exp(fl(T,P)) \quad fugl = 2.01968 \qquad fl(T,P) = {}^{-}3.20908 \qquad phil := \dfrac{fugl}{P} \qquad phil = 0.04039$

$fugv := P \cdot exp(fv(T,P)) \quad fugv = 2.01968 \qquad fv(T,P) = {}^{-}3.20908 \qquad phiv := \dfrac{fugv}{P} \quad phiv = 0.04039$

SUMMARY OF RESULTS

$T = 373.15 \quad \mathbf{K}$ **Vapor pressure, bar** $P = 50$

	LIQUID	**VAPOR**
Compressibility	$Z(T,P)_0 = 0.17187$	$Z(T,P)_2 = 0.17187$
Fugacity coefficient	$phil = 0.04039$	$phiv = 0.04039$
Fugacity, bar	$fugl = 2.01968$	$fugv = 2.01968$

5.51 (Solution using Mathcad worksheet)

$T = -200^{\circ}\text{C}$ $\qquad$ $P^{\text{vap}} = 0.10272$ bar

$Z^{\text{V}} = 0.99512$ $\qquad\qquad$ $Z^{\text{L}} = 4.414 \times 10^{-4}$

$\underline{H}^{\text{V}} = -5.5795 \times 10^{3}$ $\qquad$ $\underline{H}^{\text{L}} = -1.2994 \times 10^{4}$

$\underline{S}^{\text{V}} = 17.372$ $\qquad\qquad$ $\underline{S}^{\text{L}} = -118.74$

$T = -180^{\circ}\text{C}$ $\qquad$ $P^{\text{vap}} = 1.348$ bar

$Z^{\text{V}} = 0.96359$ $\qquad\qquad$ $Z^{\text{L}} = 4.955 \times 10^{-3}$

$\underline{H}^{\text{V}} = -5.1095 \times 10^{3}$ $\qquad$ $\underline{H}^{\text{L}} = -1.1948 \times 10^{4}$

$\underline{S}^{\text{V}} = -32.734$ $\qquad\qquad$ $\underline{S}^{\text{L}} = -106.15$

$T = -160^{\circ}\text{C}$ $\qquad$ $P^{\text{vap}} = 6.750$ bar

$Z^{\text{V}} = 0.8810$ $\qquad\qquad$ $Z^{\text{L}} = 0.02307$

$\underline{H}^{\text{V}} = -4.7953 \times 10^{3}$ $\qquad$ $\underline{H}^{\text{L}} = -1.0805 \times 10^{4}$

$\underline{S}^{\text{V}} = -42.099$ $\qquad\qquad$ $\underline{S}^{\text{L}} = -95.210$

$T = -140^{\circ}\text{C}$ $\qquad$ $P^{\text{vap}} = 20.676$ bar

$Z^{\text{V}} = 0.73096$ $\qquad\qquad$ $Z^{\text{L}} = 0.07305$

$\underline{H}^{\text{V}} = -4.7988 \times 10^{3}$ $\qquad$ $\underline{H}^{\text{L}} = -9.4328 \times 10^{3}$

$\underline{S}^{\text{V}} = -49.6785$ $\qquad\qquad$ $\underline{S}^{\text{L}} = -84.481$

$T = -130^{\circ}\text{C}$ $\qquad$ $P^{\text{vap}} = 32.310$ bar

$Z^{\text{V}} = 0.61800$ $\qquad\qquad$ $Z^{\text{L}} = 0.12528$

$\underline{H}^{\text{V}} = -5.0406 \times 10^{3}$ $\qquad$ $\underline{H}^{\text{L}} = -8.5449 \times 10^{3}$

$\underline{S}^{\text{V}} = -53.938$ $\qquad\qquad$ $\underline{S}^{\text{L}} = -78.418$

$T = -125^{\circ}\text{C}$ $\qquad$ $P^{\text{vap}} = 39.554$ bar

$Z^{\text{V}} = 0.54226$ $\qquad\qquad$ $Z^{\text{L}} = 0.16843$

$\underline{H}^{\text{V}} = -5.2985 \times 10^{3}$ $\qquad$ $\underline{H}^{\text{L}} = -7.9739 \times 10^{3}$

$\underline{S}^{\text{V}} = -56.685$ $\qquad\qquad$ $\underline{S}^{\text{L}} = -74.744$

$T = -120^{\circ}\text{C}$ $\qquad$ $P^{\text{vap}} = 47.848$ bar

$Z^{\text{V}} = 0.42788$ $\qquad\qquad$ $Z^{\text{L}} = 0.24887$

$\underline{H}^{\text{V}} = -5.8378 \times 10^{3}$ $\qquad$ $\underline{H}^{\text{L}} = -7.1281 \times 10^{3}$

$\underline{S}^{\text{V}} = -61.034$ $\qquad\qquad$ $\underline{S}^{\text{L}} = -69.459$

The Mathcad worksheet for this file is shown below.

VAPOR PRESSURE CALCULATION USING SRK EQUATION File: SRKvap.mcd

Properties of oxygen $Tc := 154.6$ $Pc := 50.46$ $om := 0.021$

Heat capacity constants

$$Cp_0 := 25.460 \quad Cp_1 := 1.519 \cdot 10^{-2} \quad Cp_2 := -0.715 \cdot 10^{-5} \quad Cp_3 := 1.311 \cdot 10^{-9}$$

Reference state and kappa calculation

$Trs := 273.15$ $Prs := 1.013$ $kap := 0.480 + 1.574 \cdot om - 0.176 \cdot om \cdot om$

S-R-K Constants: $R := 0.00008314$ $b := 0.08664 \cdot \dfrac{R \cdot Tc}{Pc}$ $ac := 0.42748 \dfrac{R^2 \cdot Tc^2}{Pc}$

Note that these are being defined as a function of temperature since we will need to interate on temperature.

$$alf(T) := 1 \cdot \left[1 + kap \cdot \left(1 - \sqrt{\frac{T}{Tc}} \right) \right]^2 \qquad a(T) := ac \cdot alf(T)$$

$$CA(T,P) := \frac{a(T) \cdot P}{(R \cdot T)^2} \qquad CB(T,P) := \frac{P \cdot b}{R \cdot T} \qquad Da(T) := \frac{d}{dT} a(T)$$

$$Z(T,P) := \begin{vmatrix} A \leftarrow CA(T,P) \\ B \leftarrow CB(T,P) \\ V \leftarrow \begin{bmatrix} -A \cdot B \\ A - B^2 - B \\ -1 \\ 1 \end{bmatrix} \\ ZZ \leftarrow polyroots(V) \\ for\ i \in 0..2 \\ \left(ZZ_i \leftarrow 0 \right)\ if\ \left(Im(ZZ_i) \neq 0 \right) \\ ZZ \leftarrow sort(ZZ) \\ ZZ_0 \leftarrow ZZ_2\ if\ \left(|ZZ_0| < 10^{-5} \right) \\ ZZ_2 \leftarrow ZZ_0\ if\ \left(|ZZ_2| < 10^{-5} \right) \\ ZZ \end{vmatrix}$$

Vector of coefficients in the SRK equation in the form
0=-A^B+(A-B^2-B)^Z-^Z^2+Z^3

Solution to the cubic

Set any imaginary roots to zero
Sort the roots

Set the value of any imaginary roots to value of the real root

Enter temperature T, and pressure P. Depending on what is specified in the Given and Find statements below, either T or P is specified and the other is an initial guess which may have to be adjusted as the other variable is changed, especially as the critical point is approached.This worksheet will probably not converge to a solution when T or P are within 3 to 5% of the critical values unless an extremely good initial guess is provided. One way to obtain a good initial is to start well below the critical region and step towards it using the result of previous calculations.

$T := -130\ C$

$T := 273.15 + T\ K$

$P := 30$

Fugacity expressions [actually ln(f/P)] for the liquid fl and vapor fv

$$fl(T,P) := \left(Z(T,P)_0 - 1\right) - \ln\left(Z(T,P)_0 - CB(T,P)\right) - \frac{CA(T,P)}{CB(T,P)} \cdot \ln\left(\frac{Z(T,P)_0 + CB(T,P)}{Z(T,P)_0}\right)$$

$$fv(T,P) := \left(Z(T,P)_2 - 1\right) - \ln\left(Z(T,P)_2 - CB(T,P)\right) - \frac{CA(T,P)}{CB(T,P)} \cdot \ln\left(\frac{Z(T,P)_2 + CB(T,P)}{Z(T,P)_2}\right)$$

GIVEN $\quad$ $fl(T,P) - fv(T,P)=0$	**Equate log of fugacity coefficients**
$P := find(P)$ $\quad$ $P = 32.31009$	**Solve equality of fugacities**

	Fugacity			Fugacity coefficient	
$fugl := P \cdot \exp(fl(T,P))$	$fugl = 23.6716$		$fl(T,P) = -0.3111$	$phil := \dfrac{fugl}{P}$	$phil = 0.73264$
$fugv := P \cdot \exp(fv(T,P))$	$fugv = 23.6716$		$fv(T,P) = -0.3111$	$phiv := \dfrac{fugv}{P}$	$phiv = 0.73264$

Residual entropy for liquid (DELSL) and vapor (DELSV) phases

$$DELSL := \left\{R \cdot \ln\left(Z(T,P)_0 - CB(T,P)\right) + \frac{Da(T)}{b} \cdot \ln\left(\frac{Z(T,P)_0 + CB(T,P)}{Z(T,P)_0}\right)\right\} \cdot 10^5$$

$$DELSV := \left\{R \cdot \ln\left(Z(T,P)_2 - CB(T,P)\right) + \frac{Da(T)}{b} \cdot \ln\left(\frac{Z(T,P)_2 + CB(T,P)}{Z(T,P)_2}\right)\right\} \cdot 10^5$$

Residual enthalpy for liquid (DELHL) and vapor (DELHV) phases

$$DELHL := \left[R \cdot T \cdot \left(Z(T,P)_0 - 1\right) + \frac{T \cdot Da(T) - a(T)}{b} \cdot \ln\left(\frac{Z(T,P)_0 + CB(T,P)}{Z(T,P)_0}\right)\right] \cdot 10^5$$

$$DELHV := \left[R \cdot T \cdot \left(Z(T,P)_2 - 1\right) + \frac{T \cdot Da(T) - a(T)}{b} \cdot \ln\left(\frac{Z(T,P)_2 + CB(T,P)}{Z(T,P)_2}\right)\right] \cdot 10^5$$

Ideal gas properties changes relative to the reference state

$$DELHIG := Cp_0 \cdot (T - Trs) + \frac{Cp_1 \cdot \left(T^2 - Trs^2\right)}{2} + \frac{Cp_2 \cdot \left(T^3 - Trs^3\right)}{3} + \frac{Cp_3 \cdot \left(T^4 - Trs^4\right)}{4}$$

$$DELSIG := Cp_0 \cdot \ln\left(\frac{T}{Trs}\right) + Cp_1 \cdot (T - Trs) + \frac{Cp_2 \cdot \left(T^2 - Trs^2\right)}{2} + \frac{Cp_3 \cdot \left(T^3 - Trs^3\right)}{3} - R \cdot 10^5 \cdot \ln\left(\frac{P}{Prs}\right)$$

Total entropy and enthalpy relative to ideal gas reference state

SL := DELSIG + DELSL   SV := DELSIG + DELSV   HL := DELHIG + DELHL   HV := DELHIG + DELHV

SUMMARY OF RESULTS

T = 143.15   K   **Vapor pressure, bar**   P = 32.31009

	LIQUID	**VAPOR**
Compressibility	$Z(T,P)_0 = 0.12528$	$Z(T,P)_2 = 0.618$
Enthalpy, J/mol	$HL = -8.5449 \cdot 10^3$	$HV = -5.04062 \cdot 10^3$
Entropy, J/mol K	$SL = -78.41775$	$SV = -53.93795$
Fugacity coefficient	$phil = 0.73264$	$phiv = 0.73264$
Fugacity, bar	$fugl = 23.6716$	$fugv = 23.6716$

5.52   (also available as a Mathcad worksheet)

5.52   Pure component properties calculation using the SRK equation of state

Read in properties for oxygen $Tc := 154.6$ $Pc := 50.46$ $om := 0.021$

Heat capacity constants

$$Cp_0 := 25.460 \quad Cp_1 := 1.519 \cdot 10^{-2} \quad Cp_2 := -0.715 \cdot 10^{-5} \quad Cp_3 := 1.311 \cdot 10^{-9}$$

Reference state and kappa calculation

$Trs := 298.15$ $Prs := 1.0$ $kap := 0.480 + 1.574 \cdot om - 0.176 \cdot om \cdot om$

S-R-K Constants: $R := 0.00008314$ $b := 0.08664 \cdot \dfrac{R \cdot Tc}{Pc}$ $ac := 0.42748 \cdot \dfrac{R^2 \cdot Tc^2}{Pc}$

Note that these are being defined as a
function of temperature for convenience.

$$alf(T) := 1 \cdot \left[1 + kap \cdot \left(1 - \sqrt{\frac{T}{Tc}}\right)\right]^2 \qquad a(T) := ac \cdot alf(T)$$

$$CA(T,P) := \frac{a(T) \cdot P}{(R \cdot T)^2} \qquad CB(T,P) := \frac{P \cdot b}{R \cdot T} \qquad Da(T) := \frac{d}{dT} a(T)$$

$$CA(T, P) := \frac{a(T) \cdot P}{(R \cdot T)^2} \qquad CB(T, P) := \frac{P \cdot b}{R \cdot T} \qquad Da(T) := \frac{d}{dT} a(T)$$

$$Z(T, P) := \begin{vmatrix} A \leftarrow CA(T, P) \\ B \leftarrow CB(T, P) \\ V \leftarrow \begin{bmatrix} -A \cdot B \\ A - B^2 - B \\ -1 \\ 1 \end{bmatrix} \\ ZZ \leftarrow polyroots(V) \\ \text{for } i \in 0..2 \\ \quad (ZZ_i \leftarrow 0) \text{ if } (Im(ZZ_i) \neq 0) \\ ZZ \leftarrow sort(ZZ) \\ ZZ_0 \leftarrow ZZ_2 \text{ if } (|ZZ_0| < 10^{-5}) \\ ZZ_2 \leftarrow ZZ_0 \text{ if } (|ZZ_2| < 10^{-5}) \\ ZZ \end{vmatrix}$$

Vector of coefficients in the SRK equation in the form
0=-A*B+(A-B^2-B)*Z-*Z^2+Z^3

Solution to the cubic

Set any imaginary roots to zero
Sort the roots

Set the value of any imaginary roots to value of the real root

Enter temperature T, and pressure P.

$$T := -125 \ \text{C} \qquad T := 273.15 + T \ \text{K} \qquad P := 100$$

Fugacity expressions [actually ln(f/P)] for the liquid fl and vapor fv

$$fl(T, P) := (Z(T, P)_0 - 1) - \ln(Z(T, P)_0 - CB(T, P)) - \frac{CA(T, P)}{CB(T, P)} \cdot \ln\left(\frac{Z(T, P)_0 + CB(T, P)}{Z(T, P)_0}\right)$$

$$fv(T, P) := (Z(T, P)_2 - 1) - \ln(Z(T, P)_2 - CB(T, P)) - \frac{CA(T, P)}{CB(T, P)} \cdot \ln\left(\frac{Z(T, P)_2 + CB(T, P)}{Z(T, P)_2}\right)$$

Fugacity		**Fugacity coefficient**

$$fugl := P \cdot \exp(fl(T, P)) \qquad fugl = 34.64672 \qquad fl(T, P) = -1.05997 \quad phil := \frac{fugl}{P} \qquad phil = 0.34647$$

$$fugv := P \cdot \exp(fv(T, P)) \qquad fugv = 34.64672 \qquad fv(T, P) = -1.05997 \quad phiv := \frac{fugv}{P} \qquad phiv = 0.34647$$

Residual entropy for liquid (DELSL) and vapor (DELSV) phases

$$\text{DELSL} := \left(R \cdot \ln\left(Z(T,P)_0 - CB(T,P) \right) + \frac{Da(T)}{b} \cdot \ln\left(\frac{Z(T,P)_0 + CB(T,P)}{Z(T,P)_0} \right) \right) \cdot 10^5$$

$$\text{DELSV} := \left(R \cdot \ln\left(Z(T,P)_2 - CB(T,P) \right) + \frac{Da(T)}{b} \cdot \ln\left(\frac{Z(T,P)_2 + CB(T,P)}{Z(T,P)_2} \right) \right) \cdot 10^5$$

Residual enthalpy for liquid (DELHL) and vapor (DELHV) phases

$$\text{DELHL} := \left[R \cdot T \cdot \left(Z(T,P)_0 - 1 \right) + \frac{T \cdot Da(T) - a(T)}{b} \cdot \ln\left(\frac{Z(T,P)_0 + CB(T,P)}{Z(T,P)_0} \right) \right] \cdot 10^5$$

$$\text{DELHV} := \left[R \cdot T \cdot \left(Z(T,P)_2 - 1 \right) + \frac{T \cdot Da(T) - a(T)}{b} \cdot \ln\left(\frac{Z(T,P)_2 + CB(T,P)}{Z(T,P)_2} \right) \right] \cdot 10^5$$

Ideal gas properties changes relative to the reference state

$$\text{DELHIG} := Cp_0 \cdot (T - Trs) + \frac{Cp_1 \cdot \left(T^2 - Trs^2 \right)}{2} + \frac{Cp_2 \cdot \left(T^3 - Trs^3 \right)}{3} + \frac{Cp_3 \cdot \left(T^4 - Trs^4 \right)}{4}$$

$$\text{DELSIG} := Cp_0 \cdot \ln\left(\frac{T}{Trs} \right) + Cp_1 \cdot (T - Trs) + \frac{Cp_2 \cdot \left(T^2 - Trs^2 \right)}{2} + \frac{Cp_3 \cdot \left(T^3 - Trs^3 \right)}{3} - R \cdot 10^5 \cdot \ln\left(\frac{P}{Prs} \right)$$

Total entropy and enthalpy relative to ideal gas reference state

$$SL := \text{DELSIG} + \text{DELSL} \qquad SV := \text{DELSIG} + \text{DELSV} \qquad HL := \text{DELHIG} + \text{DELHL} \qquad HV := \text{DELHIG} + \text{DELHV}$$

$$V_0 := Z(T,P)_0 \cdot 8.314 \cdot 10^{-2} \cdot \frac{T}{P} \qquad V_0 = 0.04081 \qquad V_2 := Z(T,P)_2 \cdot 8.314 \cdot 10^{-2} \cdot \frac{T}{P}$$

$$V_2 = 0.04081$$

SUMMARY OF RESULTS

$T = 148.15$ **K**   **Vapor pressure, bar** $P = 100$

                            LIQUID   **VAPOR**

	LIQUID	**VAPOR**
Compressibility	$Z(T, P)_0 = 0.3313$	$Z(T, P)_2 = 0.3313$
Volume, m^3/kmol	$V_0 = 0.04081$	$V_2 = 0.04081$
Enthalpy, J/mol	$HL = -9.29109 \cdot 10^3$	$HV = -9.29109 \cdot 10^3$
Entropy, J/mol K	$SL = -83.19194$	$SV = -83.19194$
Fugacity coefficient	$phil = 0.34647$	$phiv = 0.34647$
Fugacity, bar	$fugl = 34.64672$	$fugv = 34.64672$

Some representative results are shown below.

T (C)	-125	-150	-175	-200
P=1 bar				
Z	0.9923	0.9872	0.9766	0.9505
V	12.2227	10.1072	7.9693	5.7804
H	-4301.41	-4994.48	-5684.02	-6375.9
S	-19.97	-25.1	-31.35	-35.49
P=10 bar				
Z	0.9193	0.8565	0.03572	0.04292
V	1.1323	0.877	0.02914	0.0261
H	-4561.07	-5357.77	-12395.6	-13706.2
S	-40.28	-46.18	-106.11	-121.5
P=50 bar				
Z	0.1946	0.1647	0.17634	0.21349
V	0.04795	0.03373	0.02878	0.02597
H	-8938.78	-10919.2	-12338.7	-13628.9
S	-79.34	-93.79	-106.71	-121.86
P=100 bar				
Z	0.3313	0.318	0.34788	0.42446
V	0.04081	0.03256	0.02839	0.02581
H	-9291.09	-10896.8	-12261.8	-13530.9
S	-83.19	-95.02	-107.39	-122.29

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5.53   (also available as a Mathcad worksheet)

5.53   Pure component properties calculation using the SRK equation of state

Read in properties for Water $Tc := 647.3$ $Pc := 220.48$ $om := 0.344$

Heat capacity constants

$$Cp_0 := 32.218 \quad Cp_1 := 0.192 \cdot 10^{-2} \quad Cp_2 := 1.055 \cdot 10^{-5} \quad Cp_3 := -3.593 \cdot 10^{-9}$$

Reference state and kappa calculation

$\text{Trs} := 373.15 \qquad \text{Prs} := 1.013 \qquad \text{kap} := 0.480 + 1.574 \cdot \text{om} - 0.176 \cdot \text{om} \cdot \text{om}$

S-R-K Constants: $\qquad\qquad R := 0.00008314 \qquad\qquad b := 0.08664 \cdot \dfrac{R \cdot Tc}{Pc} \qquad ac := 0.42748 \cdot \dfrac{R^2 \cdot Tc^2}{Pc}$

Note that these are being defined as a function of temperature for convenience.

$\text{alf}(T) := 1 \cdot \left[1 + \text{kap} \cdot \left(1 - \sqrt{\dfrac{T}{Tc}} \right) \right]^2 \qquad a(T) := ac \cdot \text{alf}(T)$

$CA(T, P) := \dfrac{a(T) \cdot P}{(R \cdot T)^2} \qquad CB(T, P) := \dfrac{P \cdot b}{R \cdot T} \qquad Da(T) := \dfrac{d}{dT} a(T)$

$Z(T, P) :=$
$\begin{vmatrix} A \leftarrow CA(T, P) \\ B \leftarrow CB(T, P) \\ V \leftarrow \begin{bmatrix} -A \cdot B \\ A - B^2 - B \\ -1 \\ 1 \end{bmatrix} \\ ZZ \leftarrow \text{polyroots}(V) \\ \text{for } i \in 0..2 \\ \quad \left(ZZ_i \leftarrow 0 \right) \text{ if } \left(\text{Im}\left(ZZ_i \right) \neq 0 \right) \\ ZZ \leftarrow \text{sort}(ZZ) \\ ZZ_0 \leftarrow ZZ_2 \text{ if } \left(\left| ZZ_0 \right| < 10^{-5} \right) \\ ZZ_2 \leftarrow ZZ_0 \text{ if } \left(\left| ZZ_2 \right| < 10^{-5} \right) \\ ZZ \end{vmatrix}$

Vector of coefficients in the SRK equation in the form
0=-A*B+(A-B^2-B)*Z-*Z^2+Z^3

Solution to the cubic

Set any imaginary roots to zero
Sort the roots

Set the value of any imaginary roots to value of the real root

Enter temperature T, and pressure P.

$T := 50 \quad \textbf{C} \qquad\qquad T := 273.15 + T \ \textbf{K} \qquad\qquad P := 0.15$

Fugacity expressions [actually ln(f/P)] for the liquid fl and vapor fv

$\text{fl}(T, P) := \left(Z(T, P)_0 - 1 \right) - \ln\left(Z(T, P)_0 - CB(T, P) \right) - \dfrac{CA(T, P)}{CB(T, P)} \cdot \ln\left(\dfrac{Z(T, P)_0 + CB(T, P)}{Z(T, P)_0} \right)$

$\text{fv}(T, P) := \left(Z(T, P)_2 - 1 \right) - \ln\left(Z(T, P)_2 - CB(T, P) \right) - \dfrac{CA(T, P)}{CB(T, P)} \cdot \ln\left(\dfrac{Z(T, P)_2 + CB(T, P)}{Z(T, P)_2} \right)$

Fugacity   Fugacity coefficient

$\text{fugl} := P \cdot \exp(\text{fl}(T, P))$ $\text{fugl} = 0.09983$ $\text{fl}(T, P) = {}^{-}0.40721$ $\text{phil} := \dfrac{\text{fugl}}{P}$ $\text{phil} = 0.6655$

$\text{fugv} := P \cdot \exp(\text{fv}(T, P))$ $\text{fugv} = 0.14972$ $\text{fv}(T, P) = {}^{-}1.83629 \bullet 10$ $\text{phiv} := \dfrac{\text{fugv}}{P}$ $\text{phiv} = 0.99817$

Residual entropy for liquid (DELSL) and vapor (DELSV) phases

$$\text{DELSL} := \left\{ R \cdot \ln\left(Z(T, P)_0 - \text{CB}(T, P)\right) + \frac{\text{Da}(T)}{b} \cdot \ln\left(\frac{Z(T, P)_0 + \text{CB}(T, P)}{Z(T, P)_0}\right) \right\} \cdot 10^5$$

$$\text{DELSV} := \left\{ R \cdot \ln\left(Z(T, P)_2 - \text{CB}(T, P)\right) + \frac{\text{Da}(T)}{b} \cdot \ln\left(\frac{Z(T, P)_2 + \text{CB}(T, P)}{Z(T, P)_2}\right) \right\} \cdot 10^5$$

Residual enthalpy for liquid (DELHL) and vapor (DELHV) phases

$$\text{DELHL} := \left[R \cdot T \cdot \left(Z(T, P)_0 - 1\right) + \frac{T \cdot \text{Da}(T) - a(T)}{b} \cdot \ln\left(\frac{Z(T, P)_0 + \text{CB}(T, P)}{Z(T, P)_0}\right) \right] \cdot 10^5$$

$$\text{DELHV} := \left[R \cdot T \cdot \left(Z(T, P)_2 - 1\right) + \frac{T \cdot \text{Da}(T) - a(T)}{b} \cdot \ln\left(\frac{Z(T, P)_2 + \text{CB}(T, P)}{Z(T, P)_2}\right) \right] \cdot 10^5$$

Ideal gas properties changes relative to the reference state

$$\text{DELHIG} := \text{Cp}_0 \cdot (T - \text{Trs}) + \frac{\text{Cp}_1 \cdot \left(T^2 - \text{Trs}^2\right)}{2} + \frac{\text{Cp}_2 \cdot \left(T^3 - \text{Trs}^3\right)}{3} + \frac{\text{Cp}_3 \cdot \left(T^4 - \text{Trs}^4\right)}{4}$$

$$\text{DELSIG} := \text{Cp}_0 \cdot \ln\left(\frac{T}{\text{Trs}}\right) + \text{Cp}_1 \cdot (T - \text{Trs}) + \frac{\text{Cp}_2 \cdot \left(T^2 - \text{Trs}^2\right)}{2} + \frac{\text{Cp}_3 \cdot \left(T^3 - \text{Trs}^3\right)}{3} - R \cdot 10^5 \cdot \ln\left(\frac{P}{\text{Prs}}\right)$$

Total entropy and enthalpy relative to ideal gas reference state

$\text{SL} := \text{DELSIG} + \text{DELSL}$ $\text{SV} := \text{DELSIG} + \text{DELSV}$ $\text{HL} := \text{DELHIG} + \text{DELHL}$ $\text{HV} := \text{DELHIG} + \text{DELHV}$

SUMMARY OF RESULTS

$T = 323.15$ **K**   **Vapor pressure, bar** $P = 0.15$

	LIQUID	**VAPOR**
Compressibility	$Z(T, P)_0 = 1.35706 \bullet 10^{-4}$	$Z(T, P)_2 = 0.99816$
Enthalpy, J/mol	$\text{HL} = {}^{-}4.74037 \bullet 10^4$	$\text{HV} = {}^{-}1.71382 \bullet 10^3$
Entropy, J/mol K	$\text{SL} = {}^{-}127.05678$	$\text{SV} = 10.96203$
Fugacity coefficient	$\text{phil} = 0.6655$	$\text{phiv} = 0.99817$

5.54 (also available as a Mathcad worksheet)

5.54 ISENTHALPIC PENG-ROBINSON EQUATION OF STATE CALCULATION

$Tc := 154.6$ $Pc := 50.46$ $om := 0.021$ $kap := 0.37464 + 1.54226 \cdot om - 0.26992 \cdot om \cdot om$

$Cp_0 := 25.46$ $Cp_1 := 1.591 \cdot 10^{-2}$ $Cp_2 := -0.7151 \cdot 10^{-5}$ $Cp_3 := 1.311 \cdot 10^{-9}$

Peng-Robinson Constants: $R := 0.00008314$ $b := 0.07780 \cdot \dfrac{R \cdot Tc}{Pc}$ $ac := 0.45724 \cdot \dfrac{R^2 \cdot Tc^2}{Pc}$

Input initial temperature and pressure of calculation $Ti := 120.$ **K,** $Pi := 30$ **bar**

Input final pressure $Pf := 3.0$ **bar**

Initial state calculations $T := Ti$ $P := Pi$

$alf(T) := 1 \cdot \left[1 + kap \cdot \left(1 - \sqrt{\dfrac{T}{Tc}}\right)\right]^2$ $a(T) := ac \cdot alf(T)$ $CA(T,P) := \dfrac{a(T) \cdot P}{(R \cdot T)^2}$ $CB(T,P) := \dfrac{P \cdot b}{R \cdot T}$

$$Da(T) := \frac{d}{dT} a(T)$$

$Z(T,P) :=$ $\Big|$ $A \leftarrow CA(T,P)$

$B \leftarrow CB(T,P)$

$V \leftarrow \begin{bmatrix} -\left(A \cdot B - B^2 - B^3\right) \\ A - 3 \cdot B^2 - 2 \cdot B \\ -(1 - B) \\ 1 \end{bmatrix}$ **Vector of coefficients in the PR equation**
in the form
0=-(A*B-B^2-B^3)+(A-3*B^2-2*B)*Z-(1-B)*Z^2+Z^3

$ZZ \leftarrow polyroots(V)$ **Solution to the cubic**

for $i \in 0..2$

$\left(ZZ_i \leftarrow 0\right)$ if $\left(Im\left(ZZ_i\right) \neq 0\right)$ **Set any imaginary roots to zero**

$ZZ \leftarrow sort(ZZ)$ **Sort the roots**

$ZZ_0 \leftarrow ZZ_2$ if $\left(\left| ZZ_0 \right| < 10^{-5}\right)$ **Set the value of any imaginary roots**
to value of the real root

$ZZ_2 \leftarrow ZZ_0$ if $\left(\left| ZZ_2 \right| < 10^{-5}\right)$

ZZ

Calculate inital properties $Zf(T,P) := Z(T,P)$

Calculate initial molar volume
and enthalpy and entropy
departure $VL := \dfrac{Z(T,P)_0 \cdot R \cdot T}{P} \cdot 10^3$ $Z(T,P) = \begin{bmatrix} 0.0888 \\ 0 \\ 0.0888 \end{bmatrix}$

$$\text{DELHin} := \left[R \cdot T \cdot \left(Z(T,P)_0 - 1 \right) + \frac{T \cdot Da(T) - a(T)}{2 \cdot \sqrt{2} \cdot b} \cdot \ln\left[\frac{Z(T,P)_0 + \left(1 + \sqrt{2}\right) \cdot CB(T,P)}{Z(T,P)_0 + \left(1 - \sqrt{2}\right) \cdot CB(T,P)} \right] \right] \cdot 10^5$$

$$\text{DELSin} := \left[R \cdot \ln\left(Z(T,P)_0 - CB(T,P) \right) + \frac{Da(T)}{2 \cdot \sqrt{2} \cdot b} \cdot \ln\left[\frac{Z(T,P)_0 + \left(1 + \sqrt{2}\right) \cdot CB(T,P)}{Z(T,P)_0 + \left(1 - \sqrt{2}\right) \cdot CB(T,P)} \right] \right] \cdot 10^5$$

$\text{DELHin} = -5.9875 \cdot 10^3$ $\qquad\qquad$ $\text{DELSin} = -40.1647$

Guess for final state $\qquad\qquad$ $T := 0.8 \cdot Ti$ $\qquad$ $P := Pf$

Fugacity expressions [actually ln(f/P)] for the liquid fl and vapor fv

$$fl(T,P) := \left(Z(T,P)_0 - 1 \right) - \ln\left(Z(T,P)_0 - CB(T,P) \right) - \frac{CA(T,P)}{2 \cdot \sqrt{2} \cdot CB(T,P)} \cdot \ln\left[\frac{Z(T,P)_0 + \left(1 + \sqrt{2}\right) \cdot CB(T,P)}{Z(T,P)_0 + \left(1 - \sqrt{2}\right) \cdot CB(T,P)} \right]$$

$$fv(T,P) := \left(Z(T,P)_2 - 1 \right) - \ln\left(Z(T,P)_2 - CB(T,P) \right) - \frac{CA(T,P)}{2 \cdot \sqrt{2} \cdot CB(T,P)} \cdot \ln\left[\frac{Z(T,P)_2 + \left(1 + \sqrt{2}\right) \cdot CB(T,P)}{Z(T,P)_2 + \left(1 - \sqrt{2}\right) \cdot CB(T,P)} \right]$$

Given $\qquad$ $fl(T,P) - fv(T,P) = 0$ $\qquad$ $T := find(T)$ $\qquad\qquad$ $T = 101.906$

Residual entropy for liquid (DELSL) and vapor (DELSV) phases

$$\text{DELSL}(T,P) := \left[R \cdot \ln\left(Z(T,P)_0 - CB(T,P) \right) + \frac{Da(T)}{2 \cdot \sqrt{2} \cdot b} \cdot \ln\left[\frac{Z(T,P)_0 + \left(1 + \sqrt{2}\right) \cdot CB(T,P)}{Z(T,P)_0 + \left(1 - \sqrt{2}\right) \cdot CB(T,P)} \right] \right] \cdot 10^5$$

$$\text{DELSV}(T,P) := \left[R \cdot \ln\left(Z(T,P)_2 - CB(T,P) \right) + \frac{Da(T)}{2 \cdot \sqrt{2} \cdot b} \cdot \ln\left[\frac{Z(T,P)_2 + \left(1 + \sqrt{2}\right) \cdot CB(T,P)}{Z(T,P)_2 + \left(1 - \sqrt{2}\right) \cdot CB(T,P)} \right] \right] \cdot 10^5$$

Residual enthalpy for liquid (DELHL) and vapor (DELHV) phases

$$\text{DELHL}(T,P) := \left[R \cdot T \cdot \left(Z(T,P)_0 - 1 \right) + \frac{T \cdot Da(T) - a(T)}{2 \cdot \sqrt{2} \cdot b} \cdot \ln\left[\frac{Z(T,P)_0 + \left(1 + \sqrt{2}\right) \cdot CB(T,P)}{Z(T,P)_0 + \left(1 - \sqrt{2}\right) \cdot CB(T,P)} \right] \right] \cdot 10^5$$

$$\text{DELHV}(T,P) := \left[R \cdot T \cdot \left(Z(T,P)_2 - 1 \right) + \frac{T \cdot Da(T) - a(T)}{2 \cdot \sqrt{2} \cdot b} \cdot \ln\left[\frac{Z(T,P)_2 + \left(1 + \sqrt{2}\right) \cdot CB(T,P)}{Z(T,P)_2 + \left(1 - \sqrt{2}\right) \cdot CB(T,P)} \right] \right] \cdot 10^5$$

Ideal gas properties changes relative to the initial state

$$\text{DELHIG}(T, P) := Cp_0 \cdot (T - Ti) + \frac{Cp_1 \cdot \left(T^2 - Ti^2\right)}{2} + \frac{Cp_2 \cdot \left(T^3 - Ti^3\right)}{3} + \frac{Cp_3 \cdot \left(T^4 - Ti^4\right)}{4}$$

$$\text{DELSIG}(T, P) := Cp_0 \cdot \ln\left(\frac{T}{Ti}\right) + Cp_1 \cdot (T - Ti) + \frac{Cp_2 \cdot \left(T^2 - Ti^2\right)}{2} + \frac{Cp_3 \cdot \left(T^3 - Ti^3\right)}{3} - R \cdot 10^5 \cdot \ln\left(\frac{P}{Pi}\right)$$

Find vapor-liquid split $\qquad x := 0.5$

Given

$$x \cdot \text{DELHV}(T, P) + (1 - x) \cdot \text{DELHL}(T, P) + \text{DELHIG}(T, P) = \text{DELHin}$$

$\qquad x := \text{find}(x)$ $\qquad\qquad x = 0.1618$ $\qquad$ **Fraction vapor**

$\text{HV} := \text{DELHV}(T, P) + \text{DELHIG}(T, P)$ $\qquad \text{SV} := \text{DELSV}(T, P) + \text{DELSIG}(T, P)$

$\text{HL} := \text{DELHL}(T, P) + \text{DELHIG}(T, P)$ $\qquad \text{SL} := \text{DELSL}(T, P) + \text{DELSIG}(T, P)$

$\delta H := x \cdot \text{HV} + (1 - x) \cdot \text{HL} - \text{DELHin}$ $\qquad \delta S := x \cdot \text{SV} + (1 - x) \cdot \text{SL} - \text{DELSin}$

SUMMARY OF RESULTS

	FEED	**LIQUID**	**VAPOR**
Temperature, K	Ti = 120	T = 101.906	T = 101.906
Pressure, bar	Pi = 30	P = 3	P = 3
Vapor-liquid split		x = 0.1618	
Compressibility	$Z(Ti, Pi)_0 = 0.0888$	$Z(T, P)_0 = 9.3464 \cdot 10^{-3}$	$Z(T, P)_2 = 0.9309$
Enthalpy, J/mol (relative to feed)	0	$HL = {}^{-}7.0203 \cdot 10^3$	$HV = {}^{-}635.2466$
Entropy, J/mol K (relative to feed)	0	$SL = {}^{-}48.8038$	$SV = 13.8527$
Enthalpy change J/mol		$\delta H = 0$	
Entropy change J/mol K		$\delta S = 1.4957$	

5.55 (also available as a Mathcad worksheet)

ISENTROPIC PENG-ROBINSON EQUATION OF STATE CALCULATION

$Tc := 154.6$ $Pc := 50.46$ $om := 0.021$ $kap := 0.37464 + 1.54226 \cdot om - 0.26992 \cdot om \cdot om$

$Cp_0 := 25.46$ $Cp_1 := 1.591 \cdot 10^{-2}$ $Cp_2 := -0.7151 \cdot 10^{-5}$ $Cp_3 := 1.311 \cdot 10^{-9}$

Peng-Robinson Constants: $R := 0.00008314$ $b := 0.07780 \cdot \dfrac{R \cdot Tc}{Pc}$ $ac := 0.45724 \cdot \dfrac{R^2 \cdot Tc^2}{Pc}$

Input initial temperature and pressure of calculation $Ti := 120.$ **K,** $Pi := 30$ **bar**

Input final pressure $Pf := 3.0$ **bar**

Initial state calculations $T := Ti$ $P := Pi$

$$alf(T) := 1 \cdot \left[1 + kap \cdot \left(1 - \sqrt{\dfrac{T}{Tc}}\right)\right]^2$$ $a(T) := ac \cdot alf(T)$ $CA(T,P) := \dfrac{a(T) \cdot P}{(R \cdot T)^2}$ $CB(T,P) := \dfrac{P \cdot b}{R \cdot T}$

$$Da(T) := \dfrac{d}{dT} a(T)$$

$$Z(T,P) := \begin{vmatrix} A \leftarrow CA(T,P) \\ B \leftarrow CB(T,P) \\ V \leftarrow \begin{bmatrix} -\left(A \cdot B - B^2 - B^3\right) \\ A - 3 \cdot B^2 - 2 \cdot B \\ -(1 - B) \\ 1 \end{bmatrix} \\ ZZ \leftarrow polyroots(V) \\ \text{for } i \in 0..2 \\ \quad \left(ZZ_i \leftarrow 0\right) \text{ if } \left(Im(ZZ_i) \neq 0\right) \\ ZZ \leftarrow sort(ZZ) \\ ZZ_0 \leftarrow ZZ_2 \text{ if } \left(\left| ZZ_0 \right| < 10^{-5}\right) \\ ZZ_2 \leftarrow ZZ_0 \text{ if } \left(\left| ZZ_2 \right| < 10^{-5}\right) \\ ZZ \end{vmatrix}$$

Vector of coefficients in the PR equation in the form
0=-(A*B-B^2-B^3)+(A-3*B^2-2*B)*Z-(1-B)*Z^2+Z^3

Solution to the cubic

Set any imaginary roots to zero
Sort the roots

Set the value of any imaginary roots to value of the real root

Calculate inital properties

$Zf(T,P) := Z(T,P)$

Calculate initial molar volume and enthalpy and entropy departure

$VL := \dfrac{Z(T,P)_0 \cdot R \cdot T}{P} \cdot 10^3$ $Z(T,P) = \begin{bmatrix} 0.0888 \\ 0 \\ 0.0888 \end{bmatrix}$

$$\text{DELHin} := \left[R \cdot T \cdot \left(Z(T,P)_0 - 1 \right) + \frac{T \cdot Da(T) - a(T)}{2 \cdot \sqrt{2} \cdot b} \cdot \ln\left[\frac{Z(T,P)_0 + \left(1 + \sqrt{2}\right) \cdot CB(T,P)}{Z(T,P)_0 + \left(1 - \sqrt{2}\right) \cdot CB(T,P)} \right] \right] \cdot 10^5$$

$$\text{DELSin} := \left[R \cdot \ln\left(Z(T,P)_0 - CB(T,P) \right) + \frac{Da(T)}{2 \cdot \sqrt{2} \cdot b} \cdot \ln\left[\frac{Z(T,P)_0 + \left(1 + \sqrt{2}\right) \cdot CB(T,P)}{Z(T,P)_0 + \left(1 - \sqrt{2}\right) \cdot CB(T,P)} \right] \right] \cdot 10^5$$

$$\text{DELHin} = -5.9875 \cdot 10^3 \qquad\qquad \text{DELSin} = -40.1647$$

Guess for final state $T := 0.8 \cdot Ti$ $P := Pf$

Fugacity expressions [actually ln(f/P)] for the liquid fl and vapor fv

$$fl(T,P) := \left(Z(T,P)_0 - 1 \right) - \ln\left(Z(T,P)_0 - CB(T,P) \right) - \frac{CA(T,P)}{2 \cdot \sqrt{2} \cdot CB(T,P)} \cdot \ln\left[\frac{Z(T,P)_0 + \left(1 + \sqrt{2}\right) \cdot CB(T,P)}{Z(T,P)_0 + \left(1 - \sqrt{2}\right) \cdot CB(T,P)} \right]$$

$$fv(T,P) := \left(Z(T,P)_2 - 1 \right) - \ln\left(Z(T,P)_2 - CB(T,P) \right) - \frac{CA(T,P)}{2 \cdot \sqrt{2} \cdot CB(T,P)} \cdot \ln\left[\frac{Z(T,P)_2 + \left(1 + \sqrt{2}\right) \cdot CB(T,P)}{Z(T,P)_2 + \left(1 - \sqrt{2}\right) \cdot CB(T,P)} \right]$$

Given $fl(T,P) - fv(T,P) = 0$ $T := find(T)$ $T = 101.906$

Residual entropy for liquid (DELSL) and vapor (DELSV) phases

$$\text{DELSL}(T,P) := \left[R \cdot \ln\left(Z(T,P)_0 - CB(T,P) \right) + \frac{Da(T)}{2 \cdot \sqrt{2} \cdot b} \cdot \ln\left[\frac{Z(T,P)_0 + \left(1 + \sqrt{2}\right) \cdot CB(T,P)}{Z(T,P)_0 + \left(1 - \sqrt{2}\right) \cdot CB(T,P)} \right] \right] \cdot 10^5$$

$$\text{DELSV}(T,P) := \left[R \cdot \ln\left(Z(T,P)_2 - CB(T,P) \right) + \frac{Da(T)}{2 \cdot \sqrt{2} \cdot b} \cdot \ln\left[\frac{Z(T,P)_2 + \left(1 + \sqrt{2}\right) \cdot CB(T,P)}{Z(T,P)_2 + \left(1 - \sqrt{2}\right) \cdot CB(T,P)} \right] \right] \cdot 10^5$$

Residual enthalpy for liquid (DELHL) and vapor (DELHV) phases

$$\text{DELHL}(T,P) := \left[R \cdot T \cdot \left(Z(T,P)_0 - 1 \right) + \frac{T \cdot Da(T) - a(T)}{2 \cdot \sqrt{2} \cdot b} \cdot \ln\left[\frac{Z(T,P)_0 + \left(1 + \sqrt{2}\right) \cdot CB(T,P)}{Z(T,P)_0 + \left(1 - \sqrt{2}\right) \cdot CB(T,P)} \right] \right] \cdot 10^5$$

$$\text{DELHV}(T,P) := \left[R \cdot T \cdot \left(Z(T,P)_2 - 1 \right) + \frac{T \cdot Da(T) - a(T)}{2 \cdot \sqrt{2} \cdot b} \cdot \ln\left[\frac{Z(T,P)_2 + \left(1 + \sqrt{2}\right) \cdot CB(T,P)}{Z(T,P)_2 + \left(1 - \sqrt{2}\right) \cdot CB(T,P)} \right] \right] \cdot 10^5$$

Ideal gas properties changes relative to the initial state

$$\text{DELHIG}(T, P) := Cp_0 \cdot (T - Ti) + \frac{Cp_1 \cdot \left(T^2 - Ti^2\right)}{2} + \frac{Cp_2 \cdot \left(T^3 - Ti^3\right)}{3} + \frac{Cp_3 \cdot \left(T^4 - Ti^4\right)}{4}$$

$$\text{DELSIG}(T, P) := Cp_0 \cdot \ln\left(\frac{T}{Ti}\right) + Cp_1 \cdot (T - Ti) + \frac{Cp_2 \cdot \left(T^2 - Ti^2\right)}{2} + \frac{Cp_3 \cdot \left(T^3 - Ti^3\right)}{3} - R \cdot 10^5 \cdot \ln\left(\frac{P}{Pi}\right)$$

Find vapor-liquid split $x := 0.5$

Given

$$x \cdot \text{DELSV}(T, P) + (1 - x) \cdot \text{DELSL}(T, P) + \text{DELSIG}(T, P) = \text{DELSin}$$

$x := \text{find}(x)$ $x = 0.1379$ **Fraction vapor**

$HV := \text{DELHV}(T, P) + \text{DELHIG}(T, P)$ $SV := \text{DELSV}(T, P) + \text{DELSIG}(T, P)$

$HL := \text{DELHL}(T, P) + \text{DELHIG}(T, P)$ $SL := \text{DELSL}(T, P) + \text{DELSIG}(T, P)$

$\delta H := x \cdot HV + (1 - x) \cdot HL - \text{DELHin}$ $\delta S := x \cdot SV + (1 - x) \cdot SL - \text{DELSin}$

SUMMARY OF RESULTS

	FEED	LIQUID	VAPOR
Temperature, K	Ti = 120	T = 101.906	T = 101.906
Pressure, bar	Pi = 30	P = 3	P = 3
Vapor-liquid split		x = 0.1379	
Compressibility	$Z(Ti, Pi)_0 = 0.0888$	$Z(T, P)_0 = 9.3464 \cdot 10^{-3}$	$Z(T, P)_2 = 0.9309$
Enthalpy, J/mol (relative to feed)	0	$HL = -7.0203 \cdot 10^3$	$HV = -635.2466$
Entropy, J/mol K (relative to feed)	0	$SL = -48.8038$	$SV = 13.8527$
Enthalpy change J/mol		$\delta H = -152.4165$	
Entropy change J/mol K		$\delta S = 0$	

5.56   (also available as a Mathcad worksheet)

5.56 ISENTHALPIC S-R-K EQUATION OF STATE CALCULATION

$Tc := 154.6$ $Pc := 50.46$ $om := 0.021$ $kap := 0.480 + 1.574 \cdot om - 0.176 \cdot om \cdot om$

$Cp_0 := 25.46$ $Cp_1 := 1.591 \cdot 10^{-2}$ $Cp_2 := -0.7151 \cdot 10^{-5}$ $Cp_3 := 1.311 \cdot 10^{-9}$

S-R-K Constants: $R := 0.00008314$ $b := 0.08664 \cdot \dfrac{R \cdot Tc}{Pc}$ $ac := 0.42748 \cdot \dfrac{R^2 \cdot Tc^2}{Pc}$

Input initial temperature and pressure of calculation $Ti := 120.$ **K,** $Pi := 30$ **bar**

Input final pressure $Pf := 3.0$ **bar**

Initial state calculations $T := Ti$ $P := Pi$

$$alf(T) := 1 \cdot \left[1 + kap \cdot \left(1 - \sqrt{\dfrac{T}{Tc}} \right) \right]^2$$ $a(T) := ac \cdot alf(T)$ $CA(T,P) := \dfrac{a(T) \cdot P}{(R \cdot T)^2}$ $CB(T,P) := \dfrac{P \cdot b}{R \cdot T}$

$$Da(T) := \dfrac{d}{dT} a(T)$$

$Z(T,P) :=$ $\Big|$ $A \leftarrow CA(T,P)$

$B \leftarrow CB(T,P)$

$V \leftarrow \begin{bmatrix} -A \cdot B \\ A - B^2 - B \\ -1 \\ 1 \end{bmatrix}$ **Vector of coefficients in the S-R-K equation in the form**
0=-A*B+(A-B^2-B)*Z-Z^2+Z^3

$ZZ \leftarrow polyroots(V)$ **Solution to the cubic**

for $i \in 0..2$

$\left(ZZ_i \leftarrow 0 \right)$ if $\left(Im(ZZ_i) \neq 0 \right)$

$ZZ \leftarrow sort(ZZ)$ **Set any imaginary roots to zero**
Sort the roots

$ZZ_0 \leftarrow ZZ_2$ if $\left(| ZZ_0 | < 10^{-5} \right)$ **Set the value of any imaginary roots**
to value of the real root

$ZZ_2 \leftarrow ZZ_0$ if $\left(| ZZ_2 | < 10^{-5} \right)$

ZZ

Calculate inital properties $Zf(T,P) := Z(T,P)$

Calculate initial molar volume and enthalpy and entropy departure $VL := \dfrac{Z(T,P)_0 \cdot R \cdot T}{P} \cdot 10^3$ $Z(T,P) = \begin{bmatrix} 0.1004 \\ 0 \\ 0.1004 \end{bmatrix}$

$$DELHin := \left[R \cdot T \cdot \left(Z(T,P)_0 - 1 \right) + \dfrac{T \cdot Da(T) - a(T)}{b} \cdot \ln\left(\dfrac{Z(T,P)_0 + CB(T,P)}{Z(T,P)_0} \right) \right] \cdot 10^5$$

$$\text{DELSin} := \left(R \cdot \ln\left(Z(T,P)_0 - CB(T,P)\right) + \frac{Da(T)}{b} \cdot \ln\left(\frac{Z(T,P)_0 + CB(T,P)}{Z(T,P)_0}\right) \right) \cdot 10^5$$

$$\text{DELHin} = {}^{-}6.0618 \cdot 10^3 \qquad\qquad \text{DELSin} = {}^{-}40.9502$$

Guess for final state $\qquad\qquad T := 0.8 \cdot Ti \qquad\qquad P := Pf$

Fugacity expressions [actually ln(f/P)] for the liquid fl and vapor fv

$$fl(T,P) := \left(Z(T,P)_0 - 1\right) - \ln\left(Z(T,P)_0 - CB(T,P)\right) - \frac{CA(T,P)}{CB(T,P)} \cdot \ln\left(\frac{Z(T,P)_0 + CB(T,P)}{Z(T,P)_0}\right)$$

$$fv(T,P) := \left(Z(T,P)_2 - 1\right) - \ln\left(Z(T,P)_2 - CB(T,P)\right) - \frac{CA(T,P)}{CB(T,P)} \cdot \ln\left(\frac{Z(T,P)_2 + CB(T,P)}{Z(T,P)_2}\right)$$

Given $\qquad fl(T,P) - fv(T,P) = 0 \qquad\qquad T := find(T) \qquad\qquad T = 102.0671$

Residual entropy for liquid (DELSL) and vapor (DELSV) phases

$$\text{DELSL}(T,P) := \left(R \cdot \ln\left(Z(T,P)_0 - CB(T,P)\right) + \frac{Da(T)}{b} \cdot \ln\left(\frac{Z(T,P)_0 + CB(T,P)}{Z(T,P)_0}\right) \right) \cdot 10^5$$

$$\text{DELSV}(T,P) := \left(R \cdot \ln\left(Z(T,P)_2 - CB(T,P)\right) + \frac{Da(T)}{b} \cdot \ln\left(\frac{Z(T,P)_2 + CB(T,P)}{Z(T,P)_2}\right) \right) \cdot 10^5$$

Residual enthalpy for liquid (DELHL) and vapor (DELHV) phases

$$\text{DELHL}(T,P) := \left[R \cdot T \cdot \left(Z(T,P)_0 - 1\right) + \frac{T \cdot Da(T) - a(T)}{b} \cdot \ln\left(\frac{Z(T,P)_0 + CB(T,P)}{Z(T,P)_0}\right) \right] \cdot 10^5$$

$$\text{DELHV}(T,P) := \left[R \cdot T \cdot \left(Z(T,P)_2 - 1\right) + \frac{T \cdot Da(T) - a(T)}{b} \cdot \ln\left(\frac{Z(T,P)_2 + CB(T,P)}{Z(T,P)_2}\right) \right] \cdot 10^5$$

Ideal gas properties changes relative to the initial state

$$\text{DELHIG}(T,P) := Cp_0 \cdot (T - Ti) + \frac{Cp_1 \cdot \left(T^2 - Ti^2\right)}{2} + \frac{Cp_2 \cdot \left(T^3 - Ti^3\right)}{3} + \frac{Cp_3 \cdot \left(T^4 - Ti^4\right)}{4}$$

$$DELSIG(T, P) := Cp_0 \cdot \ln\left(\frac{T}{Ti}\right) + Cp_1 \cdot (T - Ti) + \frac{Cp_2 \cdot \left(T^2 - Ti^2\right)}{2} + \frac{Cp_3 \cdot \left(T^3 - Ti^3\right)}{3} - R \cdot 10^5 \cdot \ln\left(\frac{P}{Pi}\right)$$

Find vapor-liquid split $\qquad x := 0.5$

Given

$$x \cdot DELHV(T, P) + (1 - x) \cdot DELHL(T, P) + DELHIG(T, P) = DELHin$$

$\qquad x := find(x) \qquad\qquad\qquad x = 0.1661 \qquad$ **Fraction vapor**

$HV := DELHV(T, P) + DELHIG(T, P) \qquad SV := DELSV(T, P) + DELSIG(T, P)$

$HL := DELHL(T, P) + DELHIG(T, P) \qquad SL := DELSL(T, P) + DELSIG(T, P)$

$\delta H := x \cdot HV + (1 - x) \cdot HL - DELHin \qquad\qquad \delta S := x \cdot SV + (1 - x) \cdot SL - DELSin$

SUMMARY OF RESULTS

	FEED	**LIQUID**	**VAPOR**
Temperature, K	Ti = 120	T = 102.0671	T = 102.0671
Pressure, bar	Pi = 30	P = 3	P = 3
Vapor-liquid split		x = 0.1661	
Compressibility	$Z(Ti, Pi)_0 = 0.1004$	$Z(T, P)_0 = 0.0106$	$Z(T, P)_2 = 0.934$
Enthalpy, J/mol (relative to feed)	0	$HL = -7.1435 \cdot 10^3$	$HV = -630.1699$
Entropy, J/mol K (relative to feed)	0	$SL = -49.936$	$SV = 13.8781$
Enthalpy change J/mol		$\delta H = 0$	
Entropy change J/mol K		$\delta S = 1.6121$	

5.57 (also available as a Mathcad worksheet)

5.57 ISENTROPIC S-R-K EQUATION OF STATE CALCULATION

$Tc := 154.6 \qquad Pc := 50.46 \qquad om := 0.021 \qquad kap := 0.480 + 1.574 \cdot om - 0.176 \cdot om \cdot om$

$Cp_0 := 25.46 \qquad Cp_1 := 1.591 \cdot 10^{-2} \qquad Cp_2 := -0.7151 \cdot 10^{-5} \qquad Cp_3 := 1.311 \cdot 10^{-9}$

S-R-K Constants: $\qquad\qquad R := 0.00008314 \qquad b := 0.08664 \cdot \dfrac{R \cdot Tc}{Pc} \qquad ac := 0.42748 \cdot \dfrac{R^2 \cdot Tc^2}{Pc}$

Input initial temperature and pressure of calculation $\qquad Ti := 120. \quad$ **K,** $\qquad Pi := 30 \quad$ **bar**

Input final pressure $\qquad Pf := 3.0 \qquad$ **bar**

Initial state calculations $\qquad\qquad T := Ti \qquad\qquad P := Pi$

$$\text{alf}(T) := 1 \cdot \left[1 + \text{kap} \cdot \left(1 - \sqrt{\frac{T}{Tc}} \right) \right]^2 \qquad a(T) := ac \cdot \text{alf}(T) \qquad CA(T, P) := \frac{a(T) \cdot P}{(R \cdot T)^2} \qquad CB(T, P) := \frac{P \cdot b}{R \cdot T}$$

$$Da(T) := \frac{d}{dT} a(T)$$

$$Z(T, P) := \begin{vmatrix} A \leftarrow CA(T, P) \\ B \leftarrow CB(T, P) \\ V \leftarrow \begin{bmatrix} -A \cdot B \\ A - B^2 - B \\ -1 \\ 1 \end{bmatrix} \\ ZZ \leftarrow \text{polyroots}(V) \\ \text{for } i \in 0..2 \\ \quad \left(ZZ_i \leftarrow 0 \right) \text{ if } \left(\text{Im}\left(ZZ_i\right) \neq 0 \right) \\ ZZ \leftarrow \text{sort}(ZZ) \\ ZZ_0 \leftarrow ZZ_2 \text{ if } \left(\left| ZZ_0 \right| < 10^{-5} \right) \\ ZZ_2 \leftarrow ZZ_0 \text{ if } \left(\left| ZZ_2 \right| < 10^{-5} \right) \\ ZZ \end{vmatrix}$$

**Vector of coefficients in the S-R-K equation
in the form
0=-A*B+(A-B^2-B)*Z-Z^2+Z^3**

Solution to the cubic

**Set any imaginary roots to zero
Sort the roots**

**Set the value of any imaginary roots
to value of the real root**

Calculate inital properties

$$Zf(T, P) := Z(T, P)$$

**Calculate initial molar volume
and enthalpy and entropy
departure**

$$VL := \frac{Z(T, P)_0 \cdot R \cdot T}{P} \cdot 10^3 \qquad Z(T, P) = \begin{bmatrix} 0.1004 \\ 0 \\ 0.1004 \end{bmatrix}$$

$$\text{DELHin} := \left[R \cdot T \cdot \left(Z(T, P)_0 - 1 \right) + \frac{T \cdot Da(T) - a(T)}{b} \cdot \ln\left\{ \frac{Z(T, P)_0 + CB(T, P)}{Z(T, P)_0} \right\} \right] \cdot 10^5$$

$$\text{DELSin} := \left\{ R \cdot \ln\left(Z(T, P)_0 - CB(T, P) \right) + \frac{Da(T)}{b} \cdot \ln\left\{ \frac{Z(T, P)_0 + CB(T, P)}{Z(T, P)_0} \right\} \right\} \cdot 10^5$$

$$\text{DELHin} = -6.0618 \cdot 10^3 \qquad\qquad \text{DELSin} = -40.9502$$

Guess for final state $\qquad T := 0.8 \cdot Ti \qquad P := Pf$

Fugacity expressions [actually ln(f/P)] for the liquid fl and vapor fv

$$fl(T, P) := \left(Z(T, P)_0 - 1\right) - \ln\left(Z(T, P)_0 - CB(T, P)\right) - \frac{CA(T, P)}{CB(T, P)} \cdot \ln\left(\frac{Z(T, P)_0 + CB(T, P)}{Z(T, P)_0}\right)$$

$$fv(T, P) := \left(Z(T, P)_2 - 1\right) - \ln\left(Z(T, P)_2 - CB(T, P)\right) - \frac{CA(T, P)}{CB(T, P)} \cdot \ln\left(\frac{Z(T, P)_2 + CB(T, P)}{Z(T, P)_2}\right)$$

Given $\quad fl(T, P) - fv(T, P) = 0 \qquad T := find(T) \qquad T = 102.0671$

Residual entropy for liquid (DELSL) and vapor (DELSV) phases

$$DELSL(T, P) := \left(R \cdot \ln\left(Z(T, P)_0 - CB(T, P)\right) + \frac{Da(T)}{b} \cdot \ln\left(\frac{Z(T, P)_0 + CB(T, P)}{Z(T, P)_0}\right)\right) \cdot 10^5$$

$$DELSV(T, P) := \left(R \cdot \ln\left(Z(T, P)_2 - CB(T, P)\right) + \frac{Da(T)}{b} \cdot \ln\left(\frac{Z(T, P)_2 + CB(T, P)}{Z(T, P)_2}\right)\right) \cdot 10^5$$

Residual enthalpy for liquid (DELHL) and vapor (DELHV) phases

$$DELHL(T, P) := \left[R \cdot T \cdot \left(Z(T, P)_0 - 1\right) + \frac{T \cdot Da(T) - a(T)}{b} \cdot \ln\left(\frac{Z(T, P)_0 + CB(T, P)}{Z(T, P)_0}\right)\right] \cdot 10^5$$

$$DELHV(T, P) := \left[R \cdot T \cdot \left(Z(T, P)_2 - 1\right) + \frac{T \cdot Da(T) - a(T)}{b} \cdot \ln\left(\frac{Z(T, P)_2 + CB(T, P)}{Z(T, P)_2}\right)\right] \cdot 10^5$$

Ideal gas properties changes relative to the initial state

$$DELHIG(T, P) := Cp_0 \cdot (T - Ti) + \frac{Cp_1 \cdot \left(T^2 - Ti^2\right)}{2} + \frac{Cp_2 \cdot \left(T^3 - Ti^3\right)}{3} + \frac{Cp_3 \cdot \left(T^4 - Ti^4\right)}{4}$$

$$DELSIG(T, P) := Cp_0 \cdot \ln\left(\frac{T}{Ti}\right) + Cp_1 \cdot (T - Ti) + \frac{Cp_2 \cdot \left(T^2 - Ti^2\right)}{2} + \frac{Cp_3 \cdot \left(T^3 - Ti^3\right)}{3} - R \cdot 10^5 \cdot \ln\left(\frac{P}{Pi}\right)$$

Find vapor-liquid split $\qquad x := 0.5$

Given

$$x \cdot DELSV(T, P) + (1 - x) \cdot DELSL(T, P) + DELSIG(T, P) = DELSin$$

$$x := find(x) \qquad x = 0.1408 \qquad \textbf{Fraction vapor}$$

$$HV := DELHV(T,P) + DELHIG(T,P) \qquad SV := DELSV(T,P) + DELSIG(T,P)$$

$$HL := DELHL(T,P) + DELHIG(T,P) \qquad SL := DELSL(T,P) + DELSIG(T,P)$$

$$\delta H := x \cdot HV + (1-x) \cdot HL - DELHin \qquad \delta S := x \cdot SV + (1-x) \cdot SL - DELSin$$

SUMMARY OF RESULTS

	FEED	LIQUID	VAPOR
Temperature, K	$Ti = 120$	$T = 102.0671$	$T = 102.0671$
Pressure, bar	$Pi = 30$	$P = 3$	$P = 3$
Vapor-liquid split		$x = 0.1408$	
Compressibility	$Z(Ti,Pi)_0 = 0.1004$	$Z(T,P)_0 = 0.0106$	$Z(T,P)_2 = 0.934$
Enthalpy, J/mol (relative to feed)	0	$HL = -7.1435 \cdot 10^3$	$HV = -630.1699$
Entropy, J/mol K (relative to feed)	0	$SL = -49.936$	$SV = 13.8781$
Enthalpy change J/mol		$\delta H = -164.5454$	
Entropy change J/mol K		$\delta S = 7.1054 \cdot 10^{-15}$	

5.58 This problem was solved using the attached Mathcad worksheet. The results are

$T(^\circ C)$	P^{vap} with $a(T)$	P^{vap} with $a=1$ $\quad$ (P in kPa)
273.15	0.3137	166.57
283.15	0.5529	221.329
293.15	1.697	288.55
303.15	3.208	369.83
323.25	9.994	580.97
343.15	26.681	867.65
373.15	92.355	1467.0
393.15	186.67	1997.1
423.25	463.23	3016.5
448.15	886.08	4094.2
474.15	1599.4	5456.5
523.15	4065.2	8759.0

623.15	16744	18865
643.15	21060	

As can be seen, the S-R-K equation is of comparable accuracy to the P-R equation. In both cases if the α parameter is set to one, the results are not very good, indeed quite bad at low temperatures.

The Mathcad worksheet used in solving this problem is given below.

VAPOR PRESSURE CALCULATION USING SRK EQUATION

Read in properties for Water $Tc := 647.3$ $Pc := 220.48$ $om := 0.344$

kappa calculation $kap := 0.480 + 1.574 \cdot om - 0.176 \cdot om \cdot om$

S-R-K Constants: $R := 0.00008314$ $b := 0.08664 \cdot \dfrac{R \cdot Tc}{Pc}$ $ac := 0.42748 \dfrac{R^2 \cdot Tc^2}{Pc}$

Note that these are being defined as a function of temperature since we will need to interate on temperature.

$$alf(T) := 1 \cdot \left[1 + kap \cdot \left(1 - \sqrt{\frac{T}{Tc}} \right) \right]^2 \qquad a(T) := ac \cdot alf(T)$$

$$CA(T,P) := \frac{a(T) \cdot P}{(R \cdot T)^2} \qquad CB(T,P) := \frac{P \cdot b}{R \cdot T}$$

$$Z(T,P) := \begin{vmatrix} A \leftarrow CA(T,P) \\ B \leftarrow CB(T,P) \\ V \leftarrow \begin{bmatrix} -A \cdot B \\ A - B^2 - B \\ -1 \\ 1 \end{bmatrix} \\ ZZ \leftarrow polyroots(V) \\ \text{for } i \in 0..2 \\ \quad \left(ZZ_i \leftarrow 0 \right) \text{ if } \left(Im\left(ZZ_i\right) \neq 0 \right) \\ ZZ \leftarrow sort(ZZ) \\ ZZ_0 \leftarrow ZZ_2 \text{ if } \left(\left| ZZ_0 \right| < 10^{-5} \right) \\ ZZ_2 \leftarrow ZZ_0 \text{ if } \left(\left| ZZ_2 \right| < 10^{-5} \right) \\ ZZ \end{vmatrix}$$

Vector of coefficients in the SRK equation in the form
0=-A*B+(A-B^2-B)*Z-^Z^2+Z^3

Solution to the cubic

**Set any imaginary roots to zero
Sort the roots**

Set the value of any imaginary roots to value of the real root

**Enter temperature T, and pressure P.
Depending on what is specified in the Given and Find statements below, either T or P is specified and the other is an initial guess which may have to be adjusted as the other variable is changed, especially as the critical point is approached.This worksheet will probably not converge to a solution when T or P are within 3 to 5% of the critical values unless an extremely good initial guess is provided. One way to obtain a good initial is to start well below the critical region and step towards it using the result of previous calculations.**

$T := 643.15$

$P := 210$

Fugacity expressions [actually ln(f/P)] for the liquid fl and vapor fv

$$fl(T,P) := \left(Z(T,P)_0 - 1\right) - \ln\left(Z(T,P)_0 - CB(T,P)\right) - \frac{CA(T,P)}{CB(T,P)} \cdot \ln\left[\frac{Z(T,P)_0 + CB(T,P)}{Z(T,P)_0}\right]$$

$$fv(T,P) := \left(Z(T,P)_2 - 1\right) - \ln\left(Z(T,P)_2 - CB(T,P)\right) - \frac{CA(T,P)}{CB(T,P)} \cdot \ln\left[\frac{Z(T,P)_2 + CB(T,P)}{Z(T,P)_2}\right]$$

GIVEN $fl(T,P) - fv(T,P) = 0$ **Equate log of fugacity coefficients**

$P := find(P)$ $P = 210.59561$ **Solve equality of fugacities**

               Fugacity   **Fugacity coefficient**

$fugl := P \cdot \exp(fl(T,P))$ $fugl = 141.78565$ $fl(T,P) = -0.39562$ $phil := \dfrac{fugl}{P}$

$fugv := P \cdot \exp(fv(T,P))$ $fugv = 141.78565$ $fv(T,P) = -0.39562$

SUMMARY OF RESULTS

$T = 643.15$ K   **Vapor pressure, bar** $P = 210.59561$

                  LIQUID   **VAPOR**

Compressibility $Z(T,P)_0 = 0.25283$ $Z(T,P)_2 = 0.42294$

Fugacity, bar $fugl = 141.78565$ $fugv = 141.78565$

5.59   (also available as a Mathcad worksheet)
The solution is that the final temperature is 131.34 K, and the final pressure is 37.036 bar.

5.59   Using SRK EOS with the approximate two-constant heat capacity expression

Property Data $Tc := 126.2$ $Pc := 33.94$ $om := 0.04$ $Cp1 := 27.2$ $Cp2 := 0.0042$
(T in K, P in bar): $R := 0.00008314$ $kap := 0.480 + 1.574 \cdot om - 0.176 \cdot om \cdot om$

Initial Conditions (Vt=total volume, m^3): $Ti := 170$ $Pi := 100$ $Vt := 0.15$

Peng-Robinson Constants: $b := 0.08664 \cdot \dfrac{R \cdot Tc}{Pc}$ $ac := 0.42748 \cdot \dfrac{R^2 \cdot Tc^2}{Pc}$

Initial temperature $T := Ti$

Note that these are being defined as a function of temperature since we will need to interate on temperature later to obtain the final state of the system $alf(T) := 1 \cdot \left[1 + kap \cdot \left(1 - \sqrt{\dfrac{T}{Tc}}\right)\right]^2$ $a(T) := ac \cdot alf(T)$

$$Da(T) := \frac{d}{dT} a(T)$$

Find initial molar volume and number of moles
Start with initial guess for volume, m^3/mol $V := \dfrac{R \cdot Ti}{Pi}$

Solve P-R EOS for initial volume   Given $Pi = \dfrac{R \cdot T}{V - b} - \dfrac{a(T)}{(V \cdot (V + b))}$ $Vi := \text{Find}(V)$

Initial molar volume and
number of moles

$Vi = 1.02 \cdot 10^{-4}$ $Ni := \dfrac{Vt}{Vi}$ $Ni = 1.471 \cdot 10^{3}$

Entropy departure at the
initial conditions

$DELSi := \left[R \cdot \ln\left[(Vi - b) \cdot \dfrac{Pi}{R \cdot T} \right] + \dfrac{Da(T)}{b} \cdot \ln\left(\dfrac{Vi + b}{Vi} \right) \right] \cdot 10^{5}$

Now consider final state $Nf := Ni - 10 \cdot 50 \quad Vf := \dfrac{0.15}{Nf} \quad V := Vf$

Type out final number of
moles and specific volume

$Nf = 971.269$ $Vf = 1.544 \cdot 10^{-4}$

Final pressure, will change in course
of solving for the final temperature

$Pf(T) := \dfrac{R \cdot T}{V - b} - \dfrac{a(T)}{V \cdot (V + b)}$

Entropy departure
at final conditions

$DELS(T) := \left[R \cdot \ln\left[(V - b) \cdot \dfrac{Pf(T)}{R \cdot T} \right] + \dfrac{Da(T)}{b} \cdot \ln\left(\dfrac{V + b}{V} \right) \right] \cdot 10^{5}$

Solve for final
temperature using
S(final)-S(initial)=0

GIVEN $0 = 27.2 \cdot \ln\left(\dfrac{T}{Ti} \right) + 0.0042 \cdot (T - Ti) - R \cdot 10^{5} \cdot \ln\left(\dfrac{Pf(T)}{Pi} \right) + DELS(T) - DELSi$

$T := \text{FIND}(T)$

Type out solution $T = 131.34$ $Pf(T) = 37.076$

5.60   a) At a given temperature, the stability limit of a fluid is determined by the
following criterion (Note that this leads to the spinodal curve)

$$\left(\frac{\partial P}{\partial \underline{V}} \right)_{T} = 0$$

For the given EOS, the stability limit of a fluid undergoing a pressure change at
constant temperature is

$$\left(\frac{\partial P}{\partial \underline{V}} \right)_{T} = -\frac{RT}{\underline{V}^{2}} - 2\frac{BRT}{\underline{V}^{3}} - 3\frac{CRT}{\underline{V}^{4}} = 0$$

or $\underline{V}^{2} + 2B\underline{V} + 3C = 0$

In order to have a phase transition, there must be two distinct stability limits,
i.e., the above quadratic equation must have two different roots of $\underline{V}$. Therefore,

$$(2B)^{2} - 4 \times 1 \times (3C) > 0$$

or $B^{2} > 3C$

b) According to Illustration 4.2-1

$$dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P \right] dV$$

But for the given EOS $\left[T\left(\frac{\partial P}{\partial T}\right)_V - P \right] = 0$

Therefore,

$$\Delta U = \int dU = \int C_V(V, T) dT$$

Since $\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0$ (Because B and C are not functions of T)

Therefore $C_v = C_v(T) = C_V^* = a + bT$

and

$$\Delta U = \int_{T_1}^{T_2} (a + bT) dT = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2)$$

The internal energy change is the same for an ideal gas.

c) According to Eqn 4.2-19

$$d S = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV \quad \text{so that}$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{T\left(\frac{\partial P}{\partial T}\right)_V}{C_V} = \frac{P}{a + bT} = \frac{\left(\frac{RT}{V} + \frac{BRT}{V^2} + \frac{CRT}{V^3}\right)}{a + bT}$$

For an ideal gas,

$$\left(\frac{\partial T}{\partial V}\right)_S = \frac{P}{a + bT} = \frac{\left(\frac{RT}{V}\right)}{a + bT} = \frac{RT}{V(a + bT)}$$

Thermodynamic properties of n-Hexane by William Provine.

P=100 bar
P=40 bar
P=30 bar
P=26.8 bar
P=19.9 bar
P=10 bar
P=12.2 bar
P=5 bar
P=7 bar
P=4 bar

$\underline{S}$ (J/mol K)
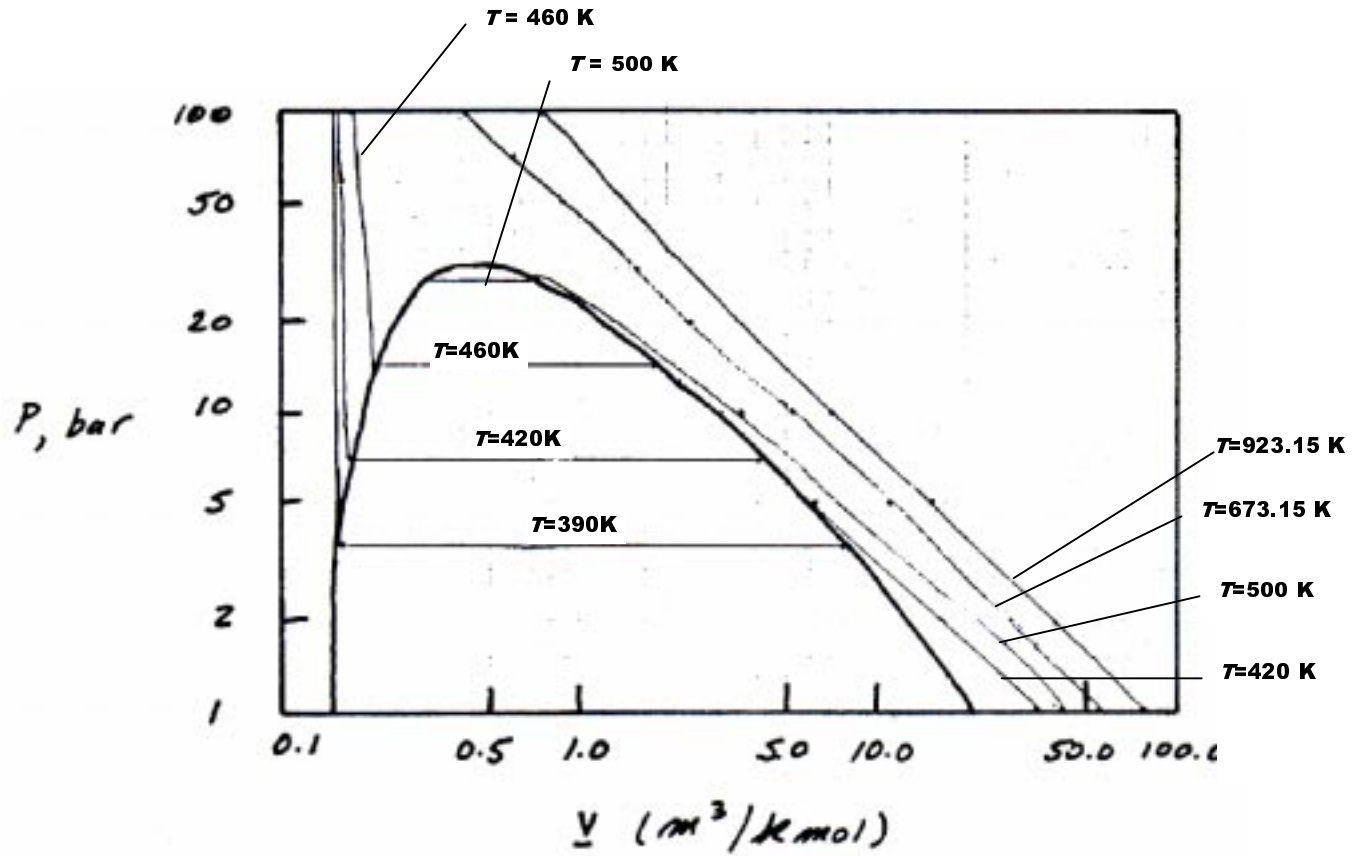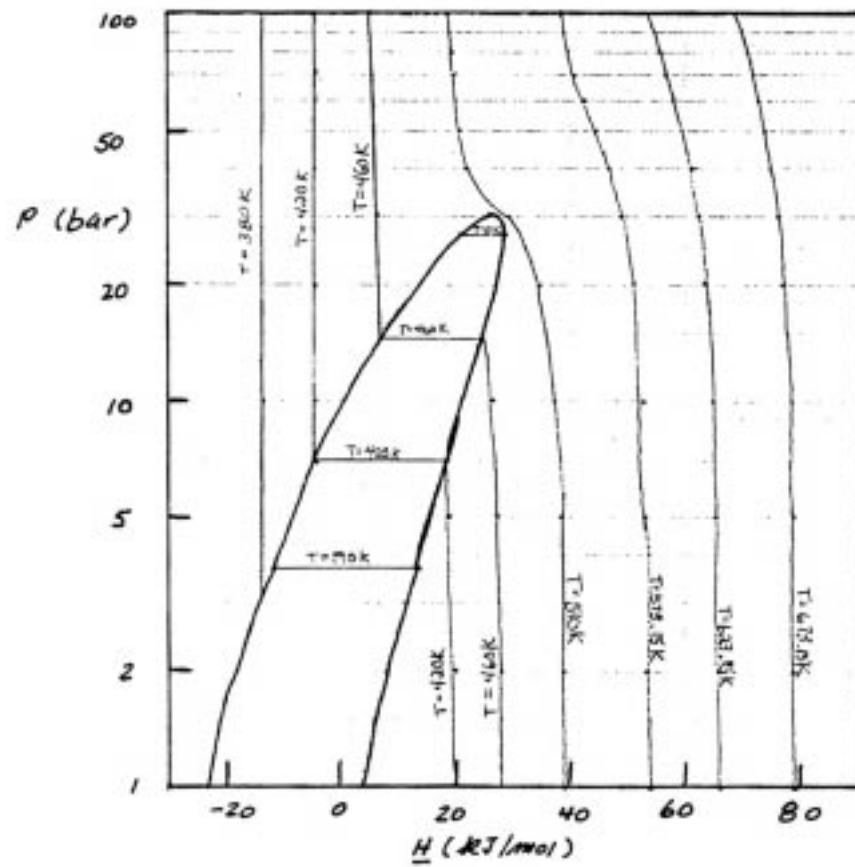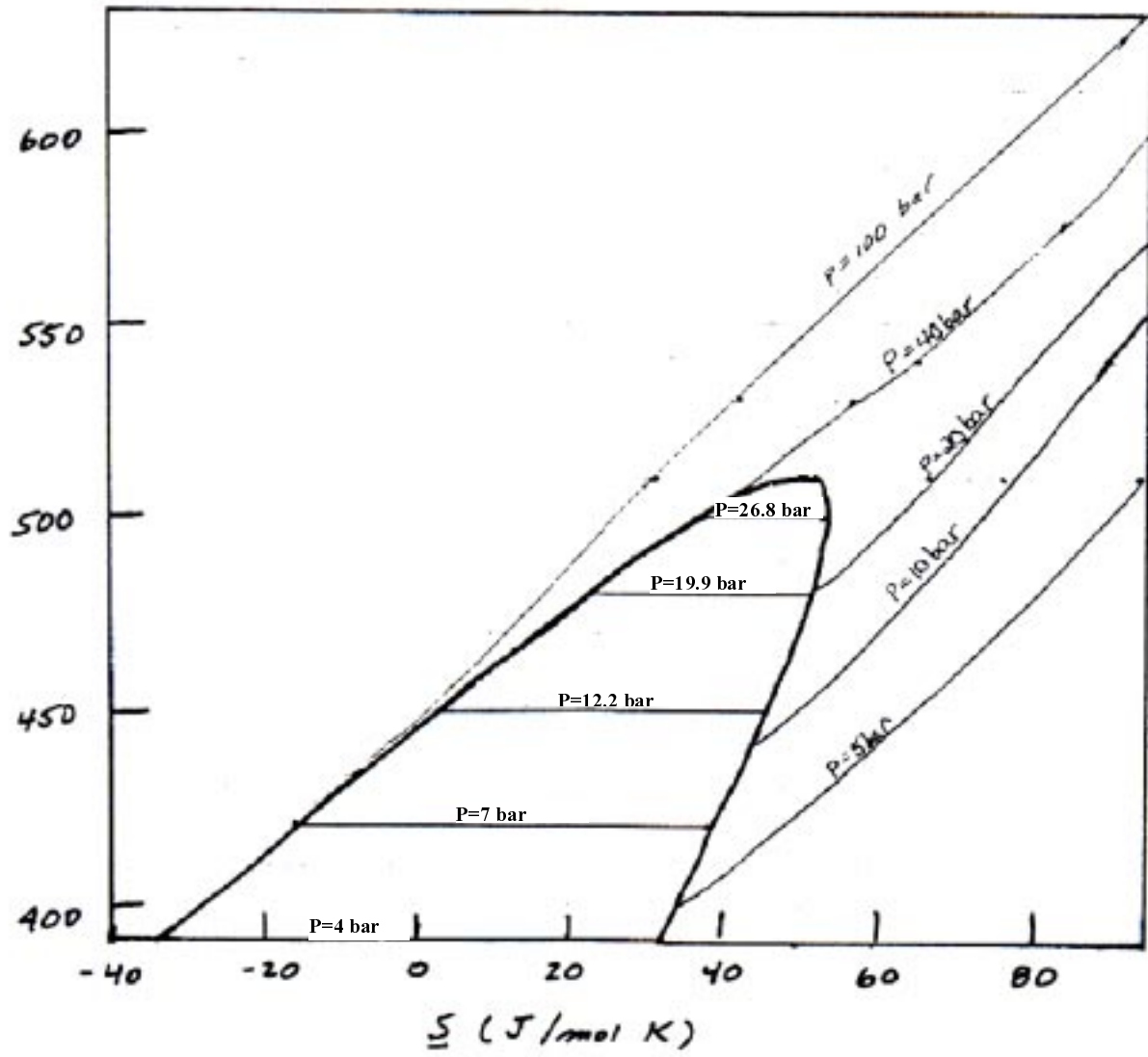
Thermodynamic properties of n-butane by Chiu Chan

T(K) vs S, J/mol K chart

P, bar vs H, kJ/mole chart
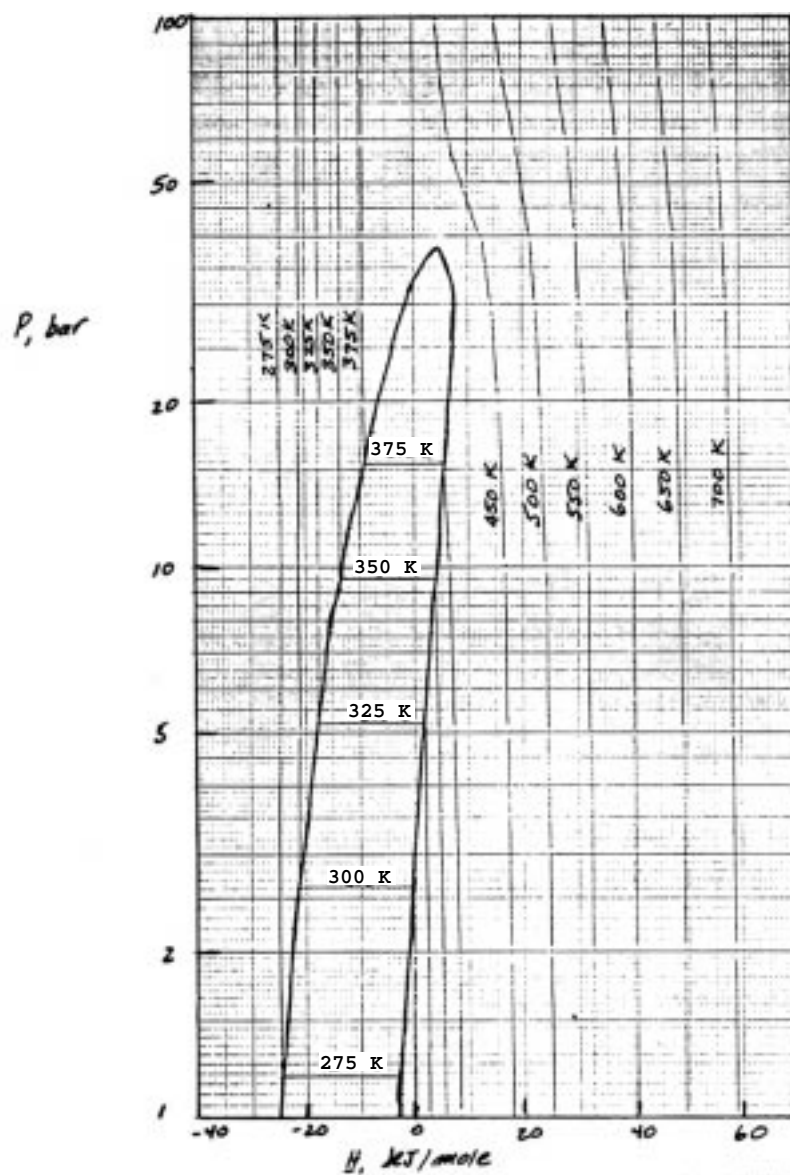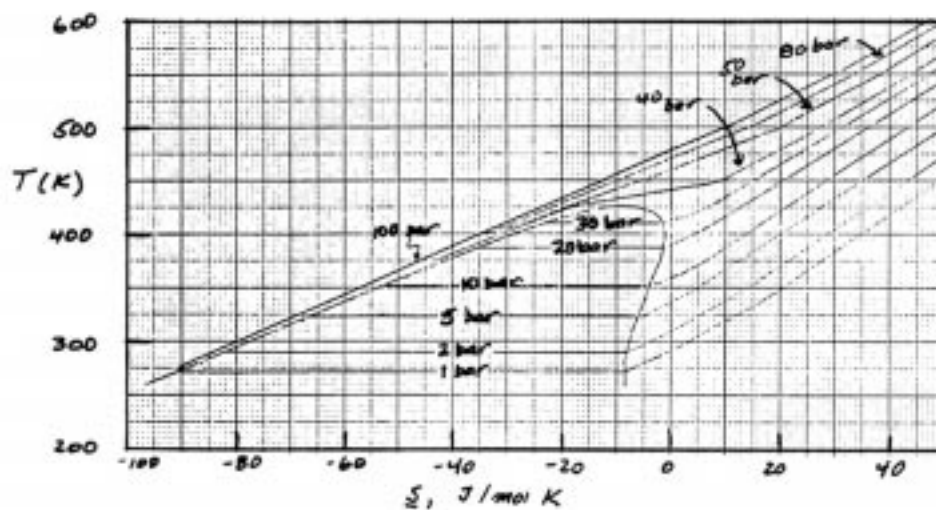
Thermodynamic properties of methane by Michael Sowa

$\underline{H}$, kJ/mol
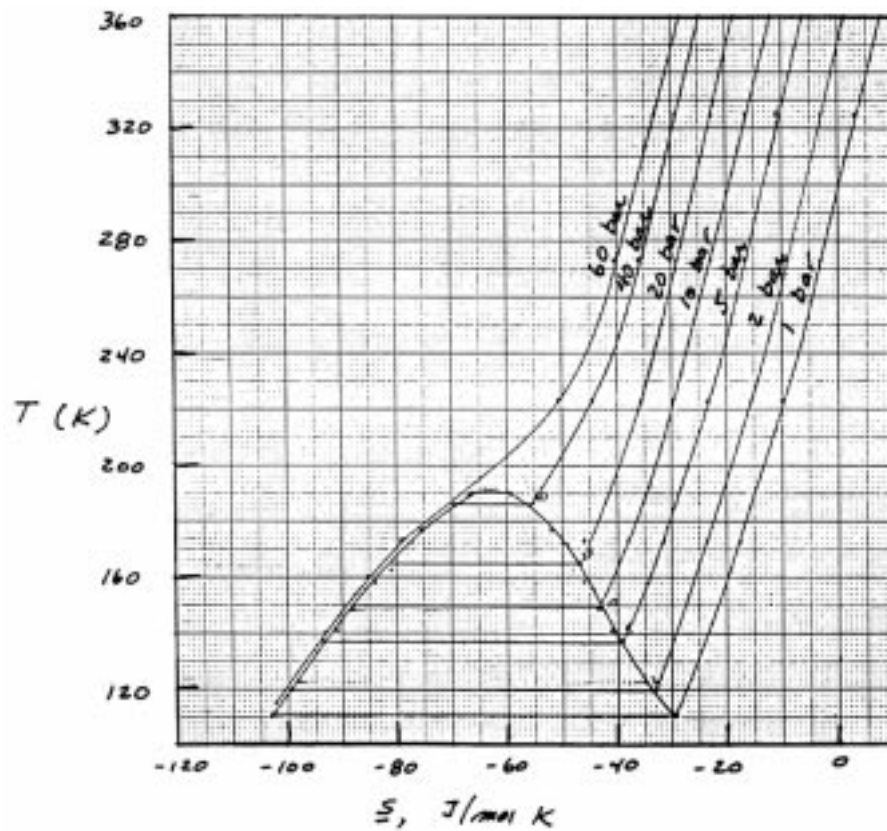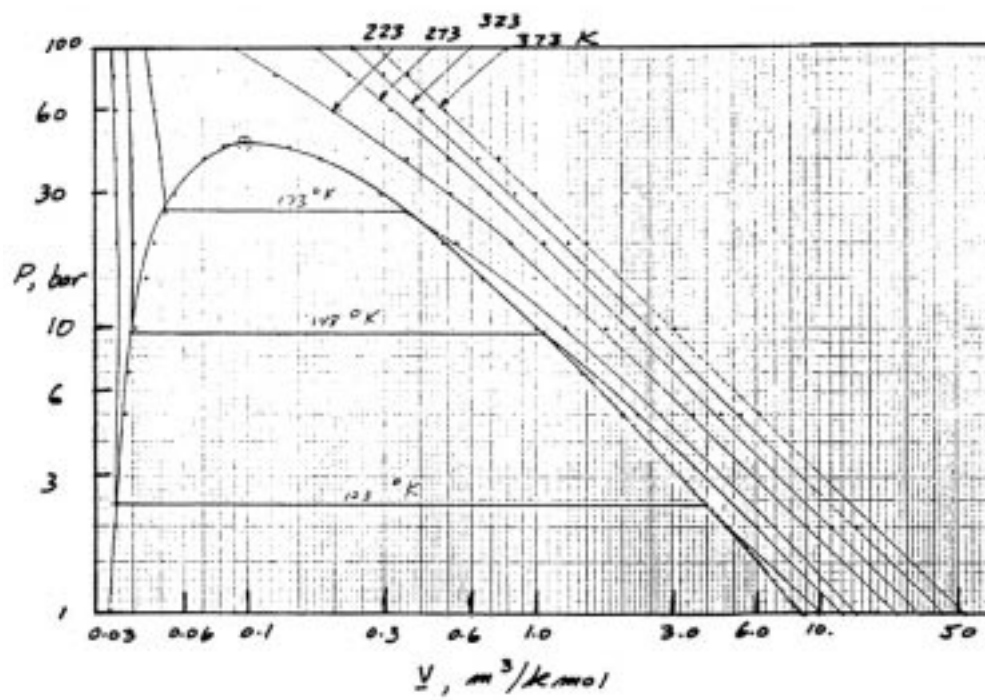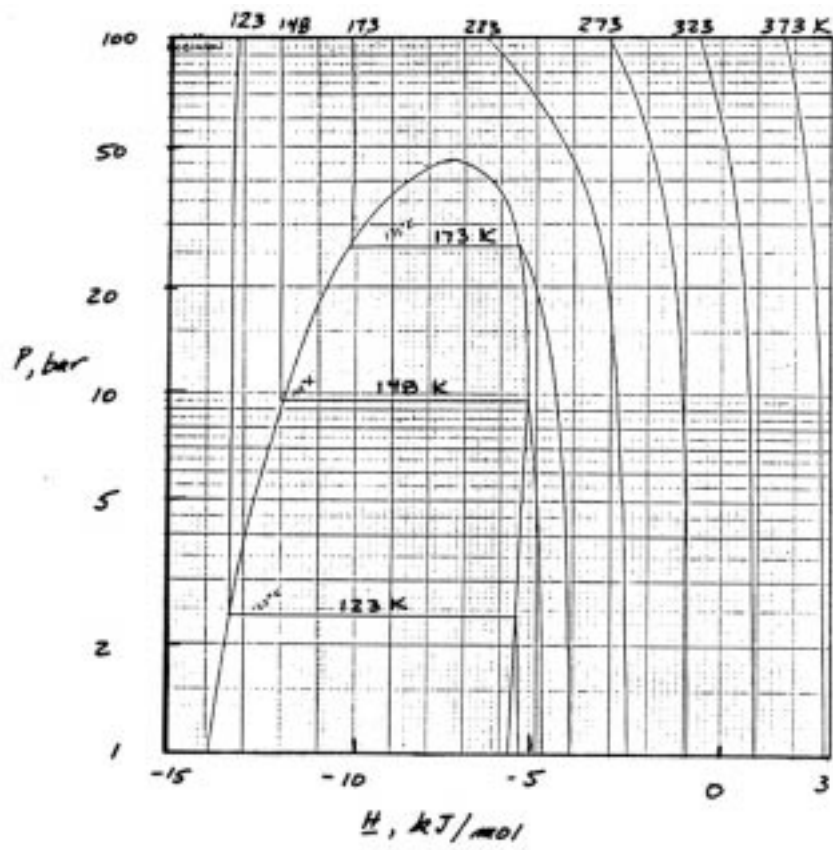
6

6.1 (a) By Eqn. (6.2-3)

$$\left(\frac{\partial H}{\partial N_i}\right)_{P,S,N_{j\neq i}} = \overline{G}_i \; ;$$

but $\overline{G}_i = \overline{H}_i - T\overline{S}_i$. Thus

$$\left(\frac{\partial H}{\partial N_i}\right)_{P,S,N_{j\neq i}} = \overline{H}_i - T\overline{S}_i$$

(b) Since $U = U(S,V,\underline{N})$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,\underline{N}} dS + \left(\frac{\partial U}{\partial V}\right)_{S,\underline{N}} dV + \sum_i \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}} dN_i$$

$$= TdS - PdV + \sum_i \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}} dN_i \qquad (1)$$

However, we also have $U = H - PV$; $dU = dH - PdV - VdP$, and, by Eqn. (6.2-3)

$$dU = VdP + TdS + \sum \overline{G}_i dN_i - PdV - VdP = TdS - PdV + \sum \overline{G}_i dN_i \qquad (2)$$

Equating (1) and (2) shows that $\overline{G}_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}}$. Next we start from

$$A = A(T,V,\underline{N})$$

$$\Rightarrow dA = \left(\frac{\partial A}{\partial T}\right)_{V,\underline{N}} dT + \left(\frac{\partial A}{\partial V}\right)_{T,\underline{N}} dV + \sum_i \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_{j\neq i}} dN_i$$

or

$$dA = -SdT - PdV + \sum_i \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_{j\neq i}} dN_i \qquad (3)$$

However, we also have that $A = U - TS$;

$$dA = dU - TdS - SdT = TdS - PdV + \sum \overline{G}_i dN_i - TdS - SdT$$

or

$$dA = -SdT - PdV + \sum \overline{G}_i dN_i \qquad (4)$$

Comparing (3) and (4) yields

$$\overline{G}_i = \left(\frac{\partial A}{\partial N_i} \right)_{T,V,N_{j\neq i}}$$

6.2 (a) General: $q = \sum N_i \overline{q}_i$ where $\overline{q}_i = \left(\partial q / \partial N_i \right)_{T,P,N_{j\neq i}}$ and

$$dq = \sum \overline{q}_i dN_i + \sum N_i d\overline{q}_i \qquad (1)$$

However, we also have that

$$dq = \left(\frac{\partial q}{\partial T} \right)_{V,\underline{N}} dT + \left(\frac{\partial q}{\partial V} \right)_{T,\underline{N}} dV + \sum \left(\frac{\partial q}{\partial N_i} \right)_{T,V,N_{j\neq i}} dN_i \qquad (2)$$

Subtracting (2) from (1) yields

$$0 = -\left(\frac{\partial q}{\partial T} \right)_{V,\underline{N}} dT - \left(\frac{\partial q}{\partial V} \right)_{T,\underline{N}} dV + \sum \left[\overline{q}_i - \left(\frac{\partial q}{\partial N_i} \right)_{T,V,N_{j\neq i}} \right] dN_i + \sum N_i d\overline{q}_i$$

At constant T and V

$$0 = \sum \left[\overline{q}_i - \left(\frac{\partial q}{\partial N_i} \right)_{T,V,\underline{N}} \right] dN_i + \sum N_i d\overline{q}_i$$

(general equation)

For $q = A$, $\overline{q}_i = \overline{A}_i$ and $\left(\frac{\partial q}{\partial N_i} \right)_{T,V,N_{j\neq i}} = \left(\frac{\partial A}{\partial N_i} \right)_{T,V,N_{j\neq i}} = \overline{G}_i$. Thus,

$$\overline{q}_i - \left(\frac{\partial q}{\partial N_i} \right)_{T,V,N_{j\neq i}} = \overline{A}_i - \overline{G}_i = -P\overline{V}_i \text{ and}$$

$$\sum N_i d\overline{A}_i \Big|_{T,V} = P \sum \overline{V}_i dN_i \Big|_{T,V} \text{ specific equation for } q = A$$

(b) Following the analysis above, we also get

$$0 = -\left(\frac{\partial q}{\partial U}\right)_{V,\underline{N}} dU - \left(\frac{\partial q}{\partial V}\right)_{U,\underline{N}} dV + \sum\left[\bar{q}_i - \left(\frac{\partial q}{\partial N_i}\right)_{U,V,N_{j\neq i}}\right]dN_i + \sum N_i d\bar{q}_i$$

and, at constant U and V

$$0 = \sum\left[\bar{q}_i - \left(\frac{\partial q}{\partial N_i}\right)_{U,V,N_{j\neq i}}\right]dN_i + \sum N_i d\bar{q}_i$$

Now, choosing $q = S$, and using that $\left(\dfrac{\partial S}{\partial N_i}\right)_{U,V,N_{j\neq i}} = -\dfrac{\overline{G}_i}{T}$, which is easily

derived, yields

$$-T\sum N_i d\overline{S}_i\big|_{U,V} = \sum \overline{H}_i dN_i\big|_{U,V}$$

(c) Following a similar analysis to those above, we obtain

$$0 = -\left(\frac{\partial q}{\partial S}\right)_{V,\underline{N}} dS - \left(\frac{\partial q}{\partial V}\right)_{S,\underline{N}} dV + \sum\left[\bar{q}_i - \left(\frac{\partial q}{\partial N_i}\right)_{S,V,N_{j\neq i}}\right]dN_i + \sum N_i d\bar{q}_i$$

which, at constant V and S, reduces to

$$0 = \sum\left[\bar{q}_i - \left(\frac{\partial q}{\partial N_i}\right)_{S,V,N_{j\neq i}}\right]dN_i + \sum N_i d\bar{q}_i$$

Finally, using $q = U$, and $(\partial U/\partial N_i)_{S,V,N_{j\neq i}} = \overline{G}_i$ yields

$$\sum N_i d\overline{U}_i\big|_{S,V} = \sum\left\{-P\overline{V}_i + T\overline{S}_i\right\}dN_i\big|_{S,V}$$

6.3 (a) At constant U and V, $S =$ maximum at equilibrium

$$S = S^{\mathrm{I}} + S^{\mathrm{II}} = \sum_{i=1}^{C} N_i^{\mathrm{I}}\overline{S}_i^{\mathrm{I}} + \sum_{i=1}^{C} N_i^{\mathrm{II}}\overline{S}_i^{\mathrm{II}}$$

but

$$dS = 0 = \left(\frac{\partial S^{\mathrm{I}}}{\partial U^{\mathrm{I}}}\right)_{V,\underline{N}} dU^{\mathrm{I}} + \left(\frac{\partial S^{\mathrm{I}}}{\partial V^{\mathrm{I}}}\right)_{U,\underline{N}} dV^{\mathrm{I}} + \sum\left(\frac{\partial S^{\mathrm{I}}}{\partial N_i^{\mathrm{I}}}\right)_{U,V,N_{j\neq i}} dN_i^{\mathrm{I}}$$

$$+ \left(\frac{\partial S^{\mathrm{II}}}{\partial U^{\mathrm{II}}}\right)_{V,\underline{N}} dU^{\mathrm{II}} + \left(\frac{\partial S^{\mathrm{II}}}{\partial V^{\mathrm{II}}}\right)_{U,\underline{N}} dV^{\mathrm{II}} + \sum\left(\frac{\partial S^{\mathrm{II}}}{\partial N_i^{\mathrm{II}}}\right)_{U,V,N_{j\neq i}} dN_i^{\mathrm{II}}$$

Since $U = U^{\mathrm{I}} + U^{\mathrm{II}} =$ constant, $dU^{\mathrm{II}} = -dU^{\mathrm{I}}$

Since $V = V^{\mathrm{I}} + V^{\mathrm{II}} =$ constant, $dV^{\mathrm{II}} = -dV^{\mathrm{I}}$

and since $N_i = N_i^{\mathrm{I}} + N_i^{\mathrm{II}} =$ constant, $dN_i^{\mathrm{II}} = -dN_i^{\mathrm{I}}$

Also,

$$\left(\frac{\partial S}{\partial U}\right)_{V,\underline{N}} = \frac{1}{T}; \quad \left(\frac{\partial S}{\partial V}\right)_{U,\underline{N}} = \frac{P}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial N_i}\right)_{U,V,N_{j\neq i}} = -\frac{\overline{G}_i}{T}$$

(see previous problem)

Thus

$$dS = 0 = \left(\frac{1}{T^{\mathrm{I}}} - \frac{1}{T^{\mathrm{II}}}\right)dU^{\mathrm{I}} + \left(\frac{P^{\mathrm{I}}}{T^{\mathrm{I}}} - \frac{P^{\mathrm{II}}}{T^{\mathrm{II}}}\right)dV^{\mathrm{I}} - \sum_i \left(\frac{\overline{G}_1^{\mathrm{I}}}{T^{\mathrm{I}}} - \frac{\overline{G}_1^{\mathrm{II}}}{T^{\mathrm{II}}}\right)dN_i^{\mathrm{I}}$$

$$\Rightarrow T^{\mathrm{I}} = T^{\mathrm{II}}; \; P^{\mathrm{I}} = P^{\mathrm{II}}; \text{ and } \overline{G}_i^{\mathrm{I}} = \overline{G}_i^{\mathrm{II}}$$

for equilibrium in a closed system at constant U and V.

(b) For a closed system at constant S and V, U has an extremum. Thus

$$dU = 0 = \left(\frac{\partial U^{\mathrm{I}}}{\partial S^{\mathrm{I}}}\right)_{V,\underline{N}} dS^{\mathrm{I}} + \left(\frac{\partial U^{\mathrm{I}}}{\partial V^{\mathrm{I}}}\right)_{S,\underline{N}} dV^{\mathrm{I}} + \sum_i \left(\frac{\partial U^{\mathrm{I}}}{\partial N_i^{\mathrm{I}}}\right)_{S,V,N_{j\neq i}} dN_i^{\mathrm{I}}$$

$$+ \left(\frac{\partial U^{\mathrm{II}}}{\partial S^{\mathrm{II}}}\right)_{V,\underline{N}} dS^{\mathrm{II}} + \left(\frac{\partial U^{\mathrm{II}}}{\partial V^{\mathrm{II}}}\right)_{S,\underline{N}} dV^{\mathrm{II}} + \sum_i \left(\frac{\partial U^{\mathrm{II}}}{\partial N_i^{\mathrm{II}}}\right)_{U,V,N_{j\neq i}} dN_i^{\mathrm{II}}$$

but S, V and N_j, $j = 1, \cdots, C$ are constant. Thus

$$dU = 0 = \left(T^{\mathrm{I}} - T^{\mathrm{II}}\right)dS^{\mathrm{I}} + \left(P^{\mathrm{I}} - P^{\mathrm{II}}\right)dV^{\mathrm{I}} + \sum_i \left(\overline{G}_i^{\mathrm{I}} - \overline{G}_i^{\mathrm{II}}\right)dN_i^{\mathrm{I}}$$

$$\Rightarrow T^{\mathrm{I}} = T^{\mathrm{II}}, \; P^{\mathrm{I}} = P^{\mathrm{II}} \text{ and } \overline{G}_i^{\mathrm{I}} = \overline{G}_i^{\mathrm{II}}$$

for equilibrium in a closed system at constant S and V.

6.4 (a) For a closed system at constant T and V, A is a minimum at equilibrium; thus $dA|_{V,T} = 0$. From Eqn. (6.2-5)

$$dA = -PdV - SdT + \sum \overline{G}_i dN_i \quad \text{or} \quad dA|_{V,T} = \sum \overline{G}_i dN_i$$

But, $N_i = N_{i,\,0} + n_i X$. Thus $dN_i = n_i dX$ and

$$dA|_{V,T} = \left(\sum n_i \overline{G}_i\right)dX = 0 \quad \text{or} \quad \left(\frac{\partial A}{\partial X}\right)_{V,T} = \sum_i n_i \overline{G}_i = 0.$$

(b) For a closed system at constant U and V, $S =$ maximum, or $dS|_{U,V} = 0$. From

Eqn. (6.2-4) $dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{1}{T}\sum \overline{G}_i dN_i$; thus

$$dS|_{U,V} = -\frac{1}{T}\sum \overline{G}_i dN_i \quad \text{or} \quad dS|_{U,V} = -\frac{1}{T}\left(\sum \overline{G}_i \boldsymbol{n}_i\right) dX$$

and

$$\left.\frac{\partial S}{\partial X}\right|_{U,V} = -\frac{1}{T}\sum_i \boldsymbol{n}_i \overline{G}_i = 0$$

6.5 Let m_i = molecular weight of species i. Multiplying Eqn. (6.3-2a) by m_i and summing over all species i yields, for a *closed* system

$$\sum m_i N_i = \text{total mass in system} = \underbrace{\sum m_i N_{i,0}}_{\substack{\text{total mass in} \\ \text{system initially}}} + X\sum \boldsymbol{n}_i m_i$$

However, since the total mass is a conserved quantity,

$$\sum m_i N_i = \sum m_i N_{i,0} \Rightarrow X\sum \boldsymbol{n}_i m_i = 0 \text{, where } X \text{ can take on any value.}$$

Consequently, if this equation is to be satisfied for all values of X, then $\sum \boldsymbol{n}_i m_i = 0$!

Similarly, in the mu lti-reaction case, starting from $N_i = N_{i,0} + \sum_{j=1}^{M} \boldsymbol{n}_{ij} X_j$, we get

$$\sum_{i=1}^{C} m_i N_i = \sum_{i=1}^{C} m_i N_{i,o} + \sum_{i=1}^{C} m_i \sum_{j=1}^{M} \boldsymbol{n}_{ij} X_j \Rightarrow \sum_{i=1}^{C} m_i \sum_{j=1}^{M} \boldsymbol{n}_{ij} X_j = 0 = \sum_{j=1}^{M} X_j \sum_{i=1}^{C} \boldsymbol{n}_{ij} m_i$$

Since the X_j's are not, in general, equal to zero, we have

$$\sum_{i=1}^{C} \boldsymbol{n}_{ij} m_i = 0$$

In particular, for the reaction $H_2O = H_2 + (1/2)O_2$, or $H_2 + (1/2)O_2 - H_2O = 0$, we have

$$\sum_i \boldsymbol{n}_{ij} m_i = (+1)(2) + \left(\frac{1}{2}\right)(32) + (-1)(18) = 0 .$$

6.6 From Eqns. (6.6-4) we have

$$\overline{V}_1 = \underline{V}_1 + \Delta\underline{V}_{\text{mix}} + x_2 \left.\frac{\partial(\Delta\underline{V}_{\text{mix}})}{\partial x_1}\right|_{T,P} \tag{1}$$

and

$$\overline{V}_2 = \underline{V}_2 + \Delta\underline{V}_{mix} + x_1 \frac{\P(\Delta\underline{V}_{mix})}{\P x_1}\bigg|_{T,P} \qquad (2)$$

Now since T, P and X, are the independent variables, we have that

0 since pure component volume is a function of
T and P only

$$d\overline{V}_1\big|_{T,P} = d\underline{V}_1\big|_{T,P} + d(\Delta\underline{v}_{mix})\big|_{T,P} + d\left[x_2 \frac{\P(\Delta\underline{V}_{mix})}{\P x_1}\right]_{T,P}$$

$$= \frac{\P(\Delta\underline{V}_{mix})}{\P x_1}\bigg|_{T,P} + \frac{\P(\Delta\underline{V}_{mix})}{\P x_1}\bigg|_{T,P}\frac{\P x_2}{\P x_1} dx_1 + x_2 \frac{\P^2(\Delta\underline{V}_{mix})}{\P x_1^2}\bigg|_{T,P} dx_1$$

$$= x_2 \frac{\P^2(\Delta\underline{V}_{mix})}{\P x_1^2}\bigg|_{T,P} dx_1 \text{ since } \frac{\P x_2}{\P x_1} = -1$$

Similarly

$$d\overline{V}_2\big|_{T,P} = -x_1 \frac{\P^2(\Delta\underline{V}_{mix})}{\P x_1^2}\bigg|_{T,P} dx_1$$

Thus

$$\sum x_i \, d\overline{V}_i\big|_{T,P} = x_1 x_2 \frac{\P^2(\Delta\underline{V}_{mix})}{\P x_1^2}\bigg|_{T,P} dx_1 - x_2 x_1 \frac{\P^2(\Delta\underline{V}_{mix})}{\P x_1^2}\bigg|_{T,P} dx_1 \equiv 0$$

Thus, $\overline{V}_1$ and $\overline{V}_2$ given by equations (1) and (2) identically satisfy the Gibbs-Duhem equation $\sum x_i d\overline{q}_i\big|_{T,P} = 0$.

A similar argument applies for the partial molar enthalpies of Eqn. (6.6-9).

6.7 (also available as a Mathcad worksheet)

The students can solve this problem by drawing tangent lines to the $\Delta\underline{V}_{mix}$ curves. Polak and Lu smoothed their data using the Redhich-Kister equation (see Eqn. (6.6-5a)). That is, they fitted their data to

$$\Delta\underline{V}_{mix} = x_1 x_2 \sum_{j=1}^{n} C_j (x_2 - x_1)^{j-1} = x_1 (1 - x_1) \sum C_j (1 - 2x)^{j-1}$$

Now

$$\frac{\P(\Delta\underline{V}_{mix})}{\P x_1} = (1 - x_1)\sum C_j(1 - 2x_1)^{j-1}$$

$$-x_1\sum C_j(1 - 2x_1)^{j-1} - 2x_1(1 - x_1)\sum C_j(j-1)(1 - 2x_1)^{j-2}$$

Thus $\quad \overline{V}_1 - \overline{V}_1 = (\Delta\underline{V}_{mix}) - x_2 \frac{\P(\Delta\underline{V}_{mix})}{\P x_1} = (1 - x_1)^2\{A - 2x_1 B\} \qquad (i)$

and

$$\overline{V}_2 - \underline{V}_2 = (\Delta\underline{V}_{\text{mix}}) - x_1 \frac{\P(\Delta\underline{V}_{\text{mix}})}{\P x_1} = x_1^2\{A + 2x_2 B\} \qquad (2)$$

where

$$A = \sum_{j=1}^{n} C_j(1 - 2x_1)^{j-1} \quad \text{and} \quad B = \sum_{j=1}^{n} C_j(j-1)(1 - 2x_1)^{j-2}$$

Taking species 1 to be methyl formate, Polak and Lu found

	C_1	C_2	C_3	C_4
methyl formate - Methanol	−0.33259	−0.10154	−0.0516	0.0264
methyl formate - Ethanol	0.81374	−0.00786	0.0846	0.0448

[units are cc/mol; multiply by 10^{-3} to get m^3/kmol]

I have used the equations above and the constants given to find $\overline{V}_1 - \underline{V}_1$ and $\overline{V}_2 - \overline{V}_2$, since this leads to more accurate results than the graphical method. The results are tabulated and plotted below.

Methyl formate - Methanol

x_{MF}	0	0.1	0.2	0.3	0.4	0.5
$\Delta\underline{V}_{\text{mix}}$ (cc/mol)	0	−0.039	−0.065	−0.080	−0.085	−0.083
$\overline{V}_1 - \underline{V}_1$		−0.459	−0.329	−0.225	−0.148	−0.093	−0.058
$\overline{V}_2 - \underline{V}_2$		0	−0.007	−0.025	−0.051	−0.080	−0.109

x_{MF}	0.6	0.7	0.8	0.9	1.0
$\Delta\underline{V}_{\text{mix}}$ (cc/mol)	−0.075	−0.063	−0.047	−0.027	0
$\overline{V}_1 - \underline{V}_1$	−0.035	−0.021	−0.011	−0.004	0
$\overline{V}_2 - \underline{V}_2$	−0.136	−0.162	−0.192	−0.236	−0.309

Thus $\overline{V}_{\text{MF}} = 62.78 + (\overline{V}_1 - \underline{V}_1)$ cc/mol or 10^{-3} m^3/kmol.
$\overline{V}_{\text{M}} = 40.73 + (\overline{V}_2 - \underline{V}_2)$.

Methyl formate - Ethanol

x_{MF}	0	0.1	0.2	0.3	0.4	0.5
$\Delta\underline{V}_{\text{mix}}$ (cc/mol)	0	0.080	0.136	0.174	0.196	0.203
$\overline{V}_1 - \underline{V}_1$		0.935	0.682	0.507	0.381	0.285	0.205
$\overline{V}_2 - \underline{V}_2$		0	0.013	0.043	0.085	0.137	0.201

x_{MF}	0.6	0.7	0.8	0.9	1.0
$\Delta\underline{V}_{\text{mix}}$ (cc/mol)	0.196	0.174	0.134	0.077	0
$\overline{V}_1 - \underline{V}_1$	0.138	0.081	0.037	0.010	0
$\overline{V}_2 - \underline{V}_2$	0.284	0.390	0.522	0.680	0.861

Thus $\overline{V}_{MF} = 62.78 + (\overline{V}_1 - \underline{V}_1)$ cc/mol. Multiply by 10^{-3} for $m^3/kmol$.

$\overline{V}_E = 58.68 + (\overline{V}_2 - \underline{V}_2)$
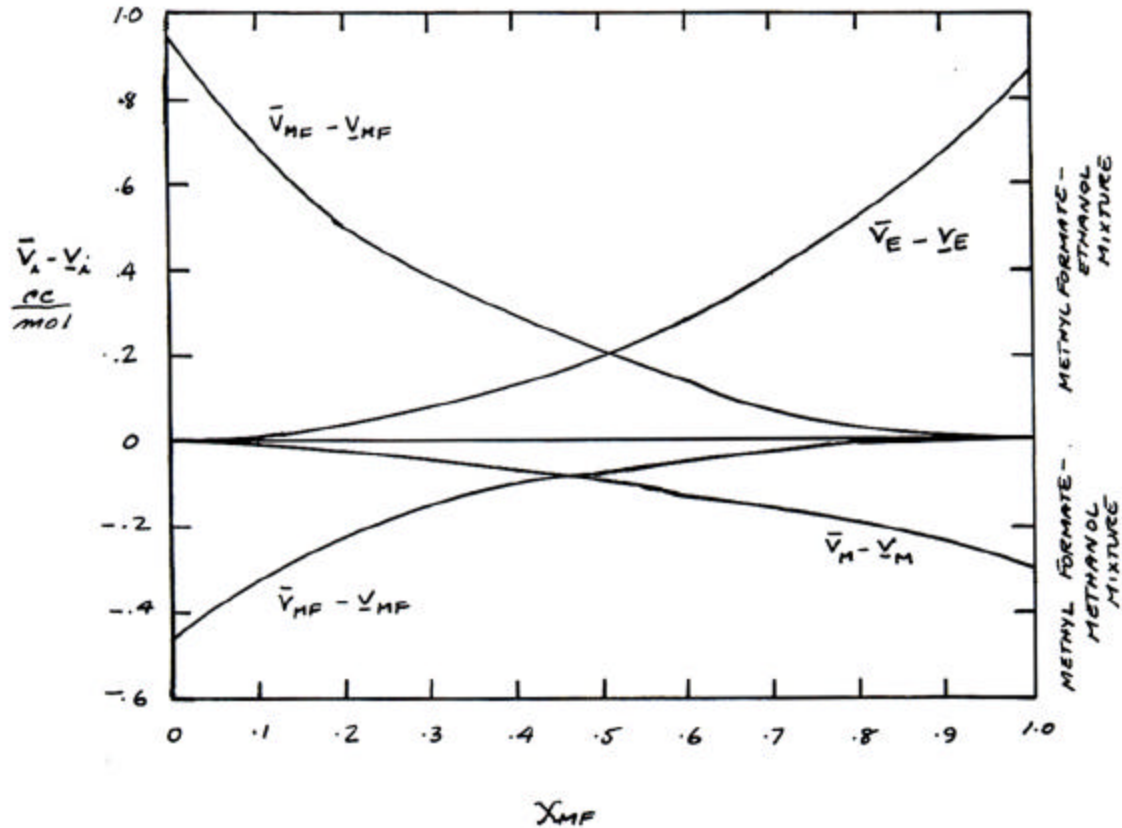
6.8 This problem is similar to the last one, and will be treated in a similar fashion. Fenby and Ruenkrairergasa give their data in the form

$$\Delta \underline{H}_{mix}(J/mol) = x_2(1-x_2)\sum_{j=1}^{n} C_j(1-2x_2)^{j-1} \qquad (1)$$

where component 2 is the fluorobenzene. The constants given in the aforementioned reference and Fenby and Scott *J. Phys. Chem* **71**, 4103 (1967) are given below

System	C_1	C_2	C_3	C_4
$C_6H_6 - C_6F_5Cl$	−2683	929	970	0
$C_6H_6 - C_6F_5Br$	−3087	356	696	0
$C_6H_6 - C_6F_5I$	−4322	−161	324	0
$C_6H_6 - C_6F_6$	−1984	+1483	+1169	0
$C_6H_6 - C_6F_5H$	230	+578	+409	+168

If we replace x_2 with $1-x_1$ in Eqn. (1), we regain the equation of the previous illustration, except for a factor of $(-1)^{j-1}$ in the sum and the corresponding places in the other equations.

$x_{C_6H_6}$	$\Delta\underline{H}_{mix}$	$(\overline{H}-\underline{H})_{C_6H_6}$	$(\overline{H}-\underline{H})_{C_6F_5Cl}$	$x_{C_6F_5Cl}$
0	0	–2642	0	1.0
0.1	–252	–2171	–39.2	0.9
0.2	–463	–1790	–130	0.8
0.3	–609	–1466	–242	0.7
0.4	–679	–1175	–349	0.6
0.5	–671	–903	–439	0.5
0.6	–590	–646	–506	0.4
0.7	–453	–409	–555	0.3
0.8	–284	–205	–601	0.2
0.9	–119	–57.8	–666	0.1
1.0	0	0	–784	0

[Note: J/mol]

	$C_6H_6-C_6F_5Br$			$C_6H_6-C_6F_5I$			
$x_{C_6H_6}$	$\Delta\underline{H}_{mix}$	$(\overline{H}-\underline{H})$ C_6H_6	$(\overline{H}-\underline{H})$ C_6F_5Br	$\Delta\underline{H}_{mix}$	$(\overline{H}-\underline{H})$ C_6H_6	$(\overline{H}-\underline{H})$ C_6F_5I	$x_{C_6F_5x}$
0	0	–2747	0	0	–3837	0	1.0
0.1	–263	–2248	–42.9	–359	–3119	–52.1	0.9
0.2	–488	–1829	–153	–657	–2489	–200	0.8
0.3	–654	–1469	–306	–883	–1937	–431	0.7
0.4	–751	–1149	–486	–1026	–1456	–740	0.6
0.5	–772	–861	–683	–1081	–1040	–1121	0.5
0.6	–717	–600	–893	–1042	–689	–1572	0.4
0.7	–595	–370	–1120	–910	–402	–2095	0.3
0.8	–420	–181	–1374	–688	–187	–2695	0.2
0.9	–212	–50.0	–1671	–382	–48.9	–3379	0.1
1.0	0	0	–2035	0	0	–4159	0

	$C_6H_6 - C_6F_6$			$C_6H_6 - C_6F_5H$			
$x_{C_6H_6}$	$\Delta\underline{H}_{mix}$	$(\overline{H}-\underline{H})$	$(\overline{H}-\underline{H})$	$\Delta\underline{H}_{mix}$	$(\overline{H}-\underline{H})$	$(\overline{H}-\underline{H})$	$x_{C_6F_5x}$
		C_6H_6	C_6F_6		C_6H_6	C_6F_5H	
0	0	–2298	0	0	61.0	0	1.0
0.1	–218	–1899	–31.2	–2.2	36.2	–1.1	0.9
0.2	–392	–1590	–93.0	–3.9	–2.8	+6.8	0.8
0.3	–502	–1332	–146	13.5	–42.3	+37.4	0.7
0.4	–536	–1097	–162	31.4	–72.3	+100	0.6
0.5	–496	–867	–125	57.5	–87.0	+202	0.5
0.6	–394	–637	–28.9	86.9	–84.5	344	0.4
0.7	–253	–413	+121	110	–66.7	524	0.3
0.8	–108	–212	+308	116	–39.4	+737	0.2
0.9	–4.5	–60.9	+503	85.9	–12.6	+973	0.1
1.0	0	0	+688	0	0	1217	0
			↑		↑	↑	

Note: Changes in sign in column

6.9 (a) Gibbs Phase Rule: $F = C - M - P + 2$

$P = 2$, $C = 2$, $M = 0 \Rightarrow F = 2 - 0 - 2 + 2 = 2$ degrees of freedom

Thus can fix two variables, usually from among T, P, x and y.

(b) $P = 1$, $C = 3$ and $M = 1 \Rightarrow F = 3 - 1 - 1 + 2 = 3$ degrees of freedom

Thus, we can fix 3 variables, for example, T, P and x_{H_2}.

(c) Formation reactions

$$C + 2O \rightarrow CO_2$$
$$C + O \rightarrow CO$$
$$2H \rightarrow H_2$$
$$C + 4H \rightarrow CH_4$$
$$2H + O \rightarrow H_2O$$

Use $O = CO - C$ and $H = \dfrac{1}{2}H_2$ to eliminate O and H from the set so that

$$C + 2(CO - C) \rightarrow CO_2 \qquad 2CO \rightarrow CO_2 + C$$
$$C + 4(1/2\ H_2) \rightarrow CH_4 \Rightarrow C + 2H_2 \rightarrow CH_4$$
$$2(1/2\ H_2) + (CO - C) \rightarrow H_2O \qquad H_2 + CO \rightarrow H_2O + C$$
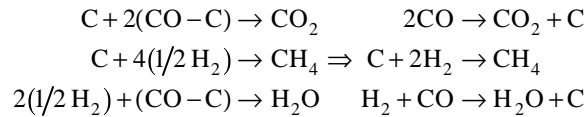
Thus we have found *a* set (there is no unique set) of three independent reactions among the six species. Consequently, $C = 6$, $M = 3$, $P = 2$ (solid carbon + gas phase).

$F = C - M - P + 2 = 6 - 3 - 2 + 2 = 3$ degrees of freedom. As a check:

$$\text{\# of unknowns} = 8\left(T^S,\ P^S,\ T^V,\ P^V,\ x_{CO_2},\ x_{CO},\ x_{H_2},\ x_{CH_4}\right)$$

$$\text{Note: } x_{H_2O} = 1 - x_{CO_2} - x_{CO} - x_{H_2} - x_{CH_4}$$

Relations among the unknowns $T^S = T^V$, $P^S = P^V$, no phase equilibrium relations, but 3 chemical equilibrium relations of the form $\sum n_{ij} \overline{G}_i = 0$.

$$8 \text{ unknowns} - 5 \text{ eqns.} = 3 \text{ unspecified unknowns or}$$
$$3 \text{ degrees of freedom}$$

6.10 (a) In general, for a binary, two-phase mixture $(C = 2,\ M = 0,\ P = 2)$

$F = C - M - P + 2 = 2 - 0 - 2 + 2 = 2$ degrees of freedom.

However, for an azeotrope there is the additional restriction $x_1 = y_1$, which eliminates one degree of freedom. Thus, there is only 1 degree of freedom for a binary, azeotropic system.

(b) In osmotic equilibrium $P^I \neq P^{II}$, since the membrane is capable of supporting a pressure difference, and $\overline{G}_2^I \neq \overline{G}_2^{II}$, where 2 is the species which does not pass through the membrane. Therefore, the independent unknowns are T^I, P^I, x_1^I, T^{II}, P^{II} and x_1^{II}. [Note, x_2^I and x_2^{II} are not independent unknowns since $x_2^I = 1 - x_1^I$ and $x_2^{II} = 1 - x_1^{II}$]. There are *two* equilibrium relations between these six unknowns: viz. $T^I = T^{II}$ and $\overline{G}_1^I = \overline{G}_1^{II}$. Consequently, there are four degrees of freedom ... that is, as we shall see in Sec. 8.7, if T, P^I, P^{II} and x_1^I are specified, x_1^{II} will be fixed.

(c) Case I: $M = 0,\ C = 2,\ P = 2 \Rightarrow F = 2 - 0 - 2 + 2 = 2$

Case II: $M = 0,\ C = 2,\ P = 3 \Rightarrow F = 2 - 0 - 3 + 2 = 1$

6.11 (a) Gibbs Phase Rule: $F = C - M - P + 2$

$C = 2,\ M = 0 \Rightarrow F = 2 - 0 - P + 2 = 4 - P$ degrees of freedom.

Therefore, a maximum of 4 phases can exist at equilibrium (for example a solid, two liquids and a vapor, or two solids, a liquid and a vapor, etc.)

(b) Gibbs Phase Rule: $F = C - M - P + 2$

$C = 2,\ M = 1 \Rightarrow F = 2 - 1 - P + 2 = 3 - P$ degrees of freedom.

Therefore, a maximum of e phases can exist at equilibrium (for example a two liquids and a vapor, or a solid, a liquid and a vapor, etc.)

6.12 (a) $\dfrac{dN_i}{dt} = \dot{N}_i + \dot{N}_{i,\text{rxn}}$

$$\frac{dU}{dt} = \sum \dot{N}_i \overline{H}_i + \dot{Q} - \cancelto{0}{\dot{W}_s} - P\frac{dV}{dt}$$

$$\frac{dS}{dt} = \sum \dot{N}_i \overline{S}_i + \frac{\dot{Q}}{T} + \dot{S}_{\text{gen}}$$

$$T\frac{dS}{dt} - T\sum \dot{N}_i \overline{S}_i - T\dot{S}_{\text{gen}} = \dot{Q}$$

$$\frac{dU}{dt} = \sum \dot{N}_i \overline{H}_i + T\frac{dS}{dt} - T\sum \dot{N}_i \overline{S}_i - T\dot{S}_{gen} - P\frac{dV}{dt}$$

$$\frac{dU}{dt} + P\frac{dV}{dt} - T\frac{dS}{dt} = \sum \dot{N}_i (\overline{H}_i - T\overline{S}_i) - T\dot{S}_{gen}$$

$$\frac{dU}{dt} + P\frac{dV}{dt} - T\frac{dS}{dt} = \sum \dot{N}_i \overline{m}_i - T\dot{S}_{gen} = \sum \left(\frac{dN_i}{dt} - \mathbf{n}_i \frac{dX}{dt}\right)\overline{m}_i - T\dot{S}_{gen}$$

General expression

Now

System is only permeable to species 1

$$\frac{dU}{dt} + P\frac{dV}{dt} - T\frac{dS}{dt} - \left(\frac{dN_1}{dt} - \mathbf{n}_1 \frac{dX}{dt}\right)\mathbf{m}_1 = -T\dot{S}_{gen} \leq 0$$

When T and P constant

$$\frac{d}{dt}(U + PV - TS) - \frac{d}{dt}[(N_1 - \mathbf{n}_1 X)\mathbf{m}_1] \leq 0$$

$$\frac{d}{dt}[G - (N_1 - \mathbf{n}_1 X)\mathbf{m}_1] \leq 0$$

$$\Rightarrow G - (N_1 - \mathbf{n}_1 X)\mathbf{m}_1 = \text{minimum at equilibrium}$$

(b) When T and V are constant

$$\frac{d}{dt}(U - TS) - \frac{d}{dt}[(N_1 - \mathbf{n}_1 X)\mathbf{m}_1] \leq 0$$

$$\Rightarrow A - (N_1 - \mathbf{n}_1 X)\mathbf{m}_1 = \text{minimum at equilibrium}$$

6.13 (a) $2N \rightarrow N_2$

$2O \rightarrow O_2$

$2N + O \rightarrow N_2O$ $N_2 + \frac{1}{2}O_2 \rightarrow N_2O$

$2N + 2O \rightarrow 2NO$ $N_2 + O_2 \rightarrow 2NO$

$2N + 4O \rightarrow N_2O_4$ $N_2 + 2O_2 \rightarrow N_2O_4$

$2N + 4O \rightarrow 2NO_2$ $N_2 + 2O_2 \rightarrow 2NO_2$

$2N + 5O \rightarrow N_2O_5$ $N_2 + \frac{5}{2}O_2 \rightarrow N_2O_5$
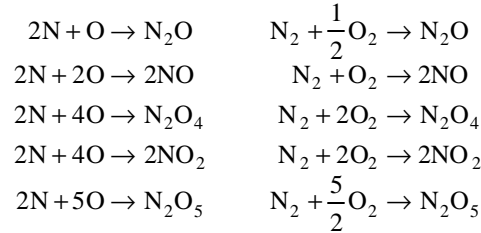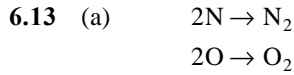
$\Rightarrow 5$ independent reactions

(b) $F = C - M - P + 2 = 7 - 5 - 1 + 2 = 9 - 6 = 3$

$F = 3$ degrees of freedom

(c) 1 degree of freedom used in $O_2:N_2$ ratio $\Rightarrow$ 2 degres of freedom

6.14 Mass balance: $M_1 + M_2 = M_f$ Molecular weight $H_2O = 18.02$ g/mol

Energy balance: $M_1\hat{U}_1 + M_2\hat{U}_2 = M_f\hat{U}_f$

In each case the system is M_1 kg of solution 1 + M_2 kg of solution 2.

Since $Q = 0$, $W_s = 0$ (adiabatic mixing)

For liquids $\hat{U} \equiv \hat{H}$. Thus we have

$$\hat{H}_f = \frac{M_1\hat{H}_1 + M_2\hat{H}_2}{M_1 + M_2}$$

when $M_1 = M_2$; $\hat{H}_f = \frac{1}{2}(\hat{H}_1 + \hat{H}_2)$.

(a) Read from Figure 6.1-1

$$\hat{H}_1 = 6.9 \times 10^3 \text{ J/kg}$$
$$\hat{H}_2 = -6.1 \times 10^3 \text{ J/kg}$$

Thus $\hat{H}_f = \frac{1}{2}(5.410 \times 10^4) = 2.705 \times 10^4 \text{ J/kg}$

To find the composition, so a sulfuric acid balance

$$r_1 M_1 + r_2 M_2 = r_f M_f \Rightarrow r_f = \frac{1}{2}(r_1 + r_2) \text{ since } M_1 = M_2$$

where r_i = weight percent of ith flow stream.

Thus $r_f = \frac{1}{2}(10 + 90) = 50 \text{ wt \%}$ sulfuric acid. From Figure 6.1-1

$$\begin{array}{c} 50 \text{ wt \% } H_2SO_4 \\ \hat{H} = \hat{U} = 2.705 \times 10^4 \text{ J/kg} \end{array} \Rightarrow T_f \sim 110°C$$

(b) Here $\hat{H}_1 = 6.9 \times 10^3 \text{ J/kg}$,

$\hat{H}_2 = -3.186 \times 10^5 \text{ J/kg} \Rightarrow \hat{H}_f = \frac{1}{2}(6.9 - 318.6) \times 10^3 = -1.56 \times 10^5 \text{ J/kg}$ and

$r_1 = 10 \text{ wt \%}$, $r_2 = 60 \text{ wt \%} \Rightarrow r_f = 35 \text{ wt \%}$. Using

Figure 6.1-1, $T_f \sim 22°C$.

Notice that there is a balance between the energy released in mixing, $\Delta \hat{H}_{mix}$, and the energy absorbed in heating the mixture, $C_P \Delta T$. In case (a), $\Delta \hat{H}_{mix}$ is very large, and $T_f > T_1$ or T_2, while in case (b) $\Delta \hat{H}_{mix}$ is smaller, so that $T_f \sim T_1$.

6.15 (a) MW $H_2O = 18.02 \text{ g/mol}$; MW $H_2SO_4 = 98.08 \text{ g/mol}$

$$100 \text{ g } H_2O = 5.55 \text{ mol}$$
$$100 \text{ g } H_2SO_4 = 1.02 \text{ mol}$$

Note: When these are mixed, a solution containing 5.44 mol H_2O /mol acid is formed. $\Delta \underline{H}_s$ for such a solution is –58,390 J/mol acid. Thus,

total heat released $= 1.02 \text{ mol acid} \times (-58,390 \text{ J/mol acid}) = -59,558 \text{ J}$

(Negative sign means that heat is released!)

(b) Adding another 100 grams of water produces a solution which contains 10.88 mol H_2O /mol acid. From the graph $\Delta \underline{H}_s = -64,850 \text{ J/mol acid}$. However, – 58,390 J/mol of acid were released in preparing the first solution, so that only – 6,460 J/mol acid, or 6,590 J, are released on this further dilution.

(c) 60 wt % $H_2SO_4 \Rightarrow \dfrac{40/18.02}{60/98.08} = 3.629$ moles H_2O/moles acid   for   which

$\Delta \underline{H}_s = -52,300$ J/mol acid , and

$$\Delta H_s = -52,300 \text{ J/mol acid} \times \frac{60 \text{ mol acid}}{98.08} = -31,990 \text{ J}$$

Note: Enthalpy of 60 WT% solution is –31,990 J relative to pure components at the same temperature. Similarly 25 wt % $H_2SO_4 \Rightarrow 16.27$ mol H_2O/mol acid , $\Delta \underline{H}_s \sim -68,830$ J/mol acid

and

$$\Delta H_s = -68,830 \text{ J/mol acid} \times \frac{0.25 \times 75}{98.08} = -13,160 \text{ J}$$

Final solution $=175$ grams; 78.75 grams acid $=0.803$ mol,

96.25 grams water $= 5.347$ mol $\Rightarrow 6.66$ mol H_2O/mol acid . So that

$$\Delta \underline{H}_s = -60,670 \text{ J/mol acid}$$
$$\Delta H_s = -48,720 \text{ J}$$

Thus, enthalpy change on mixing, ΔH_{mix} is

$$\Delta H_{mix} = -48,720 - (-31,990 - 13,160) = -3570 \text{ J}$$

Thus, $3570 \text{ J} = 357$ kJ must be *removed* to keep solution isothermal!

(d) For 1 mole of solute: $(1+ N_2)\underline{H}_{mix} = \underline{H}_1 + N_2 \underline{H}_2 + 1 \cdot \Delta \underline{H}_s\left(\dfrac{N_2}{N_1}\right)$ (argument of

$\Delta \underline{H}_s$) and for N_1 moles of solute and N_2 moles of solvent.

$$(N_1 + N_2)\underline{H}_{mix} = N_1 \underline{H}_1 + N_2 \underline{H}_2 + N_1 \Delta \underline{H}_s\left(\frac{N_2}{N_1}\right) = H_{mix}$$

Now

$$\overline{H}_1 = \left(\frac{\P H_{mix}}{\P N_1}\right)_{T,P} = \underline{H}_1 + \Delta \underline{H}_s\left(\frac{N_2}{N_1}\right) + N_1 \left.\frac{\P(\Delta \underline{H}_s)}{\P(N_2/N_1)}\right|_{T,P} \cdot \left.\frac{\P(N_2/N_1)}{\P N_1}\right|_{T,P}$$

or

$$\overline{H}_1 - \underline{H}_1 = \Delta \underline{H}_s\left(\frac{N_2}{N_1}\right) - \frac{N_2}{N_1}\left[\frac{\P \Delta \underline{H}_s(N_2/N_1)}{\P(N_2/N_1)}\right]_{T,P} \quad \text{since} \quad \frac{\P(N_2/N_1)}{\P N_1} = -\frac{N_2}{N_1^2}$$

Similarly, starting from $\overline{H}_2 = \left(\dfrac{\P H_{mix}}{\P N_2}\right)_{T,P}$ we obtain

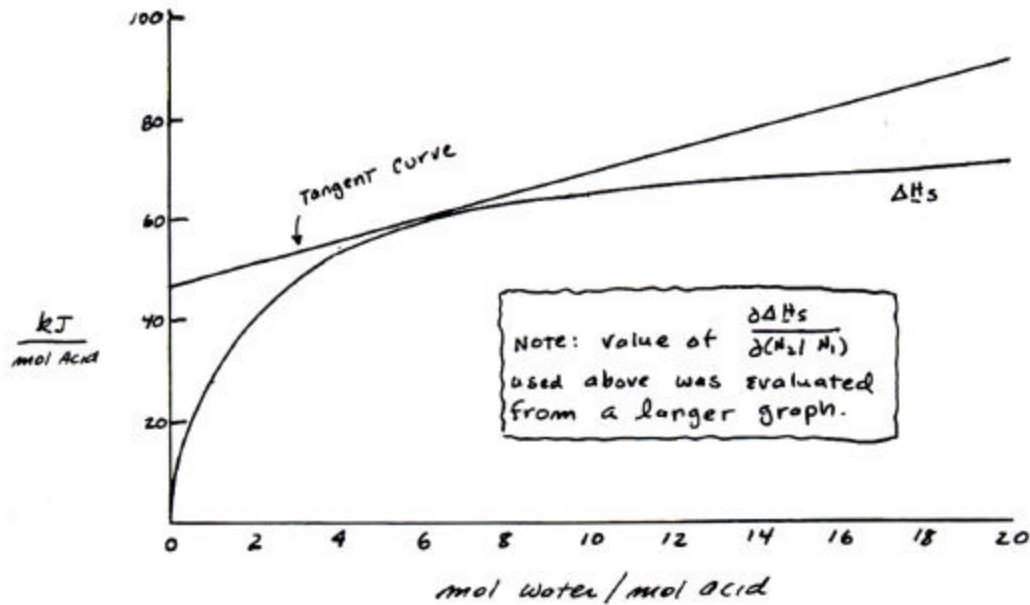$$\overline{H}_2 - \underline{H}_2 = \left.\frac{\P \Delta \underline{H}_s(N_2/N_1)}{\P(N_2/N_1)}\right|_{T,P}$$

(e) 50 wt % acid $\Rightarrow \dfrac{50/18.02}{50/98.08} = 5.443$ mol H_2O/mol acid

$\Delta \underline{H}_s(5.443) = -58,370$ J/mol and, from the accompanying graph

$$\left.\frac{\P \Delta \underline{H}_s(N_2/N_1)}{\P(N_2/N_1)}\right|_{\text{at } N_2/N_1 = 5.443} = \frac{(-91,630) - (-46,030)}{20} = -2,280 \text{ J/mol}$$

so that $\overline{H}_2 - \underline{H}_2 = -2,280$ J/mol and

$$\overline{H}_1 - \underline{H}_1 = (-58{,}370) - 5.44(-2{,}280) = -45{,}967 \ \text{J/mol} \ .$$

6.16 To get partial molar properties it is easiest to first convert all data in problem to mole fractions and properties per mole.

$$x_{\text{CCl}_4} = \frac{\text{wt \% CCl}_4/153.84}{(\text{wt \% CCl}_4/153.84) + \left[(100 - \text{wt \% CCl}_4)/78.11\right]}$$

where $\text{MW}_{\text{CCl}_4} = 153.84$; $\text{MW}_{\text{C}_6\text{H}_6} = 78.11$.

$$C_P(\text{mole mixture}) = C_P(\text{grams mixture}) \times (\text{MW of mixture})$$
$$= C_P \times \left[x_{\text{CCl}_4} \times 153.84 + \left(1 - x_{\text{CCl}_4}\right) \times 78.11\right]$$

also, compute $\sum x_i C_{P,i}$, where $C_{P,i}$ = heat capacity of pure species i and $\Delta C_{P,\text{mix}} = C_P(\text{mixture}) - \sum x_i C_{P,i}$. Results are given below:

Wt % CCl$_4$	x_{CCl_4}	C_P J/mol K	$\sum x_i C_{P,i}$	$\Delta C_{P,\text{mix}}$ (J/mol K)
0	0	137.90	137.90	0
10	0.0534	133.91	137.17	–3.26
20	0.1126	129.55	136.35	–6.80
30	0.1787	124.45	135.44	–10.99
40	0.2529	118.85	134.42	–15.67
50	0.3368	113.98	133.72	–19.74
60	0.4323	111.29	131.96	–20.67
70	0.5423	110.48	130.44	–19.96
80	0.6701	110.59	128.69	–18.10
90	0.8205	114.44	126.62	–12.18
100	1	124.15	124.15	0

Using these data, and the graphical procedure introduced in Sec. 6.6, we obtain the following results.

x_{CCl_4}	0	0.1	0.2	0.3	0.4	0.5
$\left(\overline{C}_P - C_P\right)_{CCl_4}$	–71	–60.7	–58.0	–44.5	–27.5	–17.5
$\overline{C}_{P,CCl_4}$	53.15	63.5	66.2	79.7	96.7	106.7
$\left(\overline{C}_P - C_P\right)_{C_6H_6}$	0	–0.5	–1.3	–6.7	–16.0	–24.0
$\overline{C}_{P,C_6H_6}$	137.9	137.4	136.6	131.2	121.9	113.9

x_{CCl_4}	0.6	0.7	0.8	0.9	1.0
$\left(\overline{C}_P - C_P\right)_{CCl_4}$	–11.8	–8.7	–4.1	–1.2	0
$\overline{C}_{P,CCl_4}$	112.4	115.45	120.1	123.0	124.15
$\left(\overline{C}_P - C_P\right)_{C_6H_6}$	–30.8	–36.7	–49.8	–67.5	–80.5
$\overline{C}_{P,C_6H_6}$	107.1	101.2	88.1	70.4	57.4
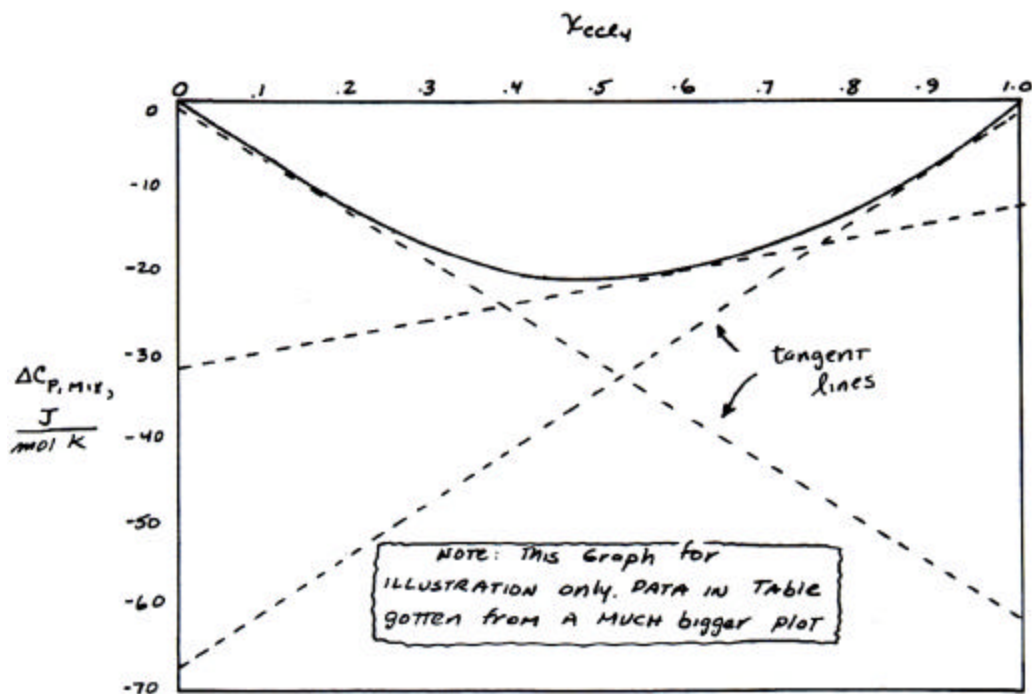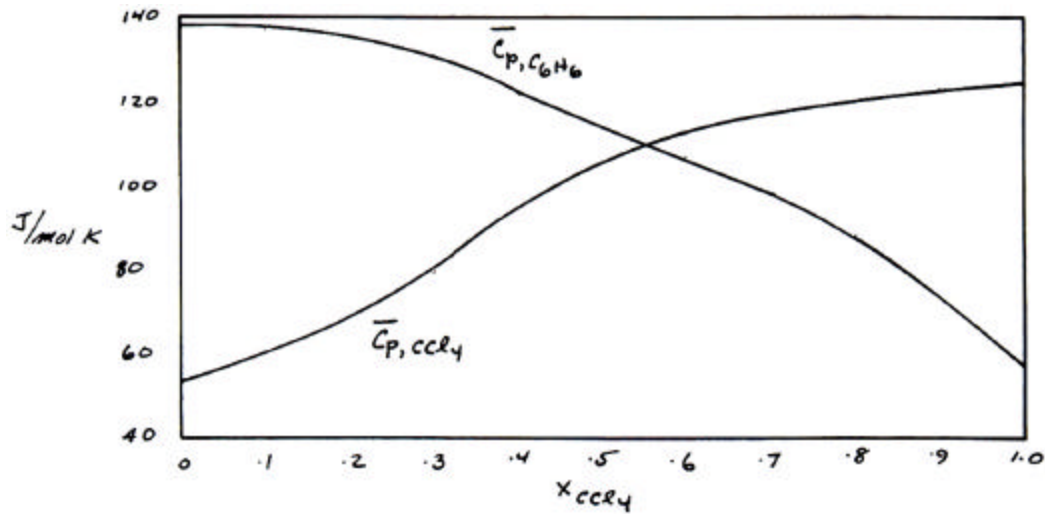
An alternate solution to this problem follows.

Alternate Solution to Problem 6.16

Instead of using Equations (6.6-10a and b) and $\Delta C_{P,\text{mix}}$ data, Equations (6.6-11a and b) and the heat capacity data for the mixture can be used. Since Equations (6.6-11a and b) are very similar to Equations (6.6-10a and b) [of which Equations (6.6-4a and b) and (6.6-9a and b) are special cases], it follows that the graphical construction discussed in Sec. 6.6 can be used. The difference, however, is that the tangents to the $C_{P,\text{mix}}$ vs. mole fraction curve will give $\overline{C}_{P,\text{CCl}_4}$ and $\overline{C}_{P,\text{C}_6\text{H}_6}$ directly, rather than $(\overline{C}_P - C_P)_{\text{CCl}_4}$ and $(\overline{C}_P - C_P)_{\text{C}_6\text{H}_6}$ as before. An illustrative graph, and the numerical results obtained using a much larger graph are given below:

x_{CCl_4}	0	0.1	0.2	0.3	0.4	0.5
$\overline{C}_{P,\text{CCl}_4}$	3.0	63.0	63.0	82.0	97.0	106.2
$\overline{C}_{P,\text{C}_6\text{H}_6}$	137.9	137.9	137.9	130.7	122.9	114.7

x_{CCl_4}	0.6	0.7	0.8	0.9	1.0
$\overline{C}_{P,\text{CCl}_4}$	113.0	117.0	120.3	123.2	124.15
$\overline{C}_{P,\text{C}_6\text{H}_6}$	105.7	97.6	87.3	70.8	55.9
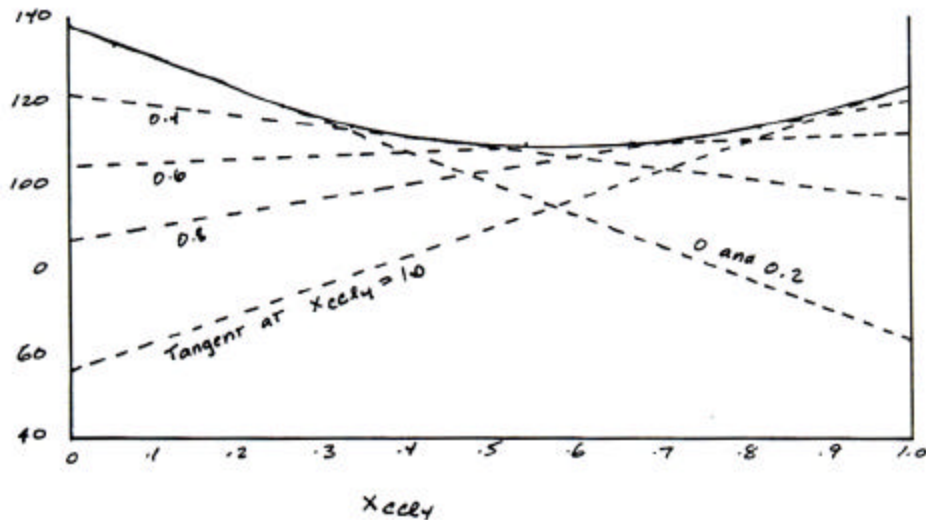
Note that these results differ from previous results by small amounts. Previous results are probably more accurate since the curvature of $\Delta C_{P,\,mix}$ vs. x_{CCl_4} is greater than that of $C_{P,\,mix}$ vs. x_{CCl_4}, so tangents are found with greater accuracy.

6.17 Let

$x = $ lbs. of 20 WT% solution $\left.\right\rbrace$ used to make 1 lb.
$y = $ lbs. of pure acid $\quad\quad$ of 60 WT% solution

(a) Total mass balance: $x + y = 1$

Species mass balance on acid: $0.2x + y = (0.6)(1)$

$\Rightarrow 0.2x + (1 - x) = 0.6$ or $x = 0.5$ kg 20 WT% solution, $y = 0.5$ kg pure acid.

(b) From Figure 6.1-1

$$\hat{H}(20 \text{ wt\%, } 5°C) = -1.22 \times 10^5 \text{ J/kg}$$

$$\hat{H}(100 \text{ wt\%, } 50°C) = 7.10 \times 10^4 \text{ J/kg}$$

$$\hat{H}(60 \text{ wt\%, } 70°C) = -1.59 \times 10^5 \text{ J/kg}$$

$$\hat{H}(60 \text{ wt\%, boiling point}) = \hat{H}(60 \text{ wt\%, } 143°C) \sim 0 \text{ J/kg}$$

Using the change over a time interval form of the energy balance equation, considering the initial state to be two 0.5 lbs. of separated 20 WT% and pure acid solutions, and the final state to be 1 lb. of mixed solution, and neglecting the difference between $\hat{H}$ and $\hat{U}$ for these liquids, yields

$$\hat{H}\left(60 \text{ wt\%, } T_f\right) - 0.5\hat{H}(20 \text{ wt\%, } 5°C) - 0.5\hat{H}(100 \text{ wt\%, } 50°C) = Q$$

at $T_f = 70^\circ C$

$$Q = \left[-1.59 \times 10^5 - 0.5 \times \left(-1.22 \times 10^5\right) - 0.5 \times \left(7.1 \times 10^4\right)\right]$$
$$= -6.25 \times 10^4 \text{ J/kg final solution}$$

at $T_f = \text{boiling point} = 143^\circ C$

$$Q = \left[0 - 0.5\left(-1.22 \times 10^5\right) - 0.5\left(7.1 \times 10^4\right)\right] = -2.55 \times 10^4 \text{ J/kg final solution}$$

6.18 Suppose there was enough information available on Δq_{mix}, where q is any extensive thermodynamic property of a mixture, as a function of the three mole numbers N_1, N_2, and N_3, that the data could be fitted to a polynomial expression in x_1, x_2 and x_3 or, equivalently, in N_1, N_2 and N_3 where $N = \sum_i N_i$. The partial molar properties could then be obtained by differentiation of the polynomial expression for Δq_{mix}. That is since

$$q = Nq = \sum_{i=1}^{3} N_i q_i + \Delta q_{mix}(N_1, N_2, N_3)$$

$$\overline{q_i} = \frac{\partial q}{\partial N_i}\bigg|_{T,P,N_{j\neq i}} = q_i + \frac{\partial(\Delta q_{mix})}{\partial N_i}\bigg|_{T,P,N_{j\neq i}}$$

so that

$$\overline{q_i} - q_i = \frac{\partial(\Delta q_{mix})}{\partial N_i}\bigg|_{T,P,N_{j\neq i}}$$

Alternately, graphical methods could be developed for finding $\overline{q_i} - q_i$ along paths where N_i is varied, and other mole numbers are fixed (i.e., x_i is varied, while the mole ratios of the other species in the mixture are fixed.)

Since it is unlikely that enough information will be available for any mixing property to obtain Δq_{mix} as an explicit function of mole fractions or species mole numbers for ternary, quaternary, etc. mixtures, it is not surprising that there is little information on partial molar properties in such systems.

6.19 (a) The Gibbs-Duhem equation is (Equation 6.2-19b)

$$x_1 \left.\frac{\partial \overline{H}_1}{\partial x_1}\right|_{T,P} + x_2 \left.\frac{\partial \overline{H}_2}{\partial x_1}\right|_{T,P} = 0$$

Now $\left.\dfrac{\partial \overline{H}_1}{\partial x_1}\right|_{T,P} = 2x_2 b_1 \dfrac{\partial x_2}{\partial x_1} = -2b_1 x_2$, and $\left.\dfrac{\partial \overline{H}_2}{\partial x_1}\right|_{T,P} = +2b_2 x_1$ so that

$$x_1 \left.\frac{\partial \overline{H}_1}{\partial x_1}\right|_{T,P} + x_2 \left.\frac{\partial \overline{H}_2}{\partial x_1}\right|_{T,P} = 2(b_2 - b_1)x_1 x_2 = 0 \text{ for all } x_1 \Rightarrow b_1 = b_2 = b$$

(b) $\displaystyle\lim_{x_i \to 1} \overline{\theta}_i = \underline{\theta}_i \Rightarrow a_1 = \underline{H}_1$ and $a_2 = \underline{H}_2$ where $\underline{H}_1$ and $\underline{H}_2$ are the pure component molar enthalpies. Thus

$$\overline{H}_1 = \underline{H}_1 + bx_2^2 ;\ \overline{H}_2 = \underline{H}_2 + bx_1^2$$

and

$$\Delta \underline{H}_{mix} = x_1(\overline{H}_1 - \underline{H}_1) + x_2(\overline{H}_2 - \underline{H}_2) = x_1 bx_2^2 + x_2 bx_1^2$$
$$\Delta \underline{H}_{mix} = (x_1 + x_2)bx_1 x_2 = bx_1 x_2$$

6.20 Note: Sorry about 1 set of data being given in alcohol wt% and other in water mole %, but this is the way the data appeared in the International Critical Tables.
(a) First will convert the data to mole fractions.

$$\text{wt\% A} = \frac{\text{kg A} \times 100}{\text{kg A} + \text{kg W}} ;\ x_A = \frac{\text{kg A}/\text{MW}_A}{\text{kg A}/\text{MW}_A + \text{kg W}/\text{MW}_W}$$

$$\Rightarrow x_A = \frac{\text{wt\% A}}{\text{wt\% A} + (100 - \text{wt\% A})\text{MW}_A/\text{MW}_W}$$

Also, $\underline{V}_{mix} = \overline{MW}/\rho_{mix}$ where ρ_{mix} = mixture density and $\overline{MW}$ is the mole fraction averaged molecular weight of mixture (i.e., $\overline{MW} = \sum x_i \overline{MW}_i$)

Also, $\underline{V}_A = \text{MW}_A/\rho(100 \text{ wt\% alcohol})$ and

$\underline{V}_W = \text{MW}_W/\rho(0\% \text{ alcohol})$.

wt% alcohol	x_A	$\overline{MW}$	$\underline{V}_{mix} - \sum x_i \underline{V}_i$	$\Delta\underline{V}_{mix}$ (cc/mol) [multiply by 10^{-3} for $m^3/kmol$]
0	0	18	18.083–18.033	0
5	0.0202	18.566	18.765–18.846	−0.081
10	0.0417	19.168	19.521–19.711	−0.190
15	0.0464	19.809	20.315–20.633	−0.318
20	0.0891	20.495	21.159–21.690	−0.531
25	0.1151	21.231	22.077–22.678	−0.601
30	0.1436	22.021	23.088–23.813	−0.725
35	0.1740	22.872	24.091–25.036	−0.945
40	0.2069	22.793	25.442–26.360	−0.918
45	0.2425	24.790	26.809–27.793	−0.984
50	0.2813	25.876	28.317–29.355	−1.038
55	0.3235	27.058	29.978–31.053	−1.075
60	0.3699	28.357	31.823–32.920	−1.097
65	0.4209	29.785	33.865–34.973	−1.108
70	0.4773	31.364	36.147–37.243	−1.096
75	0.5440	33.120	38.710–39.766	−1.056
80	0.6102	35.038	41.600–42.592	−0.992
85	0.6892	37.298	44.883–45.771	−0.888
90	0.7788	39.806	48.663–49.377	−0.714
95	0.8814	42.679	53.070–53.507	−0.437
100	1.0	46.	58.280–52.280	0

The $\Delta\underline{V}_{mix}$ data are plotted, and the graphical procedure of Sec. 6.6 used to find $(\overline{V}_A - \underline{V}_A)$ and $(\overline{V}_W - \underline{V}_W)$. Results are given in the following table.
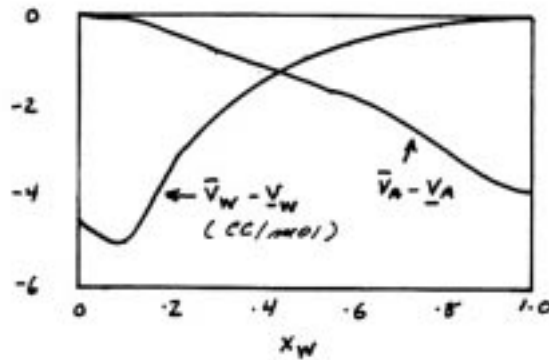
Next note that

$$\Delta \underline{H}_{\text{mix}} \left(\frac{\text{per mole}}{\text{mixture}} \right) = \frac{\text{Heat evolved}}{\text{per mole ethanol}} \times \frac{\text{Mole fraction}}{\text{of ethanol}} \times \underset{\substack{\text{Since heat is} \\ \text{evolved, } \Delta \underline{H}_{\text{mix}} \\ \text{is negative.}}}{(-1)}$$

Once $\Delta \underline{H}_{\text{mix}}$ is computed, graphical procedure is used to get $\left(\overline{H}_A - \underline{H}_A \right)$ and $\left(\overline{H}_W - \underline{H}_W \right)$. Table below gives $\left(\overline{V}_A - \underline{V}_A \right)$, $\left(\overline{V}_W - \underline{V}_W \right)$, $\left(\overline{H}_A - \underline{H}_A \right)$ and $\left(\overline{H}_W - \underline{H}_W \right)$ as a function of the water mole fraction.

x_W	$\overline{V}_W - \underline{V}_W$	$\overline{V}_A - \underline{V}_A$	$\Delta \underline{H}_{\text{mix}}$	$\overline{H}_W - \underline{H}_W$	$\overline{H}_A - \underline{H}_A$
	cc/mol			kJ/mol	
0	−4.5	0	0.	−0.85	0
0.05			−0.0400	−0.099	+0.015
0.1	−5.0	−0.05	−0.0828	−1.15	+0.039
0.15			−0.142		
0.2	−3.43	−0.42	−0.201	−1.13	+0.038
0.25			−0.251		
0.3	−2.5	−0.78	−0.296	−0.85	−0.055
0.35			−0.337		
0.4	−1.22	−1.04	−0.382	−0.88	−0.03
0.45			−0.416		
0.5	−0.82	−1.37	−0.473	−1.02	+0.087
0.55			−0.541		
0.6	−0.58	−1.67	−0.603	−1.13	+0.183
0.65			−0.674		
0.7	−0.42	−2.0	−0.743	−1.175	+0.388
0.75			−0.805		
0.8	−0.17	−2.86	−0.854	−1.02	−0.26
0.85			−0.873	−0.79	−1.36
0.9	−0.025	−3.50	−0.780	−0.30	−5.0
0.95			−0.491		
1.0	0	−3.88	0. ↑	0.	? ↑
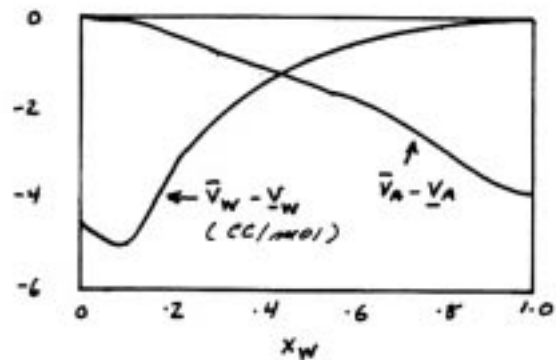
6.21

We want to evaluate $\overline{H}_A^V(T,P,\underline{y}) - \overline{H}_A^L(T,P,\underline{x})$, where x_A and y_A denote the liquid and vapor alcohol mole fractions, respectively, and the superscripts V and L designate the vapor and liquid phases. To an excellent approximation, at the temperatures here, $\overline{H}_A^V(T,P,\underline{y}) = \underline{H}_A^V(T,P)$. To proceed further we use

$$\underline{H}_A^V(T,P) - \overline{H}_A^L(T,P,\underline{x}) = \underline{H}_A^V(T,P) - \underline{H}_A^L(T,P) + \left[\underline{H}_A^L(T,P) - \overline{H}_A^L(T,P,\underline{x})\right]$$

where
$$\underline{H}_A^V(T,P) - \underline{H}_A^L(T,P) = \Delta \underline{H}^{vap}\Big|_{\substack{pure \\ ethanol}} = 44{,}770 \text{ J/mol (See Problem \textbf{5.13}a)}$$

and $\overline{H}_A^L(T,P,\underline{x}) - \underline{H}_A^L(T,P)$ was computed in Problem **6.20**. Thus,

$$\Delta \underline{H}_A^{vap}\Big|_{\substack{75 \text{ mole} \\ \% \text{ A}}} = 44{,}770 \text{ J/mol} - \left[\overline{H}_A^L(T,P,x_A = 0.75) - \underline{H}_A^L(T,P)\right]$$

$$= 44{,}770 - (\sim 0) = 44{,}770 \text{ J/mol}$$

$$\Delta \underline{H}_A^{vap}\Big|_{\substack{50 \text{ mole} \\ \% \text{ A}}} = 44{,}770 - (87) = 44{,}683 \text{ J/mol}$$

$$\Delta \underline{H}_A^{vap}\Big|_{\substack{25 \text{ mole} \\ \% \text{ A}}} = 44{,}770 - (\sim 0) = 44{,}770 \text{ J/mol}$$

To evaluate $\Delta \underline{H}_A^{vap}\Big|_{\substack{\to 0 \text{ mole} \\ \% \text{ A}}}$, care must be taken since $\left(\overline{H}_A^L - \underline{H}_A^L\right)$ becomes very large (and negative) in this limit. To avoid serious errors, we will fit the low alcohol (high water) mole fraction data with a polynomial in mole fraction, and evaluate $\left(\overline{H}_A - \underline{H}_A\right)$ analytically. I used
$$\Delta \underline{H}_{mix} = x_A x_W (A + B(x_A - x_W)) \quad \text{See Eqn. (6.6-5a)}$$
Then
$$\overline{H}_A - \underline{H}_A = \left(\frac{\partial N \Delta \underline{H}_{mix}}{\partial N_A}\right)_{T,P,N_W} = x_W \left[A x_W + B\left(3 x_W - 4 x_W^2\right)\right]$$

and $\lim_{\substack{x_W \to 1 \\ x_A \to 0}} \left(\overline{H}_A - \underline{H}_A\right) = A - B$. Fitting $\Delta \underline{H}_{mix}$ data at $x_W = 0.85$, 0.9 and 0.95, I find that $A = +5.368$ kJ/mol and $+17.45$ kJ/mol. Thus

$$\overline{H}_A - \underline{H}_A\Big|_{x_A \to 0} = +5.368 - 17.45 = -12.08 \text{ kJ/mol}$$

Thus

$$\Delta \underline{H}_A^{vap}\Big|_{x_A \to 0} = 44.77 - (-12.08) = 56.85 \text{ kJ/mol}$$

Clearly at moderate and high ethanol concentrations, an ethanol molecule must interact with the water-ethanol mixture to almost the same extent as an ethanol molecule interacts with pure ethanol. Thus its heat of vaporization from solution is about the same as from pure ethanol. However, at very low alcohol concentrations there is a dramatic change. Presumably, water (now almost pure) forms a more ordered structure (probably as a result of hydrogen-bonding). Thus, it seems reasonable that at very low ethanol concentrations, each ethanol molecule is more involved in hydrogen bonding (with water molecules) than it is in pure ethanol (with ethanol molecules).

Consequently, the heat of vaporization of ethanol from dilute alcohol solutions is greater (that is, more energy is needed) than for the pure substance.

6.22 $\underline{V}(T,P,\underline{x}) = x_1 b_1 + x_2 b_2 + x_1 x_2 \sum_{i=0}^{n} a_i (x_1 - x_2)^i$

(a) $\lim_{x_1 \to 1} \underline{V}(T,P,\underline{x}) = \underline{V}_1(T,P) = b_1$; $\lim_{x_2 \to 1} \underline{V}(T,P,x_i) = \underline{V}_2(T,P) = b_2$

(b) $\overline{V}_1 = \dfrac{\partial}{\partial N_1}(N\underline{V})_{T,P,N_2}$

$= \dfrac{\partial}{\partial N_1}\left[Nx_1 \underline{V}_1 + Nx_2 \underline{V}_2 + \dfrac{(Nx_1)(Nx_2)}{N} \sum_{i=0}^{n} a_i \dfrac{(Nx_1 - Nx_2)^i}{N^i} \right]$

$= \dfrac{\partial}{\partial N_1}\left[N_1 \underline{V}_1 + N_2 \underline{V}_2 + N_1 N_2 \sum_{i=0}^{n} a_i \dfrac{(N_1 - N_2)^i}{(N_1 + N_2)^{i+1}} \right] \qquad \{Nx_i = N_i\}$

$= \underline{V}_1 + N_2 \sum_{i}^{n} \dfrac{a_i (N_1 - N_2)^i}{(N_1 + N_2)^{i+1}} + N_1 N_2 \sum_{i=0}^{n} \dfrac{a_i i (N_1 - N_2)^{i-1}}{(N_1 + N_2)^{i+1}}$

$\quad - N_1 N_2 \sum_{i=0}^{n} a_i (i+1) \dfrac{(N_1 - N_2)^i}{(N_1 + N_2)^{i+2}}$

$= \underline{V}_1 + x_2 \sum_{i=0}^{n} a_i (x_1 - x_2)^i + x_1 x_2 \sum a_i i (x_1 - x_2)^{i-1}$

$\quad - x_1 x_2 \sum a_i (i+1)(x_1 - x_2)^i$

$= \underline{V}_1 + x_2 \sum_{i=0}^{n} a_i (x_1 - x_2)^{i-1}[x_1 - x_2 + i x_1 - (i+1)x_1(x_1 - x_2)]$

$\overline{V}_1 = \underline{V}_1 + x_2^2 \sum_{i=0}^{n} a_i (x_1 - x_2)^{i-1}[2(i+1)x_1 - 1]$

Similarly, by taking derivative with respect to N_2, we obtain

$$\overline{V}_2 = \underline{V}_2 - x_1^2 \sum a_i (x_1 - x_2)^{i-1}[2(i+1)x_2 - 1]$$

Therefore

$$\overline{V}_1^{\,\text{ex}} = \overline{V}_1 - \underline{V}_1 = x_2^2 \sum_{i=0}^{n} a_i (x_1 - x_2)^{i-1}[2(i+1)x_1 - 1]$$

and

$$\overline{V}_2^{\,\text{ex}} = \overline{V}_2 - \underline{V}_2 = -x_1^2 \sum a_i (x_1 - x_2)^{i-1}[2(i+1)x_2 - 1]$$

(c) $\quad \overline{V}_1^{\,\text{ex}}(T, P, x_1 \to 0) = \overline{V}_1^{\,\text{ex, }\infty} = \sum_{i=0}^{n} a_i (-1)^{i-1} (-1) = \sum_{i=0}^{n} a_i (-1)^i$

$$= a_0 - a_1 + a_2 - a_3 + \cdots$$

$$\overline{V}_2^{\,\text{ex}}(T, P, x_2 \to 0) = \overline{V}_2^{\,\text{ex, }\infty} = -\sum_{i=0}^{n} a_i (1)^{i-1} (-1) = \sum_{i=0}^{n} a_i$$

$$= a_0 + a_1 + a_2 + a_3 + \cdots$$

6.23 These derivations are the same as in Sec. 5.1. For example, starting with the closed system equations

$$\frac{dN}{dt} = 0 \qquad \frac{dU}{dt} = \dot{Q} + \dot{W}_\text{s} - P\frac{dV}{dt} \quad \text{and} \quad \frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{S}_\text{gen}$$

with $\dot{S}_\text{gen} \geq 0$, $U = \sum N_i \overline{U}_i$ and $S = \sum N_i \overline{S}_i$. We have first N (or M) = constant. Now for a constant volume, adiabatic system with no shaft work we have

$$\frac{dU}{dt} = 0 \Rightarrow \text{constant ; also } V = \text{constant}$$

and

$$\frac{dS}{dt} = \dot{S}_\text{gen} \geq 0 \Rightarrow S \text{ can only increase at constant } N, V \text{ and } U$$

$$\Rightarrow S = \text{ maximum at equilibrium at constant } N, V, U.$$

Similarly with $\dot{W}_\text{s} = 0$ for an isothermal system (constant N, T, and V) at constant volume we have

$$\frac{dU}{dt} = \dot{Q} \quad \text{and} \quad \frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{S}_\text{gen} \quad \text{or} \quad \dot{Q} = T\frac{dS}{dt} - T\dot{S}_\text{gen}$$

so

$$\frac{dU}{dt} = T\frac{dS}{dt} - T\dot{S}_\text{gen} \Rightarrow \frac{d(U - TS)}{dt} = \frac{dA}{dt} = -T\dot{S}_\text{gen}$$

$$\Rightarrow A = \text{minimum at equilibrium at constant } N, \ T, \text{ and } V.$$

Similarly, one can show that $\underline{G} = $ minimum at constant N, T, and P.

6.24 $\underline{M} = \underline{M}(x_1, x_2, \ldots, x_N)$

$$\overline{M}_i = \frac{\partial (N\underline{M})}{dN_i}\bigg|_{T, P, N_{j \neq i}} = \underline{M} + N\left(\frac{\partial \underline{M}}{\partial N_i}\right)_{T, P, N_{j \neq i}}$$

but

$$\left(\frac{\partial \underline{M}}{\partial N_i}\right)_{T,P,N_{j\ne i}} = \sum_j \left(\frac{\partial \underline{M}}{\partial x_j}\right)_{T,P,N_{j\ne k}} \left(\frac{\partial x_j}{\partial N_i}\right)_{T,P,N_{j\ne i}}$$

Now

$$x_j = \frac{N_j}{N}; \quad \frac{\partial}{\partial N_i} x_j = \frac{\partial}{\partial N_i}\left(\frac{N_j}{N}\right) = \begin{cases} -\dfrac{N_j}{N^2} = -\dfrac{x_j}{N}; & \text{if } j \ne i \\[2mm] \dfrac{1}{N} - \dfrac{N_i}{N^2} = \dfrac{1-x_i}{N}; & \text{if } j = i \end{cases}$$

Therefore

$$\left(\frac{\partial \underline{M}}{\partial N_i}\right)_{T,P,N_{j\ne i}} = -\sum_{j\ne i}\left(\frac{\partial \underline{M}}{\partial x_j}\right)_{T,P,N_{k\ne j}}\frac{x_j}{N} - \left(\frac{\partial \underline{M}}{\partial x_i}\right)_{T,P,N_{k\ne i}}\left(\frac{1-x_i}{N}\right)$$

$$= \frac{1}{N}\left(\frac{\partial \underline{M}}{\partial x_i}\right)_{T,P,x_{j\ne i}} - \sum_{j\ne i}\left(\frac{\partial \underline{M}}{\partial x_j}\right)_{T,P,x_{k\ne j}}\frac{x_j}{N}$$

$$\Rightarrow \overline{M}_i = \underline{M} + \left(\frac{\partial \underline{M}}{\partial x_i}\right)_{T,P,x_{j\ne i}} - \sum_j x_j\left(\frac{\partial \underline{M}}{\partial x_j}\right)_{T,P,x_{k\ne j}}$$

6.25 (See Section 8.4)

Since the stable equilibrium state of the mixture for some range of compositions is as two liquid phases, rather than a single homogeneous phase, the Gibbs free energy of the homogeneous mixture must be greater than a linear combination of the Gibbs free energies of mixtures of compositions on either side of the actual mixture composition. That is, the Gibbs free energy of the mixture must be as indicated in Figure 1 below.

Now, the Gibbs free energy of the mixture is

$$G = N_1^I \overline{G}_1^I + N_2^I \overline{G}_2^I + N_1^{II} \overline{G}_1^{II} + N_2^{II} \overline{G}_2^{II}$$

with the restrictions that

$$N_1^I + N_1^{II} = \text{constant} = N_1^o$$

and $N_2^I + N_2^{II} = \text{constant} = N_2^o$. Thus, we have that

$$G = N_1^I \overline{G}_1^I + N_2^I \overline{G}_2^I + \left(N_1^o - N_1^I\right)\overline{G}_1^{II} + \left(N_2^o - N_2^{II}\right)\overline{G}_2^{II}$$

At equilibrium

$$\left(\frac{\partial G}{\partial N_1^I}\right)_{T,P,N_2^I} = 0 \Rightarrow \overline{G}_1^I = \overline{G}_1^{II}$$

(where, in evaluating each of these derivations, we have used the Gibbs-Duhem equation) and

$$\left(\frac{\partial G}{\partial N_2^I}\right)_{T,P,N_1^I} = 0 \Rightarrow \overline{G}_2^I = \overline{G}_2^{II}$$

However, $\overline{G}_1^I = (\partial G / \partial N_1)$ is a tangent to the G versus N_1 curve. Thus, the equilibrium requirement that $\overline{G}_1^I = \overline{G}_1^{II}$ requires that the compositions of the two equilibrium phases are at the intersections of each lobe of the G versus N_1 curve with the single tangent line to both curves. See Fig. 1. [Note: See Problem **5.28**] The limit of stability of a single phase is found from the condition that $d^2 G = 0$. Here that implies

$$\left(\frac{\partial^2 G}{\partial N_1^2} \right)_{T,P,N_2} = 0 \qquad \text{Now, } G = N_1 \overline{G}_1 + N_2 \overline{G}_2$$

$$\left(\frac{\partial G}{\partial N_1} \right)_{T,P,N_2} = \overline{G}_1 + N_1 \left(\frac{\partial \overline{G}_1}{\partial N_1} \right)_{T,P,N_2} + N_2 \left(\frac{\partial \overline{G}_2}{\partial N_1} \right)_{T,P,N_2} = \overline{G}_1$$

Since the last two terms sum to zero by the Gibbs-Duhem equation. Thus

$$\left(\frac{\partial^2 G}{\partial N_1^2} \right)_{T,P,N_2} = \left(\frac{\partial \overline{G}_1}{\partial N_1} \right)_{T,P,N_2}$$

Thus, the limits of stability of a single phase are the inflection points on the G vs N_1 (or $\underline{G}$ vs x_1) curve and the local maximum and minimum on the $\overline{G}_1$ vs. N_1 (or $\overline{G}_1$ vs. x_1) curves. (See Figure 2.) The region between each coexisting phase composition and the adjacent inflection point represents a metastable region. This is illustrated in Figure 2.

Figure 1

Figure 2
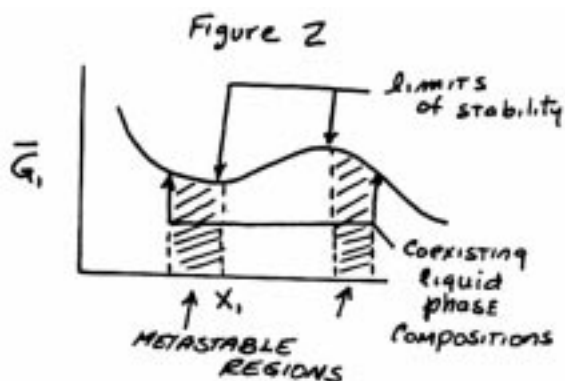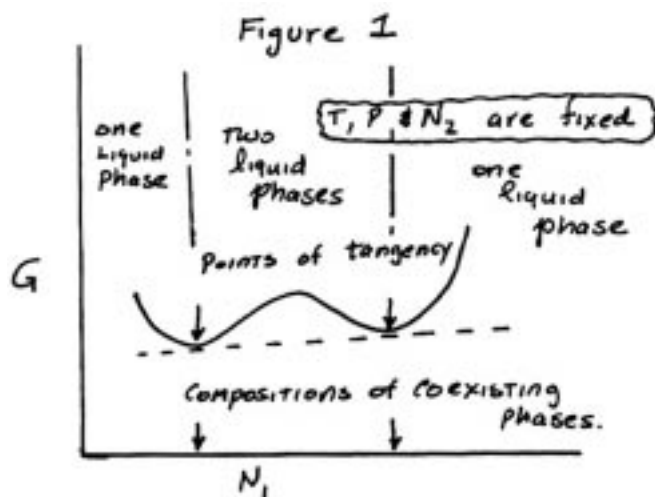
6.26 (a) $\underline{H} = x_B \underline{H}_B + (1 - x_B)\underline{H}_{EA}$

$+ x_B(1 - x_B)\left[1418 - 482.4(1 - 2x_B) + 187.4(1 - 2x_B)^3\right]$

but $\Delta\underline{H}_{\text{mix}} = \underline{H} - x_B\underline{H}_B - (1 - x_B)\underline{H}_{EA}$

$\Delta\underline{H}_{\text{mix}} = x_B(1 - x_B)\left[1418 - 482.4(1 - 2x_B) + 187.4(1 - 2x_B)^3\right]$

From Equation (6.6-9b)

$$\Delta\underline{H}_{\text{mix}} - x_B \frac{\partial(\Delta\underline{H}_{\text{mix}})}{\partial x_B} = \overline{H}_{EA} - \underline{H}_{EA} \;;\; \text{also}$$

$$\Delta\underline{H}_{\text{mix}} + (1 - x_B)\frac{\partial(\Delta\underline{H}_{\text{mix}})}{\partial x_B} = \overline{H}_B - \underline{H}_B$$

Now

$$\frac{\partial(\Delta\underline{H}_{\text{mix}})}{\partial x_B} = (1 - 2x_B)\left[1418 - 482.4(1 - 2x_B) + 187.4(1 - 2x_B)^3\right]$$

$$+ 2x_B(1 - x_B)\left[482.4 - 562.2(1 - 2x_B)^2\right]$$

Therefore,

$$\left(\overline{H}_{EA} - \underline{H}_{EA}\right) = x_B^2\left[1418 - 482.4(1 - 2x_B) + 187.4(1 - 2x_B)^3\right]$$

$$+ 2x_B^2(1 - x_B)\left[482.4 - 562.2(1 - 2x_B)^2\right]$$

and

$$\left(\overline{H}_B - \underline{H}_B\right) = (1 - x_B)^2\left[1418 - 482.4(1 - 2x_B) + 187.4(1 - 2x_B)^3\right]$$

$$+ 2x_B(1 - x_B)\left[482.4 - 562.2(1 - 2x_B)^2\right]$$

(b) At $x_B = 0.5$

$$\left(\overline{H}_{EA} - \underline{H}_{EA}\right) = \left(\frac{1}{2}\right)^2[1418] - 2\left(\frac{1}{2}\right)^2\left(\frac{1}{2}\right)(482.4) = 233.9 \text{ J/mol}$$

$$\left(\overline{H}_B - \underline{H}_B\right) = \left(\frac{1}{2}\right)^2[1418] - 2\left(\frac{1}{2}\right)\left(\frac{1}{2}\right)^2(482.4) = 475.1 \text{ J/mol}$$

(c)   Mixing process

System = 1 mole of each initial mixture (2 moles total)

Difference form of mass balance: $N_f = N_{1,\,i} + N_{2,\,i} = 1 + 1 = 2$ mol

Balance on benzene (species balance):

$$x_{B,f}N_f = x_{B,1i}N_{1i} + x_{B,2i}N_{2i} = 0.25 + 0.75$$

$$x_{B,f} = \frac{0.25 + 0.75}{2} = 0.5 \text{ (obviously!)}$$

Energy balance: $N_f\underline{U}_f = N_{1,i}\underline{U}_{1,i} + N_{2,i}\underline{U}_{2,i} + Q$

For liquid solutions, $\underline{U} \approx \underline{H}$. Consequently,

$$Q = 2\underline{H}_f - \underline{H}_{1,\,i} - \underline{H}_{2,\,i} = 2\underline{H}(x_B = 0.5) - \underline{H}(x_B = 0.25) - \underline{H}(x_B = 0.75)$$

but

$$\Delta\underline{H}_{\text{mix}} = \underline{H}_{\text{mix}} - \left[x_B\underline{H}_B + (1 - x_B)\underline{H}_{\text{EA}}\right]$$

$$\Rightarrow \underline{H}_{\text{mix}} = \underbrace{\Delta\underline{H}_{\text{mix}}}_{\substack{\text{polynomial given} \\ \text{in problem statement}}} + x_B\underbrace{\underline{H}_B}_{\downarrow} + (1 - x_B)\underbrace{\underline{H}_{\text{EA}}}_{\downarrow}$$

$$\underset{\substack{\text{pure component} \\ \text{enthalpies}}}{}$$

$$Q = 2\left[\Delta\underline{H}_{\text{mix}}(x_B = 0.5) + 0.5\underline{H}_B + 0.5\underline{H}_{\text{EA}}\right]$$
$$\quad - \left[\Delta\underline{H}_{\text{mix}}(x_B = 0.25) + 0.25\underline{H}_B + 0.75\underline{H}_{\text{EA}}\right]$$
$$\quad - \left[\Delta\underline{H}_{\text{mix}}(x_B = 0.75) + 0.75\underline{H}_B + 0.25\underline{H}_{\text{EA}}\right]$$
$$\quad = 2\Delta\underline{H}_{\text{mix}}(x_B = 0.5) - \Delta\underline{H}_{\text{mix}}(x_B = 0.25) - \Delta\underline{H}_{\text{mix}}(x_B = 0.75)$$
$$\quad = 2 \times 354.5 - 225 - 306.7 = 177.3 \text{ J}$$

6.27 $Q\left\{\dfrac{\text{kJ}}{\text{mol n-propanol}}\right\} \times \dfrac{\text{mole fraction}}{\text{of n-propanol}} = Q\left\{\dfrac{\text{kJ}}{\text{mol of solution}}\right\}$

Thus, we obtain the following

Mole % H_2O	0	5	10	15	20
Q kJ/mol propanol	0	+0.042	0.084	0.121	0.159
$\Delta\underline{H}_{\text{mix}}$ kJ/mol solution	0	0.040	0.076	0.103	0.127

Mole % H_2O	25	30	35	40	45
Q kJ/mol propanol	0.197	0.230	0.243	0.243	0.209
$\Delta\underline{H}_{\text{mix}}$ kJ/mol solution	0.148	0.161	0.158	0.146	0.115

Mole % H_2O	50	55	60	65	70	75
Q	0.167	0.084	−0.038	−0.201	−0.431	−0.778
$\Delta\underline{H}_{\text{mix}}$	0.084	0.038	−0.015	−0.070	−0.129	−0.195

Mole % H_2O	80	85	90	95	100
Q	−1.335	−2.264	−4.110	−7.985	0
$\Delta\underline{H}_{\text{mix}}$	−0.267	−0.340	−0.411	−0.399	0

$\Delta\underline{H}_{\text{mix}}$ is plotted below, and $\overline{H}_1 - \underline{H}_1$ and $\overline{H}_2 - \underline{H}_2$ are evaluated using the graphical procedure of Sec. 6.6.

Fig. 1
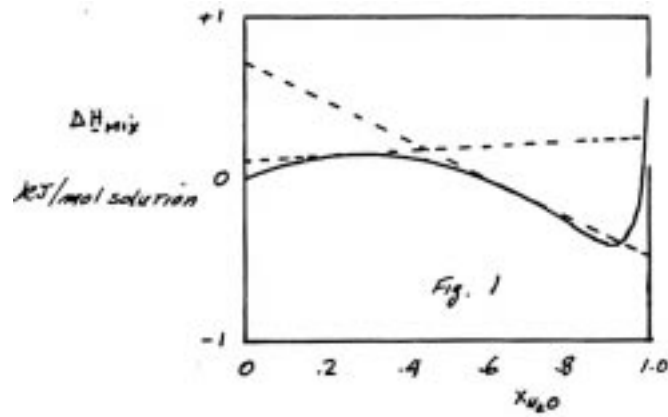
Dashed lines are sample tangent lines. [Note: Results in table and figure below gotten using a much bigger graph.]

x_{H_2O}	$\overline{H}_{nP} - \underline{H}_{nP}$	$\overline{H}_{H_2O} - \underline{H}_{H_2O}$
	kJ/mol	
0.1	0.015	0.642
0.2	0.042	0.470
0.3	0.118	0.260
0.4	0.335	−0.130
0.5	0.510	−0.340
0.6	0.610	−0.425
0.7	0.732	−0.500
0.8	0.843	−0.540
0.9	0.940	−0.565

Fig. 2
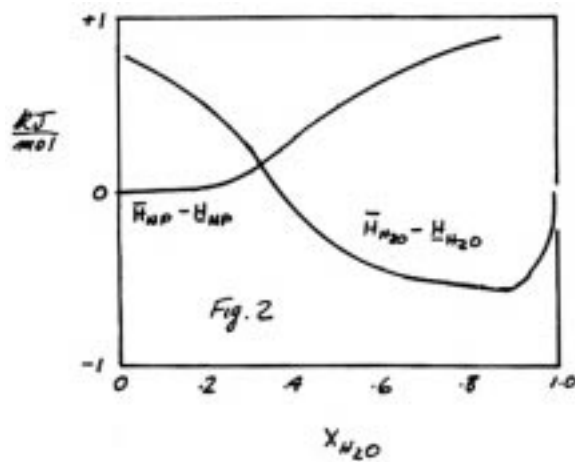
6.28 (a) $\quad \Delta \underline{H}_{\text{mix}} = x_1 x_2 [A + B(x_1 - x_2)] = x_1(1 - x_1)[A + B(2x_1 - 1)]$

$$= (x_1 - x_1^2)[A + B(2x_1 - 1)]$$

$$\left(\frac{\partial \Delta \underline{H}_{\text{mix}}}{\partial x_1} \right) = (x_2 - x_1)[A + B(x_1 - x_2)] + 2Bx_1 x_2$$

$$\Delta \underline{H}_{\text{mix}} - x_1 \left(\frac{\partial \Delta \underline{H}_{\text{mix}}}{\partial x_1} \right) = x_1 x_2 [A + B(x_1 - x_2)]$$

$$-x_1(x_2 - x_1)A - x_1(x_2 - x_1)(x_1 - x_2)B - 2Bx_1^2 x_2$$

$$= x_1^2 [A + B(4x_1 - 3)] = \overline{H}_2 - \underline{H}_2$$

at $x_1 = 0.5$, $\overline{H}_2 - \underline{H}_2 = \frac{1}{4}[A + B(2 - 3)] = \frac{1}{4}[A - B]$

$$\Delta \underline{H}_{\text{mix}} + x_2 \left(\frac{\partial \Delta \underline{H}_{\text{mix}}}{\partial x_1} \right) = \Delta \underline{H}_{\text{mix}} - x_2 \left(\frac{\partial \Delta \underline{H}_{\text{mix}}}{\partial x_2} \right)$$

$$= x_1 x_2 [A + B(x_1 - x_2)]$$

$$+ x_2(x_2 - x_1)[A + B(x_1 - x_2)] + 2Bx_1 x_2^2$$

$$= x_2^2 [A + B(3 - 4x_2)] = \overline{H}_1 - \underline{H}_1$$

at $x_1 = 0.5$, $\overline{H}_1 - \underline{H}_1 = \frac{1}{4}\left[A + B\left(3 - 4\frac{1}{2} \right) \right] = \frac{1}{4}[A + B]$

at 300 K, $A = -12{,}974 + 51.505 \times 300 = 2477.5$
$$B = 8782.8 - 34.129 \times 300 = -1455.9$$

$$\Rightarrow \overline{H}_2 - \underline{H}_2 = \frac{1}{4}[2477.5 + 1455.9] = 983.4 \ \text{J/mol}$$

$$\overline{H}_1 - \underline{H}_1 = \frac{1}{4}[2477.5 - 1455.9] = 255.4 \ \text{J/mol}$$

(b) $\quad \overline{C}_{P,i} - C_{P,i} = \frac{\partial}{\partial T}(\overline{H}_i - \underline{H}_i)$; $\quad \frac{\partial A}{\partial T} = 51.505$; $\quad \frac{\partial B}{\partial T} = -34.129$

$$\Rightarrow \overline{C}_{P,2} - C_{P,2}\big|_{0.5} = \frac{\partial}{\partial T}(\overline{H}_2 - \underline{H}_2) = \frac{1}{4}\left(\frac{\partial A}{\partial T} - \frac{\partial B}{\partial T} \right) = \frac{1}{4}(51.505 + 34.129)$$

$$= 21.409 \ \text{J/mol K}$$

$$\overline{C}_{P,1} - C_{P,1}\big|_{0.5} = \frac{1}{4}(51.505 - 34.129) = 4.344 \ \text{J/mol K}$$

(c) Overall mass balance: $\quad 0 = \dot{N}_1 + \dot{N}_2 + \dot{N}_3$

n-octanol mass balance: $\quad 0 = x_1 \dot{N}_1 + x_2 \dot{N}_2 + x_3 \dot{N}_3$

Also (problem information): $\quad \dot{N}_1 = 2\dot{N}_2$

Basis of calculation: $\dot{N}_2 = 1 \Rightarrow \dot{N}_3 = -3;\ \dot{N}_1 = 2$

$$x_3 = \frac{0.2 \times 2 + 0.9 \times 1}{3} = 0.4333$$

Energy balance: $0 = \dot{N}_1(\underline{H})_1 + \dot{N}_2(\underline{H})_2 + \dot{N}_3(\underline{H})_3 + \dot{Q}$

$$\Delta\underline{H}_{mix} = \underline{H} - x_1\underline{H} - x_2\underline{H}_2$$

$$(\underline{H})_1 = \Delta\underline{H}_{mix} - x_1\underline{H}_1 - x_2\underline{H}_2$$

$$\Rightarrow -\dot{Q} = \dot{N}_1(\Delta\underline{H}_{mix})_1 + \dot{N}_2(\Delta\underline{H}_{mix})_2 - (\dot{N}_1 + \dot{N}_2)(\Delta\underline{H}_{mix})_3$$
$$= 2(\Delta\underline{H}_{mix})_1 + 1(\Delta\underline{H}_{mix})_2 - 3(\Delta\underline{H}_{mix})_3$$

$\Delta\underline{H}_{mix} = x_1 x_2[2477.5 - 1455.9(x_1 - x_2)]$

$(\Delta\underline{H}_{mix})_1 = 0.2 \times 0.8[2477.5 - 1455.9(0.2 - 0.8)] = 536.17$ J/mol

$(\Delta\underline{H}_{mix})_2 = 0.9 \times 0.1[2477.5 - 1455.9(0.9 - 0.1)] = 118.15$ J/mol

$(\Delta\underline{H}_{mix})_3 = 0.433 \times 0.567[2477.5 - 1455.9(0.433 - 0.567)] = 655.79$ J/mol

$-\dot{Q} = 2 \times 536.17 + 1 \times 118.15 - 3 \times 655.79 = -776.89$

$\Rightarrow \dot{Q} = 776.89$ J/3 mol solution

$\Rightarrow$ Heat must be added

$\dot{Q} = 258.96$ J/mol solution

6.29 The mass balance of the acetic acid-pyridine streams at steady-state is

$$0 = \dot{N}_P + \dot{N}_A + \dot{N}_{mix} \quad \Rightarrow \quad -\dot{N}_{mix} = \dot{N}_P + \dot{N}_A \quad \Rightarrow \quad \dot{N}_{mix} = -2\,\frac{kmol}{min}$$

The energy balance is

$$0 = \dot{N}_P \underline{H}_P + \dot{N}_A \underline{H}_A + \dot{N}_{mix} \underline{H}_{mix} + \dot{Q}$$
$$= \dot{N}_P \underline{H}_P + \dot{N}_A \underline{H}_A + \dot{N}_{mix}\left(x_P \underline{H}_P + x_A \underline{H}_A + \Delta \underline{H}_{mix}\right) + \dot{Q}$$
$$= 1\cdot\left(\underline{H}_P - \underline{H}_P\right) + 1\cdot\left(\underline{H}_A - \underline{H}_A\right) - 2\cdot\Delta\underline{H}_{mix}\left(x_P = 0.5\right) + \dot{Q}$$

so

$$\dot{Q} = 2\cdot\Delta\underline{H}_{mix}\left(x_P = 0.5\right)$$

Now from the table

$$\Delta\underline{H}_{mix}\left(x_P = 0.4786\right) = -4833\ \text{J / mol} \quad \text{and}$$
$$\Delta\underline{H}_{mix}\left(x_P = 0.5029\right) = -4765\ \text{J / mol}$$

By interpolation

$$\Delta\underline{H}_{mix}\left(x_P = 0.5\right) \approx -4773\ \text{J / mol}$$

$$\dot{Q} = 2\,\frac{kmol}{min}\cdot(-4773)\frac{J}{mol}\cdot\frac{1\,kJ}{1000\,J}\cdot\frac{1000\,mol}{kmol}$$
$$= -9546\,\frac{kJ}{min}$$

Negative sign means that heat must be removed (or cooling supplied) to keep the process at a constant temperature. Since ethylene glycol has a value of $C_P = $ 2.8 kJ/kg K. From an energy balance we have that

$$2.8\,\frac{kJ}{kg\cdot K}\times 20\ K \times \dot{M} = 9546\,\frac{kJ}{min}$$

Therefore

$$\dot{M} = \frac{9546\,\dfrac{kJ}{min}}{2.8\,\dfrac{kJ}{kg\cdot K}\times 20\ K} = 170.5\ \frac{\text{kg ethylene glycol}}{min}$$

6.30 (also available as an Mathcad worksheet)

Problem 6.30

$x_0 := 0$	$H_0 := 0$	$x_1 := 0.0371$	$H_1 := -1006$	$x_2 := 0.0716$	$H_2 := -1851$
$x_3 := 0.1032$	$H_3 := -2516$	$x_4 := 0.1340$	$H_4 := -3035$	$x_5 := 0.1625$	$H_5 := -3427$
$x_6 := 0.1896$	$H_6 := -3765$	$x_7 := 0.2190$	$H_7 := -4043$	$x_8 := 0.2494$	$H_8 := -4271$
$x_9 := 0.2760$	$H_9 := -4440$	$x_{10} := 0.3006$	$H_{10} := -4571$	$x_{11} := 0.3234$	$H_{11} := -4676$
$x_{12} := 0.3461$	$H_{12} := -4760$	$x_{13} := 0.3671$	$H_{13} := -4819$	$x_{14} := 0.3874$	$H_{14} := -4863$
$x_{15} := 0.3991$	$H_{15} := -4832$	$x_{16} := 0.4076$	$H_{16} := -4880$	$x_{17} := 0.4235$	$H_{17} := -4857$
$x_{18} := 0.4500$	$H_{18} := -4855$	$x_{19} := 0.4786$	$H_{19} := -4833$	$x_{20} := 0.5029$	$H_{20} := -4765$

$x_{21} := 0.5307$ $H_{21} := -4669$ $x_{22} := 0.5621$ $H_{22} := -4496$ $x_{23} := 0.5968$ $H_{23} := -4253$

$x_{24} := 0.6372$ $H_{24} := -3920$ $x_{25} := 0.6747$ $H_{25} := -3547$ $x_{26} := 0.7138$ $H_{26} := -3160$

$x_{27} := 0.7578$ $H_{27} := -2702$ $x_{28} := 0.8083$ $H_{28} := -2152$ $x_{29} := 0.8654$ $H_{29} := -1524$

$x_{30} := 0.9277$ $H_{30} := -806$ $x_{31} := 1.0$ $H_{31} := 0$

$i := 0, 1 .. 31$
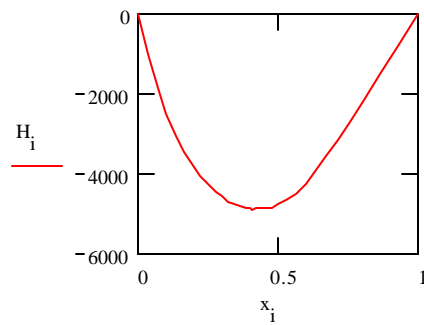
One-constant Margules fit

$f(x) := x \cdot (1 - x)$ $S := \text{linfit}(x, H, f)$ $S = -1.961 \cdot 10^4$

Two-constant Margules fit

$$f(x) := \begin{bmatrix} x \cdot (1 - x) \\ x \cdot (1 - x) \cdot (2 \cdot x - 1) \end{bmatrix}$$ $SS := \text{linfit}(x, H, f)$ $$SS = \begin{bmatrix} -1.893 \cdot 10^4 \\ 8.068 \cdot 10^3 \end{bmatrix}$$

Three-constant Margules fit

$$f(x) := \begin{bmatrix} x \cdot (1 - x) \\ x \cdot (1 - x) \cdot (2 \cdot x - 1) \\ x \cdot (1 - x) \cdot (2 \cdot x - 1)^2 \end{bmatrix}$$ $SS := \text{linfit}(x, H, f)$ $$SS = \begin{bmatrix} -1.88 \cdot 10^4 \\ 7.983 \cdot 10^3 \\ -1.143 \cdot 10^3 \end{bmatrix}$$

$$HH(x) := \left[-1.88 \cdot 10^4 \cdot (x \cdot (1 - x)) + 7.983 \cdot 10^3 \cdot (x \cdot (1 - x) \cdot (2 \cdot x - 1)) \right] - 1.143 \cdot 10^3 \cdot \left[x \cdot (1 - x) \cdot (2 \cdot x - 1)^2 \right]$$

$$dHH(x) := \frac{d}{dx} HH(x)$$

$\Delta H1(x) := HH(x) + (1 - x) \cdot dHH(x)$ $\Delta H2(x) := HH(x) - x \cdot dHH(x)$
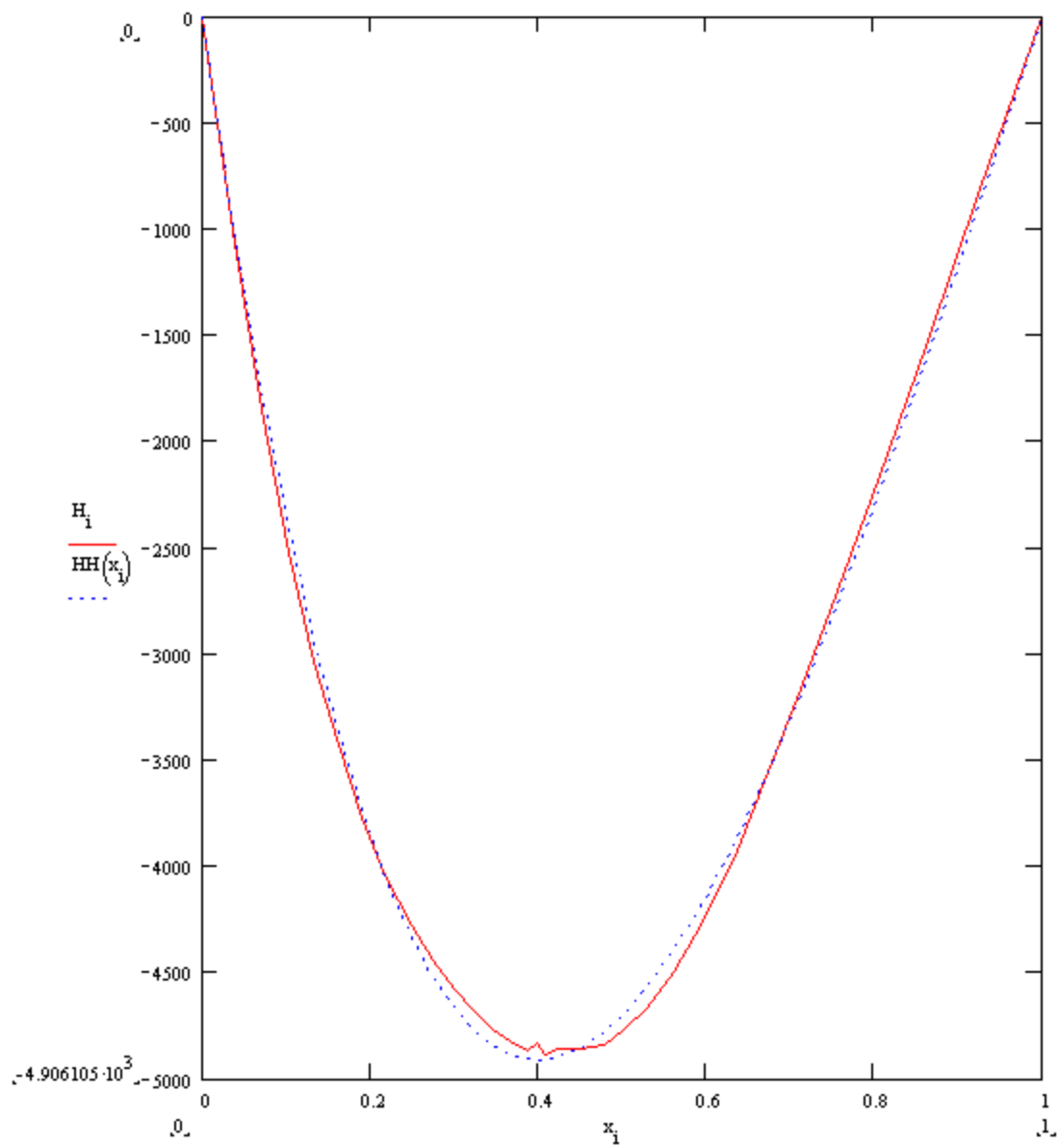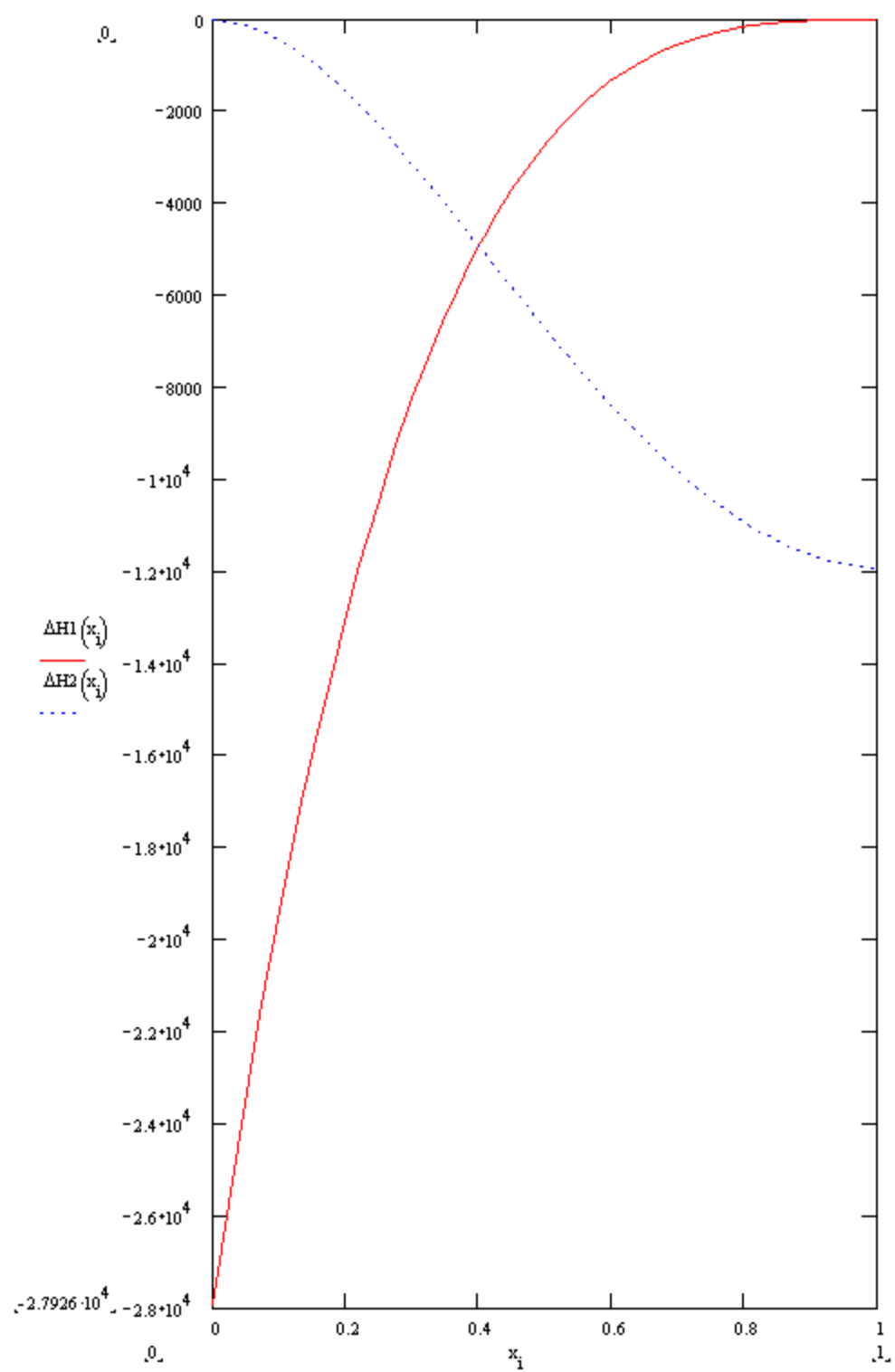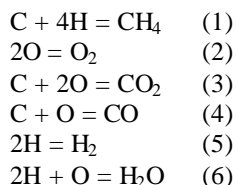
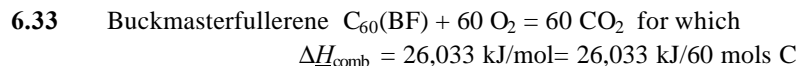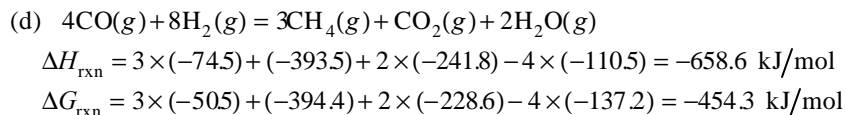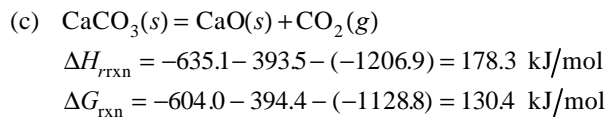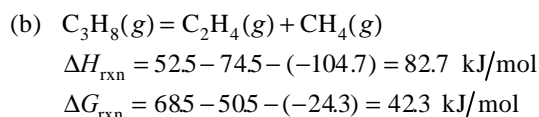| $HH(x_i)$	$\Delta H1(x_i)$	$\Delta H2(x_i)$
0	$-2.793 \cdot 10^4$	0
- 970.622	$-2.45 \cdot 10^4$	- 64.168
$-1.76 \cdot 10^3$	$-2.16 \cdot 10^4$	- 230.38
$-2.393 \cdot 10^3$	$-1.917 \cdot 10^4$	- 462.512
$-2.931 \cdot 10^3$	$-1.7 \cdot 10^4$	- 753.807
$-3.363 \cdot 10^3$	$-1.516 \cdot 10^4$	$-1.074 \cdot 10^3$
$-3.718 \cdot 10^3$	$-1.355 \cdot 10^4$	$-1.418 \cdot 10^3$
$-4.045 \cdot 10^3$	$-1.195 \cdot 10^4$	$-1.828 \cdot 10^3$
$-4.322 \cdot 10^3$	$-1.044 \cdot 10^4$	$-2.288 \cdot 10^3$
$-4.517 \cdot 10^3$	$-9.243 \cdot 10^3$	$-2.716 \cdot 10^3$
$-4.66 \cdot 10^3$	$-8.227 \cdot 10^3$	$-3.127 \cdot 10^3$
$-4.762 \cdot 10^3$	$-7.36 \cdot 10^3$	$-3.52 \cdot 10^3$
$-4.835 \cdot 10^3$	$-6.565 \cdot 10^3$	$-3.92 \cdot 10^3$
$-4.88 \cdot 10^3$	$-5.886 \cdot 10^3$	$-4.296 \cdot 10^3$
$-4.902 \cdot 10^3$	$-5.281 \cdot 10^3$	$-4.663 \cdot 10^3$
$-4.906 \cdot 10^3$	$-4.953 \cdot 10^3$	$-4.875 \cdot 10^3$
$-4.905 \cdot 10^3$	$-4.724 \cdot 10^3$	$-5.03 \cdot 10^3$
$-4.895 \cdot 10^3$	$-4.317 \cdot 10^3$	$-5.319 \cdot 10^3$
$-4.853 \cdot 10^3$	$-3.696 \cdot 10^3$	$-5.8 \cdot 10^3$
$-4.777 \cdot 10^3$	$-3.102 \cdot 10^3$	$-6.315 \cdot 10^3$
$-4.688 \cdot 10^3$	$-2.653 \cdot 10^3$	$-6.747 \cdot 10^3$
$-4.561 \cdot 10^3$	$-2.2 \cdot 10^3$	$-7.231 \cdot 10^3$
$-4.388 \cdot 10^3$	$-1.759 \cdot 10^3$	$-7.763 \cdot 10^3$
$-4.162 \cdot 10^3$	$-1.349 \cdot 10^3$	$-8.327 \cdot 10^3$
$-3.86 \cdot 10^3$	- 963.67	$-8.946 \cdot 10^3$
$-3.545 \cdot 10^3$	- 683.156	$-9.48 \cdot 10^3$
$-3.186 \cdot 10^3$	- 458.239	$-9.989 \cdot 10^3$
$-2.751 \cdot 10^3$	- 274.249	$-1.05 \cdot 10^4$
$-2.218 \cdot 10^3$	- 135.442	$-1.1 \cdot 10^4$
$-1.581 \cdot 10^3$	- 48.028	$-1.144 \cdot 10^4$
- 859.046	- 8.49	$-1.177 \cdot 10^4$
0	0	$-1.196 \cdot 10^4$

6.31   Starting by writing the equation for the formation of each of the six compounds present from their elements

$$C + 4H = CH_4 \quad (1)$$
$$2O = O_2 \quad\quad (2)$$
$$C + 2O = CO_2 \quad (3)$$
$$C + O = CO \quad\quad (4)$$
$$2H = H_2 \quad\quad (5)$$
$$2H + O = H_2O \quad (6)$$

Now using eqn. (2) to eliminate the oxygen atom, and eqn. (5) to eliminate the hydrogen atom. We obtain

$$C + 2H_2 = CH_4$$
$$C + O_2 = CO_2$$
$$C + 1/2O_2 = CO$$
$$H_2 + 1/2O_2 = H2O$$
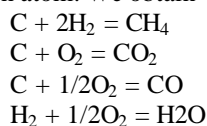
Thus from the Denbigh method, we find there are four independent reactions. One such set is listed above.

6.32   (a) $N_2(g) + H_2(g) = 2NH_3(g)$ $\Delta H_{rxn} = 2 \times (-46.1) = -92.2 \ \text{kJ}/\text{mol}$

$\Delta G_{rxn} = 2 \times (-16.5) = -33.0 \ \text{kJ}/\text{mol}$

(b) $C_3H_8(g) = C_2H_4(g) + CH_4(g)$

$\Delta H_{rxn} = 52.5 - 74.5 - (-104.7) = 82.7 \ \text{kJ}/\text{mol}$

$\Delta G_{rxn} = 68.5 - 50.5 - (-24.3) = 42.3 \ \text{kJ}/\text{mol}$

(c) $CaCO_3(s) = CaO(s) + CO_2(g)$

$\Delta H_{rrxn} = -635.1 - 393.5 - (-1206.9) = 178.3 \ \text{kJ}/\text{mol}$

$\Delta G_{rxn} = -604.0 - 394.4 - (-1128.8) = 130.4 \ \text{kJ}/\text{mol}$

(d) $4CO(g) + 8H_2(g) = 3CH_4(g) + CO_2(g) + 2H_2O(g)$

$\Delta H_{rxn} = 3 \times (-74.5) + (-393.5) + 2 \times (-241.8) - 4 \times (-110.5) = -658.6 \ \text{kJ}/\text{mol}$

$\Delta G_{rxn} = 3 \times (-50.5) + (-394.4) + 2 \times (-228.6) - 4 \times (-137.2) = -454.3 \ \text{kJ}/\text{mol}$

6.33   Buckmasterfullerene $C_{60}(BF) + 60 \ O_2 = 60 \ CO_2$ for which

$$\Delta \underline{H}_{comb} = 26{,}033 \ \text{kJ/mol} = 26{,}033 \ \text{kJ/60 mols C}$$

Graphite $60C + 60 \ O_2 = 60CO_2$ for which $\Delta \underline{H}_{comb} = 60 \times 393.513 = 23{,}611 \ \text{kJ/60 mols C}$

For these reactions sice only carbon, carbon dioxide and oxygen are involved,
$\Delta \underline{H}_f = -\Delta \underline{H}_{comb}$

Subtracting the first chemical reaction above from the second yields

$$60C > C_{60}(BF) \Rightarrow -26033 - (-23611) = \ -2422 \ \text{kJ/mol} \ C_{60}(BF)$$
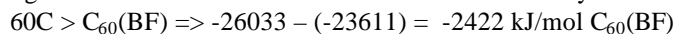
6.34 (also available as an Mathcad worksheet)

Problem 6.34 Partial molar enthalpies   File: 6-34.MCD

$x_0 := 0$	$H_0 := 0$	$x_1 := 0.0120$	$H_1 := -68.8$	$x_2 := 0.0183$	$H_2 := -101.3$

$x_3 := 0.0340$ $\quad$ $H_3 := -179.1$ $\quad$ $x_4 := 0.0482$ $\quad$ $H_4 := -244.4$ $\quad$ $x_5 := 0.0736$ $\quad$ $H_5 := -344.6$

$x_6 := 0.1075$ $\quad$ $H_6 := -451.1$ $\quad$ $x_7 := 0.1709$ $\quad$ $H_7 := -565.3$ $\quad$ $x_8 := 0.1919$ $\quad$ $H_8 := -581.0$

$x_9 := 0.2301$ $\quad$ $H_9 := -585.0$ $\quad$ $x_{10} := 0.2636$ $\quad$ $H_{10} := -566.1$ $\quad$ $x_{11} := 0.2681$ $\quad$ $H_{11} := -561.9$

$x_{12} := 0.2721$ $\quad$ $H_{12} := -557.8$ $\quad$ $x_{13} := 0.3073$ $\quad$ $H_{13} := -519.6$ $\quad$ $x_{14} := 0.3221$ $\quad$ $H_{14} := -508.0$

$x_{15} := 0.3486$ $\quad$ $H_{15} := -468.5$ $\quad$ $x_{16} := 0.3720$ $\quad$ $H_{16} := -424.4$ $\quad$ $x_{17} := 0.3983$ $\quad$ $H_{17} := -369.1$

$x_{18} := 0.4604$ $\quad$ $H_{18} := -197.1$ $\quad$ $x_{19} := 0.4854$ $\quad$ $H_{19} := -135.4$ $\quad$ $x_{20} := 0.5137$ $\quad$ $H_{20} := -66.1$

$x_{21} := 0.5391$ $\quad$ $H_{21} := -1.9$ $\quad$ $x_{22} := 0.5858$ $\quad$ $H_{22} := 117.1$ $\quad$ $x_{23} := 0.6172$ $\quad$ $H_{23} := 186.5$

$x_{24} := 0.6547$ $\quad$ $H_{24} := 266.9$ $\quad$ $x_{25} := 0.7041$ $\quad$ $H_{25} := 360.3$ $\quad$ $x_{26} := 0.7519$ $\quad$ $H_{26} := 436.6$

$x_{27} := 0.7772$ $\quad$ $H_{27} := 470.5$ $\quad$ $x_{28} := 0.7995$ $\quad$ $H_{28} := 495.9$ $\quad$ $x_{29} := 0.8239$ $\quad$ $H_{29} := 510.0$

$x_{30} := 0.8520$ $\quad$ $H_{30} := 515.8$ $\quad$ $x_{31} := 0.8784$ $\quad$ $H_{31} := 505.3$ $\quad$ $x_{32} := 0.8963$ $\quad$ $H_{32} := 486.0$

$x_{33} := 0.9279$ $\quad$ $H_{33} := 420.5$ $\quad$ $x_{34} := 0.9532$ $\quad$ $H_{34} := 329.2$ $\quad$ $x_{35} := 0.9778$ $\quad$ $H_{35} := 184.7$

$x_{36} := 0.9860$ $\quad$ $H_{36} := 123.3$ $\quad$ $x_{37} := 0.9971$ $\quad$ $H_{37} := 25.1$ $\quad$ $x_{38} := 1.0$ $\quad$ $H_{38} := 0.0$

$i := 0, 1.. 38$
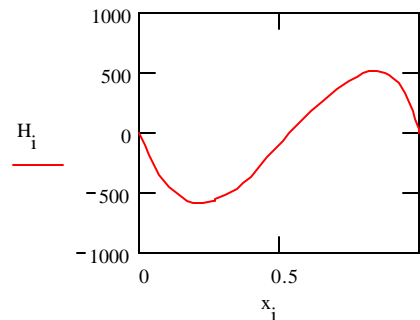
One-constant Margules fit

$f(x) := x \cdot (1 - x)$ $\qquad$ $SS := linfit(x, H, f)$ $\qquad$ $SS = -528.45491$

$HH(x) := SS_0 \cdot x \cdot (1 - x)$

$dHH(x) := \dfrac{d}{dx} HH(x)$

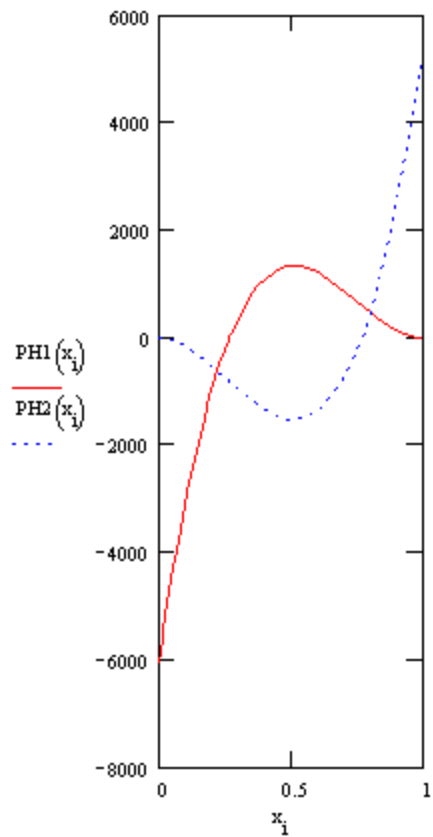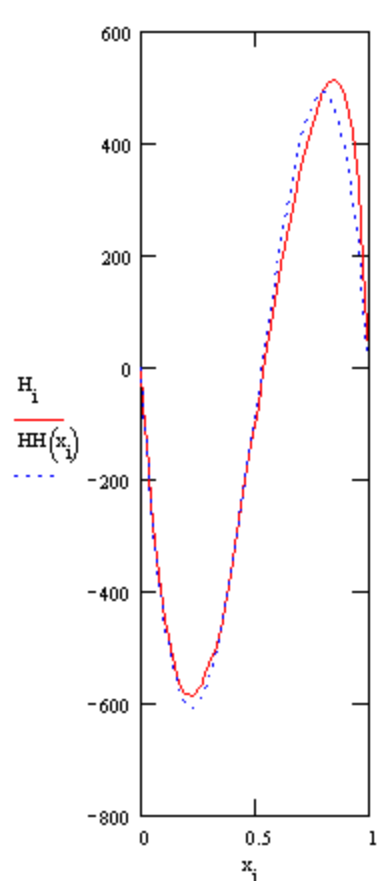$PH1(x) := HH(x) + (1 - x) \cdot dHH(x)$ $\qquad$ $PH2(x) := HH(x) - x \cdot dHH(x)$
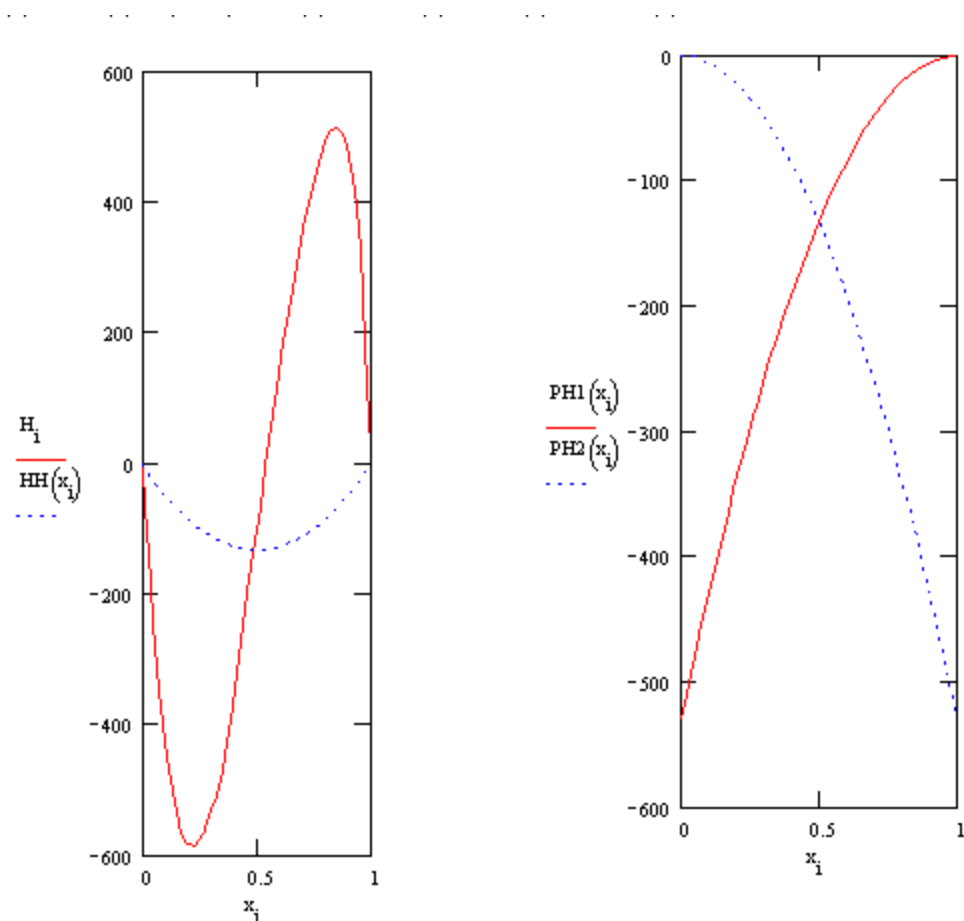
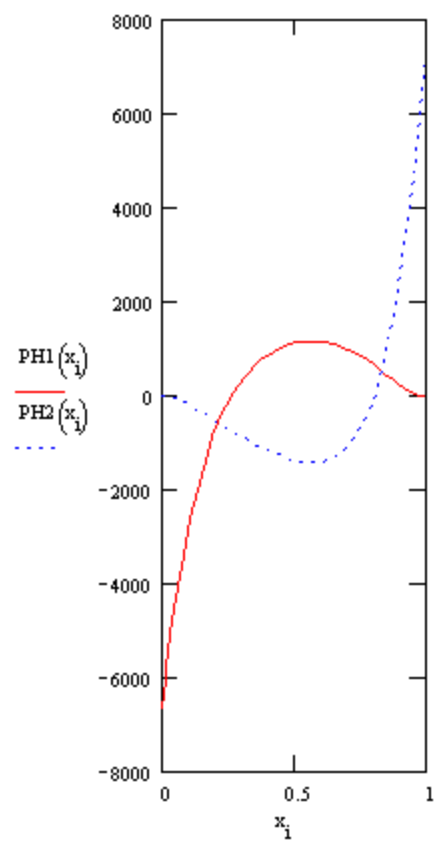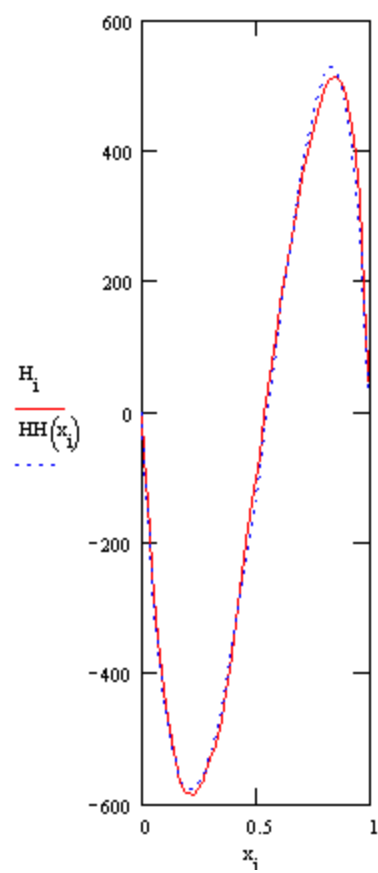Two-constant Margules fit

$$f(x) := \begin{bmatrix} x \cdot (1-x) \\ x \cdot (1-x) \cdot (2 \cdot x - 1) \end{bmatrix} \qquad SS := \text{linfit}(x, H, f) \qquad SS = \begin{bmatrix} -337.24041 \\ 5707.44046 \end{bmatrix}$$

$$HH(x) := x \cdot (1-x) \cdot \left[SS_0 + SS_1 \cdot (2 \cdot x - 1) \right] \qquad\qquad dHH(x) := \frac{d}{dx} HH(x)$$

$$PH1(x) := HH(x) + (1-x) \cdot dHH(x) \qquad PH2(x) := HH(x) - x \cdot dHH(x)$$

Three-constant Margules fit

$$f(x) := \begin{bmatrix} x \cdot (1-x) \\ x \cdot (1-x) \cdot (2 \cdot x - 1) \\ x \cdot (1-x) \cdot (2 \cdot x - 1)^2 \end{bmatrix}$$

$$SS := linfit(x, H, f)$$

$$SS = \begin{bmatrix} -488.57112 \\ 5672.45617 \\ 970.2807 \end{bmatrix}$$

$$HH(x) := \left[SS_0 \cdot (x \cdot (1-x)) + SS_1 \cdot (x \cdot (1-x) \cdot (2 \cdot x - 1)) \right] + SS_2 \cdot x \cdot (1-x) \cdot (2\,x - 1)^2$$

$$dHH(x) := \frac{d}{dx} HH(x)$$

$$PH1(x) := HH(x) + (1-x) \cdot dHH(x)$$
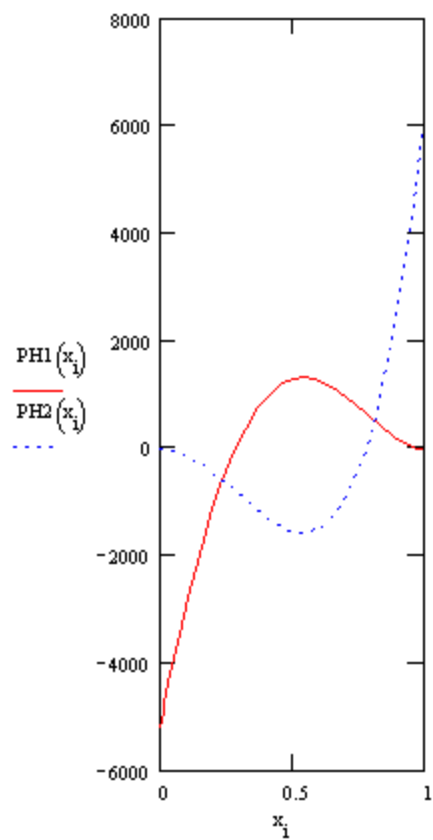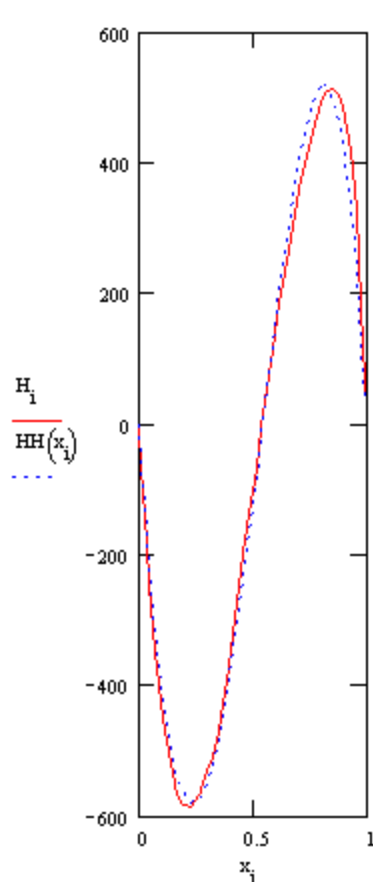
$$PH2(x) := HH(x) - x \cdot dHH(x)$$

Four-constant Margules fit

$$f(x) := \begin{bmatrix} x \cdot (1 - x) \\ x \cdot (1 - x) \cdot (2 \cdot x - 1) \\ x \cdot (1 - x) \cdot (2 \cdot x - 1)^2 \\ x \cdot (1 - x) \cdot (2 \cdot x - 1)^3 \end{bmatrix} \qquad SS := linfit(x, H, f)$$

$$HH(x) := x \cdot (1 - x) \cdot \left[SS_0 + SS_1 \cdot (2 \cdot x - 1) + SS_2 \cdot (2 \cdot x - 1)^2 + SS_3 \cdot (2 \cdot x - 1)^3 \right]$$

$$dHH(x) := \frac{d}{dx} HH(x) \qquad PH1(x) := HH(x) + (1 - x) \cdot dHH(x) \qquad PH2(x) := HH(x) - x \cdot dHH(x)$$

HH(x_i)	PH1(x_i)	PH2(x_i)
0	- 6620.61619	0
- 75.89284	- 6037.1938	- 3.48837
- 112.97104	- 5746.57438	- 7.95429
- 197.51978	- 5066.79383	- 26.13746
- 264.87861	- 4503.47003	- 50.23256
- 365.61955	- 3607.09619	- 108.09291
- 465.07305	- 2606.80402	- 207.10545
- 563.45181	- 1219.73582	- 428.17388
- 575.52278	- 871.2077	- 505.3063
- 576.41179	- 347.75299	- 644.75104
- 558.17713	14.29521	- 763.09798
- 554.54726	57.06648	- 778.58558
- 551.10303	94.0214	- 792.26028
- 512.60889	379.84612	- 908.52549
- 492.43244	481.19324	- 955.04467
- 451.15379	638.98059	- 1034.5447
- 409.80542	756.15737	- 1100.47128
- 358.55983	866.44984	- 1169.46453
- 221.37494	1052.07298	- 1307.91205
- 161.16559	1101.2544	- 1351.95197
- 90.55115	1140.97708	- 1391.46839
- 25.5922	1162.73326	- 1415.53852
95.51229	1169.06642	- 1422.80738
176.23404	1148.81031	- 1391.88005
269.19976	1098.66681	- 1303.49667
380.26243	990.04823	- 1070.73515
466.63265	841.94903	- 670.81348
500.06403	748.83482	- 367.73066
520.4105	660.0669	- 36.47376
530.95404	557.74661	405.60256
525.02317	436.6149	1033.96809
498.49631	323.9931	1759.05242
467.10138	250.96992	2335.16915
380.96262	135.3294	3542.17012
279.46841	62.11408	4706.43722
148.70801	15.16587	6030.57744
97.36045	6.1957	6517.96343
21.20369	0.27562	7216.85219
0	0	7407.10877

6.35 Assume reactor operates in steady state. Then the mass balance is

$$0 = N_{i,\text{in}} - N_{i,\text{out}} + \boldsymbol{n}_i X$$

or

$$N_{i,\text{in}} = +N_{i,\text{out}} - \boldsymbol{n}_i X$$

and the energy balance is

$$0 = \sum_i N_{i,\text{in}} \underline{H}_{i,\text{in}} - \sum_i N_{i,\text{out}} \underline{H}_{i,\text{out}} + Q$$

or

$$
\begin{aligned}
Q &= -\sum_i N_{i,\text{in}} \underline{H}_{i,\text{in}} + \sum_i N_{i,\text{out}} \underline{H}_{i,\text{out}} \\
&= -\sum_i (N_{i,\text{out}} - \boldsymbol{n}_i X) \underline{H}_{i,\text{in}} + \sum_i N_{i,\text{out}} \underline{H}_{i,\text{out}} \\
&= \sum_i N_{i,\text{out}} \left(\underline{H}_{i,\text{out}} - \underline{H}_{i,\text{in}} \right) + \Delta \underline{H}_{\text{rxn}}(T_{\text{in}}) X
\end{aligned}
$$

Using a Mathcad worksheet, the heats of formation and heat capacities in the appendices of the textbook, we find that 59.93 kJ must be supplied per mole of N2 entering reactor. See Mathcad worksheet for this problem.

6.36 (also available as an Mathcad worksheet)

6.36

				Nomenclature
$x25_0 := 0$	$H25_0 := 0$	$x50_0 := 0$	$H50_0 := 0$	H25 = enthalpy at 25C
$x25_1 := 0.027$	$H25_1 := -223.16$	$x50_1 := 0.031$	$H50_1 := -76.20$	H50 = enthalpy at 50C
$x25_2 := 0.034$	$H25_2 := -290.15$	$x50_2 := 0.043$	$H50_2 := -121.84$	HH25 and HH50 are
$x25_3 := 0.054$	$H25_3 := -329.50$	$x50_3 := 0.082$	$H50_3 := -97.55$	correlated enthalpies.
$x25_4 := 0.094$	$H25_4 := -384.25$	$x50_4 := 0.098$	$H50_4 := -52.75$	ΔH125 = difference
$x25_5 := 0.153$	$H25_5 := -275.07$	$x50_5 := 0.206$	$H50_5 := 125.60$	between partial molar
$x25_6 := 0.262$	$H25_6 := -103.41$	$x50_6 := 0.369$	$H50_6 := 370.53$	and pure component
$x25_7 := 0.295$	$H25_7 := -81.22$	$x50_7 := 0.466$	$H50_7 := 435.43$	enthalpies of species
$x25_8 := 0.349$	$H25_8 := -11.35$	$x50_8 := 0.587$	$H50_8 := 473.11$	1 at 25C,
$x25_9 := 0.533$	$H25_9 := 133.98$	$x50_9 := 0.707$	$H50_9 := 460.55$	etc.
$x25_{10} := 0.602$	$H25_{10} := 168.31$	$x50_{10} := 0.872$	$H50_{10} := 238.23$	
$x25_{11} := 0.739$	$H25_{11} := 177.94$	$x50_{11} := 0.9999$	$H50_{11} := 0.0$	
$x25_{12} := 1.0$	$H25_{12} := 0.0$	$x50_{12} := 1.0$	$H50_{12} := 0.0$	

$i := 0.. 12$
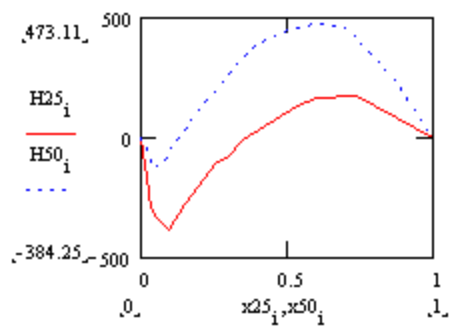
Three-constant Margules fit

$$f(x) := \begin{bmatrix} x \cdot (1 - x) \\ x \cdot (1 - x) \cdot (2 \cdot x - 1) \\ x \cdot (1 - x) \cdot (2 \cdot x - 1)^2 \end{bmatrix}$$
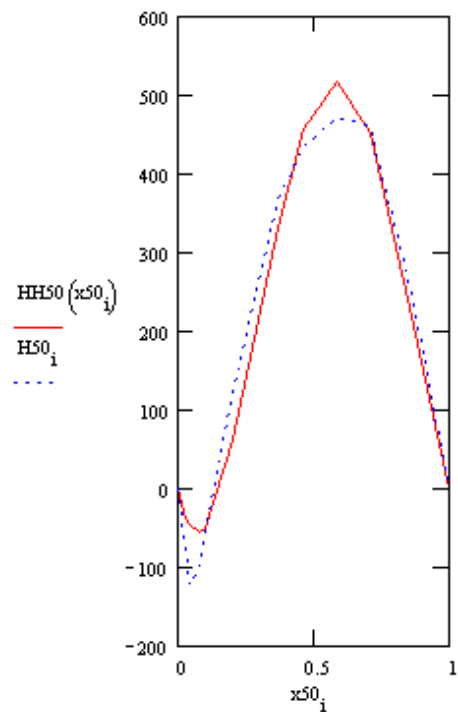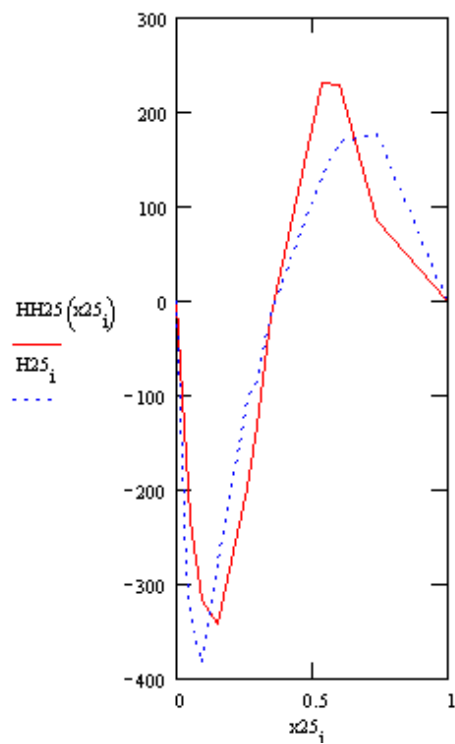
$s25 := \text{linfit}(x25, H25, f)$

$$s25 = \begin{bmatrix} 851.268 \\ 1.543 \cdot 10^3 \\ -5.027 \cdot 10^3 \end{bmatrix}$$

$s50 := \text{linfit}(x50, H50, f)$

$$s50 = \begin{bmatrix} 1.95 \cdot 10^3 \\ 1.443 \cdot 10^3 \\ -2.099 \cdot 10^3 \end{bmatrix}$$

$$HH25(x) := s25_0 \cdot x \cdot (1 - x) + s25_1 \cdot x \cdot (1 - x) \cdot (2 \cdot x - 1) + s25_2 \cdot x \cdot (1 - x) \cdot (2 \cdot x - 1)^2$$

$$HH50(x) := s50_0 \cdot x \cdot (1 - x) + s50_1 \cdot x \cdot (1 - x) \cdot (2 \cdot x - 1) + s50_2 \cdot x \cdot (1 - x) \cdot (2 \cdot x - 1)^2$$
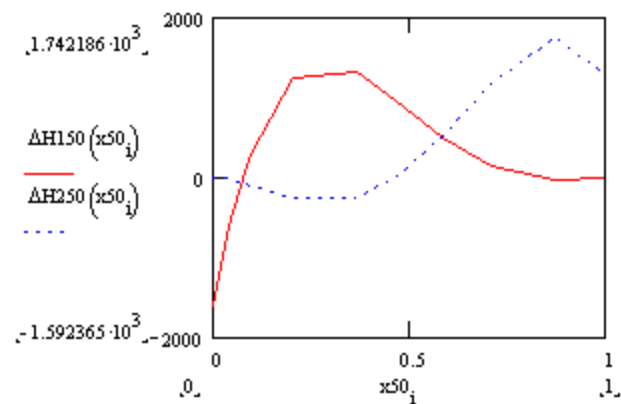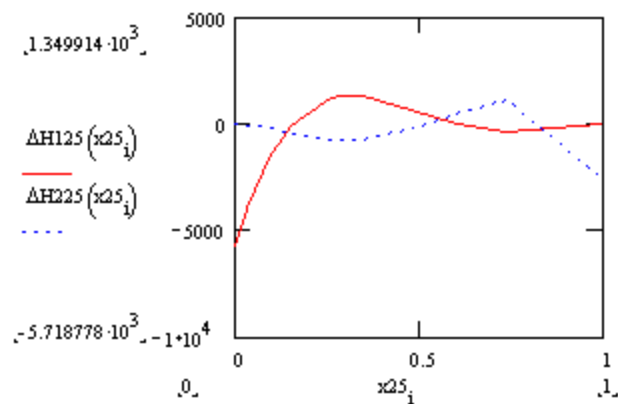
$$HH50(x) := s50_0 \cdot x \cdot (1 - x) + s50_1 \cdot x \cdot (1 - x) \cdot (2 \cdot x - 1) + s50_2 \cdot x \cdot (1 - x) \cdot (2 \cdot x - 1)^2$$

$$dHH25(x) := \frac{d}{dx}HH25(x) \quad dHH50(x) := \frac{d}{dx}HH50(x)$$

$$\Delta H150(x50) := HH50(x50) + (1 - x50) \cdot dHH50(x50)$$

$$\Delta H125(x25) := HH25(x25) + (1 - x25) \cdot dHH25(x25)$$

$$\Delta H250(x50) := HH50(x50) - x50 \cdot dHH50(x50)$$
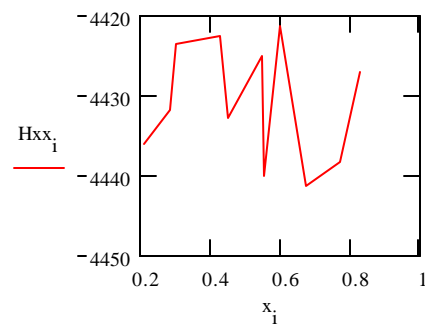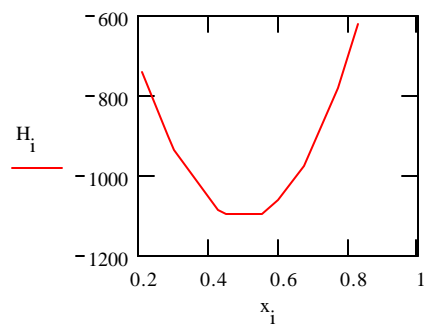
$$\Delta H225(x25) := HH25(x25) - x25 \cdot dHH25(x25)$$

6.37 (also available as an Mathcad worksheet)

6.37

$x_0 := 0.2108$	$H_0 := -738$	$x_1 := 0.2834$	$H_1 := -900$	$x_2 := 0.3023$	$H_2 := -933$
$x_3 := 0.4285$	$H_3 := -1083$	$x_4 := 0.4498$	$H_4 := -1097$	$x_5 := 0.5504$	$H_5 := -1095$
$x_6 := 0.5562$	$H_6 := -1096$	$x_7 := 0.6001$	$H_7 := -1061$	$x_8 := 0.6739$	$H_8 := -976$
$x_9 := 0.7725$	$H_9 := -780$	$x_{10} := 0.8309$	$H_{10} := -622$		

$i := 0.. \ 10$

$$Hxx_i := \frac{H_i}{x_i \cdot (1 - x_i)}$$

$$\Delta H1_i := -4430 \cdot \left(1 - x_i\right)^2 \qquad\qquad \Delta H2_i := -4430 \cdot \left(x_i\right)^2$$

$\Delta H1_i$	$\Delta H2_i$	Hxx_i
$-2.759 \cdot 10^3$	-196.854	$-4.436 \cdot 10^3$
$-2.275 \cdot 10^3$	-355.798	$-4.432 \cdot 10^3$
$-2.156 \cdot 10^3$	-404.837	$-4.424 \cdot 10^3$
$-1.447 \cdot 10^3$	-813.402	$-4.422 \cdot 10^3$
$-1.341 \cdot 10^3$	-896.278	$-4.433 \cdot 10^3$
-895.481	$-1.342 \cdot 10^3$	$-4.425 \cdot 10^3$
-872.526	$-1.37 \cdot 10^3$	$-4.44 \cdot 10^3$
-708.446	$-1.595 \cdot 10^3$	$-4.421 \cdot 10^3$
-471.092	$-2.012 \cdot 10^3$	$-4.441 \cdot 10^3$
-229.28	$-2.644 \cdot 10^3$	$-4.438 \cdot 10^3$
-126.675	$-3.058 \cdot 10^3$	$-4.427 \cdot 10^3$

6.38 (a) $C_8H_{18} + 12\dfrac{1}{2}O_2 + 47.02N_2 \rightarrow 8CO_2 + 9H_2O + 47.02N_2$

$$\Delta H_{rxn} = 8\Delta\underline{H}_{f,\,CO_2} + 9\Delta\underline{H}_{f,\,H_2O} - \Delta H_{f,\,C_8H_{18}}$$

$$= 8(-393.5) + 9(-241.8) - (-208.4) = -5115.8 \text{ kJ}$$

$$\Delta U_{rxn} = \Delta H_{rxn} - \Delta NRT = -5115.8 \text{ kJ}(17 - 13.5) \times 8.314 \times \frac{298.15}{1000} \text{ kJ}$$

$$= -5115.8 - 8.7 \text{ kJ} = -5124.5 \text{ kJ}$$

C_P of mixture $= 8 \times 51.25 + 9 \times 39.75 + 47.02 \times 32.43 = 2292.61 \text{ J/mol K}$

C_V of mixture $= C_P - \underset{\substack{\uparrow \\ \text{\# of} \\ \text{moles}}}{N}R = 2292.61 - 64.02 \times 8.314 = 1760.35 \text{ J/mol K}$

$$T_{final} = T_{in} + \frac{\Delta U_{rxn}}{C_V} = 298.15 + \frac{5124.5 \times 10^3}{1760.35} = 298.15 + 2911.07 = 3209.2 \text{ K}$$

by ideal gas law

$$PV = NRT \Rightarrow \frac{N_i T_i}{P_i} = \frac{N_f T_f}{P_f}; \ P_f = P_i \frac{N_f}{N_i} \frac{T_f}{T_i}$$

$$P_f = 1 \text{ bar} \frac{64.02}{60.52} \times \frac{3209.2}{298.15} = 11.386 \text{ bar}$$

(b) Adiabatic expansion

$$C_P(\text{per mole}) = \frac{2292.61}{8 + 9 + 47.02} = \frac{2292.61}{64.02} = 35.81$$

$$T_2 = T_1 \left(\frac{P_2}{P_1}\right)^{R/C_P} = 3209.2 \times \left(\frac{1}{11.386}\right)^{8.314/35.81}$$

$$T_2 = 3209.2(0.087827)^{0.23217} = 1824.5 \text{ K}$$

$$\frac{dU}{dt} = \dot{W} \; ; \; \frac{dS}{dt} = 0 + \dot{S}_{\text{gen}}\!\!\nearrow^{0}$$

$$W = C_V \Delta T = -2.438 \times 10^6 \text{ J/mol of octane}$$

(c)   This is like Carnot cycle with a varying upper T

$$\frac{dU}{dt} = \dot{Q} + \dot{W} = C_V \frac{dT}{dt} \; ; \; \frac{dS}{dt} = \frac{\dot{Q}}{T_L} + \dot{S}_{\text{gen}}\!\!\nearrow^{0} = \frac{C_P}{T}\frac{dT}{dt} \; ; \; T_2 = 150°\text{C}$$

$$\frac{dU}{dt} = T_L \frac{dS}{dt} + \dot{W} \qquad \text{or}$$

$$\Delta U - T_L \Delta S = W$$

$$W = C_V \Delta T - T_L \cdot C_P \ln \frac{T_L}{T_H}$$

$$W = 1760.35(423.15 - 1824.5) - 423.15 \times 2292.61 \ln \frac{423.15}{1824.5}$$

$$= -1.049 \times 10^6 \text{ J/mol of octane}$$

$$C_V \frac{dT}{dt} = T_L \frac{C_P}{T}\frac{dT}{dt} + \dot{W} \Rightarrow \dot{W} = C_V \frac{dT}{dt} - T_L \frac{C_P}{T}\frac{dT}{dt}$$

$$W_S = C_V(T_L - T_H) - T_L C_P \ln \frac{T_L}{T_H}$$

$$\frac{dU}{dt} = \sum \dot{N}_{i,\text{in}} \overline{H}_{i,\text{in}} - \sum \dot{N}_{i,\text{out}} \overline{H}_{i,\text{out}} + \dot{Q} + \dot{W} = 0$$

$$\frac{dS}{dt} = \sum \dot{N}_{i,\text{in}} \overline{S}_{i,\text{in}} - \sum \dot{N}_{i,\text{out}} \overline{S}_{i,\text{out}} + \frac{\dot{Q}}{T_{\text{amb}}} + \dot{S}_{\text{gen}}\!\!\nearrow^{0} = 0$$

(for maximum work)

$$\dot{Q} = -T_{\text{amb}} \left[\sum \dot{N}_{i,\text{in}} \overline{S}_{i,\text{in}} - \sum \dot{N}_{i,\text{out}} \overline{S}_{i,\text{out}}\right]$$

$$0 = \sum \dot{N}_{i,\text{in}}(\overline{H}_{i,\text{in}} - T_{\text{amb}} \overline{S}_{i,\text{in}}) - \sum \dot{N}_{i,\text{out}}(\overline{H}_{i,\text{out}} - T_{\text{amb}} \overline{S}_{i,\text{out}}) + \dot{W}$$

$$-\dot{W} = \sum \dot{N}_{i,\text{in}}(\overline{H}_{i,\text{in}} - T_{\text{amb}} \overline{S}_{i,\text{in}}) - \sum \dot{N}_{i,\text{out}}(\overline{H}_{i,\text{out}} - T_{\text{amb}} \overline{S}_{i,\text{out}})$$

$$= \sum \dot{N}_{i,\text{in}}(\overline{H}_{i,\text{in}} - T_{\text{amb}} \overline{S}_{i,\text{in}}) - \sum (\dot{N}_{i,\text{in}} + X\boldsymbol{n}_i)(\overline{H}_{i,\text{out}} - T_{\text{amb}} \overline{S}_{i,\text{out}})$$

Absolute maximum work $T_{\text{in}} = T_{\text{out}} = T_{\text{amb}}$

Ideal gas $\overline{H}_i = \underline{H}_i$; $\underline{G}_{i,\text{in}} = \underline{G}_{i,\text{out}}$; $\overline{S}_i = \underline{S}_i - R \ln x_i$

$$-\dot{W} = \sum_i N_{i,\text{in}} \underline{G}_{i,\text{in}} - RT_{\text{amb}} \sum_i N_{i,\text{in}} \ln x_{i,\text{in}} - \sum_i N_{i,\text{in}} \underline{G}_{i,\text{in}} +$$

$$RT_{\text{amb}} \sum_i N_{i,\text{in}} \ln x_{i,\text{out}} + X \sum_i \boldsymbol{n}_i (\underline{G}_i - RT_{\text{amb}} \ln x_{i,\text{out}})$$

$$-\dot{W} = RT_{amb} \sum N_{i,in} \ln\frac{x_{i,in}}{x_{i,out}} + X \sum \boldsymbol{n_i} \underline{G}_i - RT_{amb} \sum \ln x_{i,out}^{n_i}$$

$$= RT_{amb} \sum N_{i,in} \ln\frac{x_{i,in}}{x_{i,out}} + X\Delta G_{rxn} - RT_{amb} \sum \ln x_{i,out}^{n_i}$$

6.39

C is the number of components, and M is the number of phases.

Then the unknowns are

N_i^K (number of moles of species i in phase K)

$\quad = C \times P$ unknowns

P^K (pressure in phase K) $= P$ unknowns

T^K (temperature in phase K) $= P$ unknowns.

Total number of unknowns is $C \times P + P + P = P \times (C+2)$

Then restrictions are that

T is the same in all phases, i.e., $T^I = T^{II} = T^{III} =.....$

$\quad$ P-1 restrictions

P is the same in all phases, i.e., $P^I = P^{II} = P^{III} =.....$

$\quad$ P-1 restrictions

$\overline{G}_i^K$ must be the same for species i in all phases

$\quad = C \times (P-1)$ restrictions

In addition we have the stoichiometric relation for each species that

$N_i = \sum_{k=1}^{K} N_i^k = N_{i,o} + \sum_{j=1}^{M} \boldsymbol{n}_{ij} X_j$ which provides an addition C restrictions.
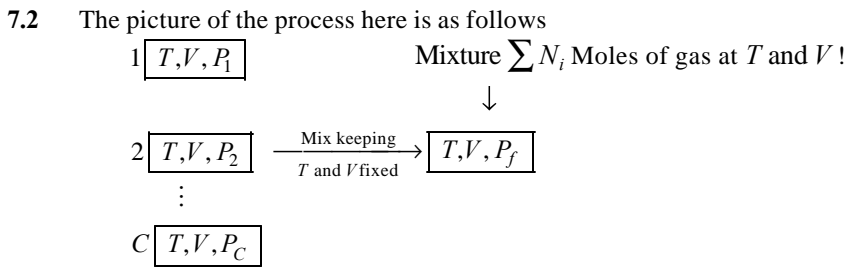
Therefore the number of degrees of freedom F are

$F = (C+2) \cdot P - (C+2) \cdot (P-1) - C = C + 2 - C = 2$

independent of the number of components, phases or independent chemical reactions.

Therefore Duhem's theorem is valid.

7

7.1 $PV(T,P,N_1,N_2...) = \sum N_i RT \quad \Rightarrow \quad \overline{V}_i(T,P,\underline{x}) = \underline{V}_i(T,P)$

$U(T,P,N_1,N_2...) = \sum N_i \underline{U}_i(T,P) \quad \Rightarrow \quad \overline{U}_i(T,P,\underline{x}) = \underline{U}_i(T,P)$

Also $\overline{S}_i(T,P,\underline{x}) = \underline{S}_i(T,P) - R\ln x_i$

$\Delta\underline{U}_{\text{mix}} = \sum_i x_i [\overline{U}_i(T,P,\underline{x}) - \underline{U}_i(T,P)] = \sum_i x_i[0] = 0$

$\Delta\underline{V}_{\text{mix}} = \sum_i x_i [\overline{V}_i(T,P,\underline{x}) - \underline{V}_i(T,P)] = \sum_i x_i[0] = 0$

$\Delta\underline{H}_{\text{mix}} = \Delta\underline{U}_{\text{mix}} + P\Delta\underline{V}_{\text{mix}} = 0$

$\Delta\underline{S}_{\text{mix}} = \sum x_i [\overline{S}_i(T,P,\underline{x}) - \underline{S}_i(T,P)] = \sum x_i[-R\ln x_i] = -R\sum x_i \ln x_i$

$\Delta\underline{G}_{\text{mix}} = \sum x_i [\overline{G}_i(T,P,\underline{x}) - \underline{G}_i(T,P)] = \sum x_i[(\overline{H}_i - T\overline{S}_i) - (\underline{H}_i - T\underline{S}_i)]$

$\qquad = \sum x_i(\overline{H}_i - \underline{H}_i) - T\sum x_i(\overline{S}_i - S_i)$

$\qquad = \Delta\underline{H}_{\text{mix}} - T\Delta\underline{S}_{\text{mix}} = RT\sum x_i \ln x_i$

Similarly

$\Delta\underline{A}_{\text{mix}} = \Delta\underline{U}_{\text{mix}} - T\Delta\underline{S}_{\text{mix}} = RT\sum x_i \ln x_i$

.

7.2 The picture of the process here is as follows

$1\ \boxed{T,V,P_1}$ $\qquad\qquad$ Mixture $\sum N_i$ Moles of gas at T and V !

$\qquad\qquad\qquad\qquad\qquad\qquad\downarrow$

$2\ \boxed{T,V,P_2} \quad \xrightarrow[\text{T and V fixed}]{\text{Mix keeping}} \quad \boxed{T,V,P_f}$

$\qquad \vdots$

$C\ \boxed{T,V,P_C}$

(a) Let

P_i = initial pressure of species i (pressure in unmixed state)

P = final pressure of mixed gas

$P^i = x_i P$ = partial pressure of species i in final state

want to show that $P_i = P^i$

$P = NRT/V = \left(\sum N_i\right)RT/V$

$P_i = N_i RT/V$

and

$\downarrow$ initial pressure of pure i

$$P^i = x_i P = x_i NRT/V = N_i RT/V = P_i$$

$\uparrow$ partial pressure of species i Q.E.D.

(b) Since the internal energy of an ideal gas is independent of total pressure, it follows that $\overline{U}_i^{IGM}(T,\underline{x}) = \underline{U}_i^{IG}(T)$ for mixing at constant total pressure or constant partial pressure. Thus, $\Delta\underline{U}_{mix}^{IGM} = 0$.

Next,

$$\overline{V}_i^{IGM}(T,P,\underline{x}) = \frac{\P V}{\P N_i}\bigg|_{T,P}\left\{\frac{\sum N_j RT}{P}\right\} = \frac{RT}{P} = \frac{RTx_i}{Px_i} = \frac{RTx_i}{P^i}$$

$$= x_i\frac{RT}{P_i} = x_i\frac{V^{IG}(P_i,T)}{N_i} = x_i\underline{V}_i^{IG}(T,P_i)$$

Thus $\overline{V}_i^{IGM}(T,P,\underline{x}) = x_i\underline{V}_i^{IG}(T,P_i)$

Can now define two $\Delta\boldsymbol{q}_{mix}^{IGM}$

$$\Delta\boldsymbol{q}_{mix}^{IGM}\Big|_1 = \sum x_i\{\overline{\boldsymbol{q}}_i(T,P,\underline{x})-\boldsymbol{q}_i(T,P)\} \text{ and } \Delta\boldsymbol{q}_{mix}^{IGM}\Big|_2 = \sum x_i\{\overline{\boldsymbol{q}}_i(T,P,\underline{x})-\boldsymbol{q}(T,P_i)\}$$

$\Delta\boldsymbol{q}_{mix}^{IGM}\Big|_1$ was computed in Section 7.1 and will not be considered here. We will be concerned with $\Delta\boldsymbol{q}_{mix}^{IGM}\Big|_2$!

$$\Delta\underline{V}_{mix}^{IGM} = \sum x_i\{\overline{V}_i^{IGM}(T,P,\underline{x})-\underline{V}_i(T,P_i)\} = \sum x_i\{x_i\underline{V}_i(T,P_i)-\underline{V}_i(T,P_i)\}$$

$$= \sum x_i(x_i-1)\frac{V}{N_i} = \sum x_i(x_i-1)\frac{V}{x_i N} = \frac{V}{N}\sum_{i=1}^{C}(x_i-1)$$

$$= \frac{V}{N}(1-C) = \frac{V(1-C)}{\displaystyle\sum_{i=1}^{C}N_i}$$

Note: $\displaystyle\sum_{i=1}^{C}1 = C$

where C = number of components.

For enthalpy we have

$$\overline{H}_i^{IGM}(T,P,\underline{x}) = \overline{U}_i^{IGM}(T,P,\underline{x})+P\overline{V}_i^{IGM}(T,P,\underline{x}) = \underline{U}_i^{IG}(T,P)+Px_i\underline{V}_i^{IG}(T,P_i)$$

$$= \underline{U}_i^{IG}(T,P)+P\overline{V}_i^{IG}(T,P) = \underline{H}_i^{IG}(T,P)$$

Thus

$$\Delta\underline{H}_{mix}^{IGM}\Big|_1 = \sum x_i\left(\overline{H}_i^{IGM}(T,P,\underline{x})-\underline{H}_i^{IG}(T,P)\right) = 0$$

and

$$\Delta \underline{H}^{\text{IGM}}_{\text{mix}}\Big|_2 = \sum_{i=1}^{C} x_i \left(\overline{H}_i^{\text{IGM}}(T,P,\underline{x}) - \underline{H}_1^{\text{IG}}(T,P_i) \right)$$

$$= \sum_i x_i \left\{ \underline{U}_i^{\text{IG}}(T,P) + P\underline{V}_i(T,P) - \underline{U}_i^{\text{IG}}(T,P) - P_i\underline{V}_i(T,P_i) \right\}$$

$$= \sum_i x_i \left\{ 0 + P\underline{V}_i(T,P) - P_i\underline{V}_i(T,P_i) \right\} = \sum_i x_i \{ RT - RT \} = 0$$

To compute $\Delta\underline{S}^{\text{IGM}}_{\text{mix}}$ we use the same sort of argument as in Section 7.1, but noting here that the volume occupied by each gas in the initial and final states are the same. Therefore $\overline{S}_i^{\text{IGM}}(T,P,\underline{x}) = \underline{S}_i^{\text{IG}}(T,P_i)$. Since T and V of each species is unchanged (see eqn. (3.4-2)). Therefore

$$\Delta\underline{S}^{\text{IGM}}_{\text{mix}}\Big|_2 = \sum_i x_i \left\{ \overline{S}_i^{\text{IGM}}(T,P,\underline{x}) - \underline{S}_i^{\text{IG}}(T,P_i) \right\} = 0$$

For the Helmholtz free energy we note that

$$A = U - TS \Rightarrow \overline{A}_i^{\text{IGM}}(T,P,\underline{x}) = \overline{U}_i^{\text{IGM}}(T,P,\underline{x}) - T\overline{S}_i^{\text{IGM}}(T,P,\underline{x})$$

$$= \underline{U}_i^{\text{IG}}(T) - T\underline{S}_i^{\text{IG}}(T,P_i) = \underline{A}_i^{\text{IG}}(T,P_i)$$

Thus, $\Delta\underline{A}^{\text{IGM}}_{\text{mix}}\Big|_2 = 0$. Finally $\underline{G} = \underline{A} + P\underline{V}$, $\Rightarrow$

$$\overline{G}_i^{\text{IGM}}(T,P,\underline{x}) = \overline{A}_i^{\text{IGM}}(T,P,\underline{x}) + P\overline{V}_i^{\text{IGM}}(T,P,\underline{x}) = \underline{A}_i^{\text{IG}}(T,P_i) + Px_i\underline{V}_i^{\text{IG}}(T,P_i)$$

$$= \underline{A}_i^{\text{IG}}(T,P_i) + P_i V_i^{\text{IG}}(T,P_i) = \underline{G}_i^{\text{IG}}(T,P_i)$$

So that

$$\Delta\underline{G}^{\text{IGM}}_{\text{mix}}\Big|_2 = 0$$

7.3   Generally mixing at constant T and P and mixing at constant T and V are quite *different*. However, for the *ideal gas* we have

$$PV_i = N_i RT \quad \text{(pure fluids)} \quad \text{and} \quad PV = \sum N_i RT \quad \text{(mixtures)}$$

Thus for the pure fluids (same T and P)

$$V_1 = \frac{N_1 RT}{P} \quad \text{and} \quad V_2 = \frac{N_2 RT}{P}$$

$$\Rightarrow (V_1 + V_2) = \frac{N_1 RT}{P} + \frac{N_2 RT}{P} = (N_1 + N_2)\frac{RT}{P} = V$$

So for the ideal gas the mixing process described in problem statement is also a mixing process at constant T and P and Table 7.1-1 applies here also.

7.4   We have the following properties for a mixture for mixing at constant T and P:

$$U(T,P,\underline{x}) = \sum N_i \underline{U}_i(T,P)$$

$$V(T,P,\underline{x}) = \sum N_i \underline{V}_i(T,P)$$

$$S(T,P,\underline{x}) = \sum N_i \underline{S}_i(T,P) - R\sum N_i \ln x_i$$

and $\underline{S}_i = \underline{S}_i^0 + C_{V,i} \ln \frac{\underline{U}_i}{\underline{U}_i^0} + R\ln \frac{\underline{V}_i}{\underline{V}_i^0}$

$\underline{S}_i^0$, $\underline{U}_i^0$, $\underline{V}_i^0$ are at some reference state.

(a) Find $\overline{V}_i$, $\overline{U}_i$, $\overline{S}_i$ and $\overline{G}_i$ in terms of $\underline{S}_i^0$, $\underline{U}_i^0$, $\underline{V}_i^0$, $C_{V,i}$, R, T, and $\underline{P}$. Need $\underline{U}_i$, $\underline{V}_i$.

We know $d\underline{U} = Td\underline{S} - Pd\underline{V} \rightarrow \left.\dfrac{\partial \underline{S}}{\partial \underline{U}}\right|_{\underline{V}} = \dfrac{1}{T}$; $\left.\dfrac{\partial \underline{S}}{\partial \underline{V}}\right|_{\underline{U}} = \dfrac{P}{T}$ and $\underline{S}_i = \underline{S}_i^0 + C_{V,i} \ln\dfrac{\underline{U}_i}{\underline{U}_i^0} + R\ln\dfrac{\underline{V}_i}{\underline{V}_i^0}$ for

pure component i.

$$\left.\dfrac{\partial \underline{S}}{\partial \underline{U}}\right|_{\underline{V}} = \dfrac{1}{T} = C_{V,i}\dfrac{1}{\underline{U}_i} \rightarrow \underline{U}_i = C_{V,i}T$$

$$\left.\dfrac{\partial \underline{S}}{\partial \underline{V}}\right|_{\underline{U}} = R\dfrac{1}{\underline{V}_i} \text{ and } \left.\dfrac{\partial \underline{S}}{\partial \underline{V}}\right|_{\underline{U}} \cdot \left.\dfrac{\partial \underline{U}}{\partial \underline{S}}\right|_{\underline{V}} \cdot \left.\dfrac{\partial \underline{V}}{\partial \underline{U}}\right|_{\underline{S}} = -1$$

$$\left.\dfrac{\partial \underline{U}}{\partial \underline{S}}\right|_{\underline{V}} = T\left.\dfrac{\partial \underline{V}}{\partial \underline{U}}\right|_{\underline{S}} = -\dfrac{1}{P} \Rightarrow \left.\dfrac{\partial \underline{S}}{\partial \underline{V}}\right|_{\underline{U}} = T\cdot\dfrac{-1}{P} = -1 \rightarrow \left.\dfrac{\partial \underline{S}}{\partial \underline{V}}\right|_{\underline{U}} = \dfrac{R}{\underline{V}_i} = \dfrac{P}{T}$$

$$\Rightarrow \underline{V}_i = \dfrac{RT}{P}$$

So $\overline{U}_i = \left.\dfrac{\partial \underline{U}}{\partial N_i}\right|_{T,P,N_{j\neq i}} = \dfrac{\partial}{\partial N_i}\sum N_i C_{V,i}T = C_{V,i}T = \underline{U}_i$

$$\overline{U}_i = C_{V,i}T$$

$$\overline{V}_i = \left.\dfrac{\partial \underline{V}}{\partial N_i}\right|_{T,P,N_{j\neq i}} = \dfrac{\partial}{\partial N_i}\sum N_i \underline{V}_i = \dfrac{RT}{P} = \overline{V}_i = \underline{V}_i$$

7.5   (a) Start with eqn. 7.2-13

$$\ln\dfrac{\overline{f}_i}{x_i P} = \ln \overline{f}_i = \dfrac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}=ZRT/P}\left[\dfrac{RT}{\underline{V}} - N\left(\dfrac{dP}{\partial N_i}\right)_{\underline{V}}\right]d\underline{V} - \ln Z$$

$$P = \dfrac{RT}{\underline{V}-b} - \dfrac{a}{\underline{V}^2} = \dfrac{NRT}{V-Nb} - \dfrac{N^2 a}{V^2} = \dfrac{NRT}{V-\sum N_i b_i} - \dfrac{\sum\sum N_i N_j a_{ij}}{V^2}$$

$$\left.\dfrac{\partial P}{\partial N_i}\right|_V = \dfrac{RT}{V-\sum N_i b_i} - \dfrac{NRT}{\left(V-\sum N_i b_i\right)^2}(-b_i) - \dfrac{2\sum N_j a_{ij}}{V^2}$$

$$= \dfrac{RT}{V-Nb} + \dfrac{NRTb_i}{(V-b)^2} - \dfrac{2\sum N_j a_{ij}}{V^2}$$

$$N\left.\dfrac{\partial P}{\partial N_i}\right|_V = \dfrac{RT}{\underline{V}} + \dfrac{RTb_i}{(\underline{V}-b)^2} - \dfrac{2\sum x_j a_{ij}}{V^2}$$

$$\ln \bar{\pmb{f}_i} = \ln \frac{\bar{f}_i}{x_i P} = \frac{1}{RT} \int\limits_{\underline{V}=\infty}^{ZRT/P} \left[\frac{RT}{\underline{V}} - \frac{RT}{\underline{V}-b} - \frac{RTb_i}{(\underline{V}-b)^2} + \frac{2\sum_j x_j a_{ij}}{\underline{V}^2} \right] d\underline{V} - \ln Z$$

$$= \frac{1}{RT} \left[RT \ln \frac{\underline{V}}{\underline{V}-b} \right]_{\underline{V}=\infty}^{ZRT/P} + \frac{RTb_i}{(\underline{V}-b)}\bigg|_{\underline{V}=\infty}^{ZRT/P} - \frac{2\sum_j x_j a_{ij}}{\underline{V}^2}\bigg|_{\underline{V}=\infty}^{ZRT/P} - \ln Z$$

$$= \ln \frac{Z}{Z-B} + \frac{B_i}{(Z-B)} - \frac{2\sum_j x_j a_{ij}}{RT\underline{V}} - \ln Z \qquad \left(\text{where } B_i = \frac{Pb_i}{RT} \right)$$

$$\Rightarrow \ln \bar{\pmb{f}_i} = \ln \frac{\bar{f}_i}{x_i P} = \frac{B_i}{Z-B} - \ln(Z-B) - \frac{2\sum_j x_j a_{ij}}{RT\underline{V}}$$

(b) For a pure van der Waals fluid (Eqn. 5.4-13)

$$\ln \frac{f_i}{P} = (Z-1) - \ln(Z-B_i) - \frac{a_i}{RT\underline{V}}$$

and, by definition of the activity coefficient

$$\bar{f}_i = x_i f_i \pmb{g}_i \Rightarrow$$

$$\bar{f}_i = x_i P \exp \left\{ \frac{B_i}{Z-B} - \ln(Z-B) - \frac{2\sum_j x_j A_{ij}}{Z} \right\}_{\text{mixture}}$$

$$f_i = P \exp \left\{ (Z-1) - \ln(Z-B_i) - \frac{A_{ii}}{Z} \right\}_{\text{pure fluid } i}$$

so

$$\frac{\bar{f}_i}{x_i f_i} = \frac{\exp \left\{ [B_i/(Z-B)] - \ln(Z-B) - \left[\left(2\sum_j x_j A_{ij} \right) \Big/ Z \right] \right\}_{\text{mixture}}}{\exp \left\{ (Z-1) - \ln(Z-B_i) - [(A_{ii})/Z] \right\}_{\text{pure fluid}}} = \pmb{g}_i$$

Note that the compressibilities in pure fluid and mixture will generally be different at the same T and P.

7.6   As a preliminary note that, from Eqns. (4.4-27 and 28)

$$\underline{H}(T,P) - \underline{H}^{IG}(T,P) = RT(Z-1) + \int\limits_{\underline{V}=\infty}^{\underline{V}=ZRT/P} \left[T \left(\frac{\partial P}{\partial T} \right)_{\underline{V}} - P \right] d\underline{V}$$

and

$$\underline{S}(T,P) - \underline{S}^{IG}(T,P) = R \ln Z + \int\limits_{\underline{V}=\infty}^{\underline{V}=ZRT/P} \left[\left(\frac{\partial P}{\partial T} \right)_{\underline{V}} - \frac{R}{\underline{V}} \right] d\underline{V}$$

vdw E.O.S. $P = \dfrac{RT}{\underline{V}-b} - \dfrac{a}{\underline{V}^2}$ so

$$\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} = \frac{R}{\underline{V}-b} \; ; \; T\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - P = \frac{RT}{\underline{V}-b} - \frac{RT}{(\underline{V}-b)} + \frac{a}{\underline{V}^2} = \frac{a}{\underline{V}^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_{\underline{V}} - \frac{R}{\underline{V}} = \frac{R}{(\underline{V}-b)} - \frac{R}{\underline{V}} \; ;$$

$$\Rightarrow \underline{H}(T,P) - \underline{H}^{IG}(T,P) = RT(Z-1) + \int_{\underline{V}=\infty}^{\underline{V}=ZRT/P} \frac{a}{\underline{V}^2} d\underline{V} = RT(Z-1) - \frac{a}{\underline{V}} = RT(Z-1) - \frac{RTA}{Z}$$

and

$$\underline{S}(T,P) - \underline{S}^{IG}(T,P) = R\ln Z + \int_{\underline{V}=\infty}^{\underline{V}=ZRT/P} \left[\frac{R}{\underline{V}-b} - \frac{R}{\underline{V}}\right] d\underline{V}$$

$$= R\ln Z + R\ln\frac{(\underline{V}-b)}{\underline{V}}\Bigg|_{\underline{V}=\infty}^{ZRT/P} = R\ln(Z-B)$$

Now on to solution of problem.

(a) $\underline{V}^{ex} = \underline{V}_{mix} - \sum x_i \underline{V}_i = \dfrac{RT}{P}\left(Z_{mix} - \sum x_i Z_i\right) = \Delta\underline{V}_{mix}$

$Z_{mix} =$ compressibility of mixture at T and P

$Z_i =$ compressibility of pure fluid i at T and P

Will leave answer to this part in this form since the analytic expression for Z_i and Z_{mix} (solution to cubic) is messy. Though it can be analytically and symbolically with a computer algebra program such as Mathcad, Mathematica, Maple, etc.)

(b) $\underline{H}^{ex} = \underline{H}_{mix} - \sum x_i \underline{H}_i = \dfrac{RT}{Z_{mix}-1} - \dfrac{RTA_{mix}}{Z_{mix}} - \sum_i x_i\left[RT(Z_i-1) - \dfrac{RTA_i}{Z_{mix}}\right]$

$$= RT\left(Z_{mix} - \sum x_i Z_i\right) + \sum RT\left(\frac{x_i A_i}{Z_i}\right) - \frac{RTA_{mix}}{Z_{mix}}$$

$$= RT\left(Z_{mix} - \sum x_i Z_i\right) + RT\left(\sum \frac{x_i A_i}{Z_i} - \frac{A_{mix}}{Z_{mix}}\right)$$

$\underline{U}^{ex} = \left(\underline{H}_{mix} - P\underline{V}_{mix}\right) - \sum x_i\left(\underline{H}_i - P\underline{V}_i\right)$

$$= \left(\underline{H}_{mix} - \sum x_i\underline{H}_i\right) - P\left(\underline{V}_{mix} - \sum x_i\underline{V}_i\right)$$

$$= RT\left(Z_{mix} - \sum x_i Z_i\right) + RT\left(\sum \frac{x_i A_i}{Z_i} - \frac{A_{mix}}{Z_{mix}}\right) - RT\left(Z_{mix} - \sum x_i Z_i\right)$$

$$= +RT\left(\sum \frac{x_i A_i}{Z_i} - \frac{A_{mix}}{Z_{mix}}\right)$$

(c) $\underline{S}_{\text{mix}} - \sum x_i S_i - R\sum x_i \ln x_i$

$= \underline{S}^{ex}$

$= P\ln(Z_{\text{mix}} - B_{\text{mix}}) - R\big[X_i \ln(Z_i - B_i) - R\sum x_i \ln x_i\big]$

$= R\ln(Z_{\text{mix}} - B_{\text{mix}}) - R\sum x_i\big[\ln(Z_i - B_i) + \ln x_i\big]$

$= R\ln(Z_{\text{mix}} - B_{\text{mix}}) - R\big[x_i\big[\ln x_i(Z_i - B_i)\big]\big]$

$= R\ln\dfrac{Z_{\text{mix}} - B_{\text{mix}}}{\prod\limits_i (Z_i - B_i)^{x_i}}$

(d) $\underline{G}^{ex} = \underline{H}^{ex} - T\underline{S}^{ex} = RT\big(Z_{\text{mix}} - \sum x_i Z_i\big) + RT\left(\sum \dfrac{x_i A_i}{Z_i} - \dfrac{A_{\text{mix}}}{Z_{\text{mix}}}\right)$

$\qquad - RT\ln\dfrac{Z_{\text{mix}} - B_{\text{mix}}}{\prod\limits_i (Z_i - B_i)^{x_i}}$

$\underline{A}^{ex} = \underline{U}^{ex} - T\underline{S}^{ex} = +RT\left(\sum \dfrac{x_i A_i}{Z_i} - \dfrac{A_{\text{mix}}}{Z_{\text{mix}}}\right) - RT\ln\dfrac{Z_{\text{mix}} - B_{\text{mix}}}{\prod\limits_i (Z_i - B_i)^{x_i}}$

7.7   (a) Start from eqn. (7.2-13)

$$\ln \boldsymbol{f}_i = \ln\frac{\bar{f}_i}{y_i P} = \frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}=ZRT/P}\left[\frac{RT}{\underline{V}} - N\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_{j\neq i}}\right]d\underline{V} - \ln Z$$

but

$$\frac{P\underline{V}}{RT} = 1 + \frac{B_{\text{mix}}}{\underline{V}} = 1 + \frac{\sum\sum y_i y_j B_{ij}}{\underline{V}}$$

$$P = \frac{RT}{\underline{V}} + \frac{B_{\text{mix}}RT}{\underline{V}^2} = \frac{\sum N_i RT}{V} + \frac{RT\sum\sum N_i N_j B_{ij}}{V^2}$$

$$\frac{\partial P}{\partial N_i} = \frac{RT}{V} + \frac{2\sum\limits_j N_j B_{ij} RT}{V^2}$$

$$N\frac{\partial P}{\partial N_i} = \frac{NRT}{V} + \frac{2N\sum\limits_j N_j B_{ij} RT}{V^2} = \frac{RT}{\underline{V}} + \frac{2\sum x_j B_{ij}}{\underline{V}^2}RT$$

$$\Rightarrow$$

$$\ln\frac{f_i}{y_i P} = \frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}=ZRT/P}\left[\frac{RT}{\underline{V}} - \frac{RT}{\underline{V}} - \frac{2RT\sum\limits_j x_j B_{ij}}{\underline{V}^2}\right]d\underline{V} - \ln Z$$

$$= \frac{2}{\underline{V}}\sum x_j B_{ij} - \ln Z \quad \text{(eqn. 7.4 - 6)}$$

Note also that

$$\frac{P\underline{V}}{RT} = 1 + \frac{B}{\underline{V}} \quad \text{or} \quad \frac{P\underline{V}^2}{RT} = \underline{V} + B \quad \frac{P\underline{V}^2}{RT} - \underline{V} - B = 0$$

$$\Rightarrow \underline{V} = \frac{1 \pm \sqrt{1 + 4PB/RT}}{2P/RT} \quad \text{or} \quad \frac{P\underline{V}}{RT} = Z = \frac{1}{2}\left(1 \pm \sqrt{1 + 4PB/RT}\right)$$

as $P \rightarrow 0$, $Z \rightarrow 1$ (ideal gas limit) so only + sign allowed

$$Z = \frac{1}{2}\left(1 + \sqrt{1 + 4PB/RT}\right)$$

Note that at low pressures we can obtain a simpler expression.
At low pressures

$$\frac{P\underline{V}}{RT} = 1 + \frac{B_{\text{mix}}}{\underline{V}} \approx 1 + \frac{B_{\text{mix}}P}{RT}$$

Then

$$\underline{V} = \frac{RT}{P} + B_{\text{mix}} = \frac{RT}{P} + \left\{y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22}\right\}$$

$$\underline{V} - \underline{V}^{IG} = \frac{RT}{P} + B_{\text{mix}} - \frac{RT}{P} = \sum\sum y_i y_j B_{ij} = \underline{V}^{\text{ex}}$$

Also

$$V = N\underline{V} = (N_1 + N_2)\frac{RT}{P} + \frac{1}{N_1 + N_2}\left\{N_1^2 B_{11} + N_2^2 B_{12} + 2N_1 N_2 B_{22}\right\}$$

$$\overline{V}_1 = \frac{\partial}{\partial N_1}V = \frac{RT}{P} - \frac{1}{N_1 + N_2}\sum_i\sum N_i N_j B_{ij} + \frac{2\sum_j N_j B_{ij}}{N_1 + N_2}$$

$$= \frac{RT}{P} - \sum\sum y_i y_j B_{ij} + 2\sum y_j B_{ij}$$

$$= \frac{RT}{P} + \left[2y_1 B_{11} + 2y_2 B_{12} - y_1^2 B_{11} - 2y_1 y_2 B_{12} - y_2^2 B_{22}\right]$$

$$= \frac{RT}{P} + \left[y_1(2 - y_1)B_{11} + 2y_2(1 - y_1)B_{12} - y_2^2 B_{22}\right]$$

$$= \frac{RT}{P} + \left[y_1(2 - y_1)B_{11} + 2y_2^2 B_{12} - y_2^2 B_{22}\right]$$

$$\overline{V}_1 - \overline{V}_1^{IGM} = \frac{RT}{P} + \left[y_1(2 - y_1)B_{11} + 2y_2^2 B_{12} - y_2^2 B_{22}\right] - \frac{RT}{P}$$

$$\ln\frac{\overline{f}_1}{y_1 P} = \frac{1}{RT}\int_0^P \left(\overline{V}_1 - \overline{V}_1^{IGM}\right)dP = \left[y_1(2 - y_1)B_{11} + 2y_2^2 B_{12} - y_2^2 B_{22}\right]\frac{P}{RT}$$

$$\Rightarrow \frac{\overline{f}_1}{y_1 P} = \exp\left\{\left[y_1(2 - y_1)B_{11} + 2y_2^2 B_{12} - y_2^2 B_{22}\right]\frac{P}{RT}\right\}$$

This is an alternate, some approximate expression that we will use in what follows. Also, for the pure component we have

$$\frac{f_1}{P} = \exp\left[\frac{B_{11}P}{RT}\right]$$

Note that these expressions are slightly easier to use then the full expressions since we don't have to solve for $\underline{V}$ (or Z) first

$$\frac{\overline{f}_1}{y_1 f_1} = \mathbf{g}_1 = \frac{\exp\{[y_1(2-y_1)B_{11}+2y_2^2 B_{12}-y_2^2 B_{22}](P/RT)\}}{\exp\{B_{11}P/RT\}}$$

$$= \exp\left\{[-(1-2y_1+y_1^2)B_{11}+2y_2^2 B_{12}-y_2^2 B_{22}]\frac{P}{RT}\right\}$$

$$= \exp\left[y_2^2(2B_{12}-B_{11}-B_{22})\frac{P}{RT}\right] = \mathbf{g}_1$$

or $\ln \mathbf{g}_1 = \dfrac{\mathbf{d}_{12}y_2^2 P}{RT}$ where $\mathbf{d}_{12} = 2B_{12}-B_{11}-B_{22}$

(b) Repeating the argument for a ternary mixture

$$\ln \mathbf{g}_1 = \frac{P}{RT}\left[y_2^2 \mathbf{d}_{12} + y_2 y_3(\mathbf{d}_{12}+\mathbf{d}_{13}-\mathbf{d}_{22})+y_3^2 \mathbf{d}_{13}\right]$$

By simple generalization

$$\ln \mathbf{g}_1 = \frac{P}{2RT}\sum_{\substack{i \\ i\neq 1 \\ i\neq j}}\sum_{\substack{j \\ j\neq 1}} y_i y_j \left(\mathbf{d}_{1i}+\mathbf{d}_{ij}-\mathbf{d}_{ij}\right) \qquad \boxed{\text{Note: } \mathbf{d}_{ii}=0}$$

7.8 (a) $\underline{G}^{ex} = x_1 x_2\{A+B(x_1-x_2)\}$

$$\underline{G}^{ex} = N\underline{G}^{ex} = \frac{N_1 N_2}{N_1+N_2}\left\{A+B\left(\frac{N_1-N_2}{N_1+N_2}\right)\right\}$$

$$\overline{G}_1^{ex} = \left(\frac{\P \underline{G}^{ex}}{\P N_1}\right)_{T,P} = \frac{N_2}{N_1+N_2}\left\{A+B\left(\frac{N_1-N_2}{N_1+N_2}\right)\right\}$$

$$-\frac{N_1 N_2}{(N_1+N_2)^2}\left\{A+B\frac{(N_1-N_2)}{N_1+N_2}\right\}$$

$$+\frac{N_1 N_2}{N_1+N_2}\left\{\frac{B}{N_1+N_2}-\frac{B(N_1-N_2)}{(N_1+N_2)^2}\right\}$$

$$= x_2\{A+B(x_1-x_2)\}-x_1 x_2\{A+B(x_1-x_2)\}+x_1 x_2 B(1-x_1+x_2)$$

$$= Ax_2^2+Bx_2^2-2Bx_2^3+2Bx_2^2-2Bx_2^3$$

Thus $\overline{G}_1^{ex} = RT\ln \mathbf{g}_1 = (A+3B)x_2^2-4Bx_2^3$.

Now by repeating the calculation, or by using the symmetry of $\underline{G}^{ex}$ and replacing B by $-B$ and interchanging the subscripts 1 and 2 we obtain

$$\overline{G}_2^{ex} = RT\ln \mathbf{g}_2 = (A-3B)x_1^2+4Bx_1^3$$

(b) $\underline{G}^{ex} = \dfrac{2RTa_{12}x_1 q_1 x_2 q_2}{x_1 q_1+x_2 q_2} \implies G^{ex} = N\underline{G}^{ex} = \dfrac{2RTa_{12}q_1 q_2 N_1 N_2}{N_1 q_1+N_2 q_2}$

After some algebra

$$\overline{G}_1^{\text{ex}} = \frac{\P(N\underline{G}^{\text{ex}})}{\P N_1}\Bigg|_{T,P,N_2} = \frac{2RTa_{12}q_1}{\left[1+(x_1q_1/x_2q_2)\right]^2}$$

$$\Rightarrow \ln \boldsymbol{g}_1 = \frac{\overline{G}_1^{\text{ex}}}{RT} = \frac{2a_{12}q_1}{\left[1+(x_1q_1/x_2q_2)\right]^2} = \frac{\boldsymbol{a}}{\left[1+(\boldsymbol{a}x_1/\boldsymbol{b}x_2)\right]^2}$$

Similarly $\ln \boldsymbol{g}_2 = \dfrac{\boldsymbol{b}}{\left[1+(\boldsymbol{b}x_2/\boldsymbol{a}x_1)\right]^2}$.

(c) $\dfrac{G^{\text{ex}}}{RT} = 2a_{12}z_1z_2 + 2a_{13}z_1z_3 + 2a_{23}z_2z_3$; where $z_i = \dfrac{x_iq_i}{\displaystyle\sum_j x_jq_j}$ and

$$G^{\text{ex}} = N\underline{G}^{\text{ex}} = RT\left(\sum_k N_kq_k\right)^{-1}\sum_k\sum_j a_{kj}N_kN_jq_kq_j \text{ ; thus}$$

$$\ln \boldsymbol{g}_i = \frac{\overline{G}_i^{\text{ex}}}{RT}\frac{\P}{\P N_i}G^{\text{ex}}\Bigg|_{T,P,N_{j\ne i}} = \frac{-q_i\displaystyle\sum_{j,\,k}a_{kj}q_kq_jx_kx_j}{\left(\displaystyle\sum_k x_kq_k\right)^2} + \frac{2\displaystyle\sum_j a_{ij}q_iq_jx_j}{\displaystyle\sum_k x_kq_k}$$

Now setting

$$\boldsymbol{a}_{12} = 2q_1a_{12},\ \boldsymbol{b}_{12} = 2q_2a_{21} = 2q_2a_{12} = \boldsymbol{a}_{21} \Rightarrow q_2 = \frac{q_1\boldsymbol{b}_{12}}{\boldsymbol{a}_{12}};$$

similarly, $q_3 = \dfrac{q_1\boldsymbol{b}_{13}}{\boldsymbol{a}_{13}}$, etc. For the case $i=1$

$$\ln \boldsymbol{g}_1 = \frac{\left\{x_2^2\boldsymbol{a}_{12}(\boldsymbol{b}_{12}/\boldsymbol{a}_{12})^2 + x_3^2\boldsymbol{a}_{13}(\boldsymbol{b}_{13}/\boldsymbol{a}_{13})^2\right\} + x_2x_3(\boldsymbol{b}_{12}/\boldsymbol{a}_{12})(\boldsymbol{b}_{13}/\boldsymbol{a}_{13})[\boldsymbol{a}_{12} + \boldsymbol{a}_{13} - \boldsymbol{a}_{23}(\boldsymbol{a}_{12}/\boldsymbol{b}_{12})]}{\left\{x_1 + x_2(\boldsymbol{b}_{12}/\boldsymbol{a}_{12}) + x_3(\boldsymbol{b}_{13}/\boldsymbol{a}_{13})\right\}^2}$$

Interchanging indices 1 and 2

$$\ln \boldsymbol{g}_2 = \frac{\left\{x_1^2\boldsymbol{b}_{12}(\boldsymbol{a}_{12}/\boldsymbol{b}_{12})^2 + x_3^2\boldsymbol{a}_{23}(\boldsymbol{b}_{23}/\boldsymbol{a}_{23})^2\right\} + x_1x_3(\boldsymbol{a}_{12}/\boldsymbol{b}_{12})(\boldsymbol{b}_{23}/\boldsymbol{a}_{23})[\boldsymbol{b}_{12} + \boldsymbol{a}_{13} - \boldsymbol{a}_{23}(\boldsymbol{b}_{12}/\boldsymbol{a}_{12})]}{\left\{x_2 + x_1(\boldsymbol{a}_{12}/\boldsymbol{b}_{12}) + x_3(\boldsymbol{b}_{23}/\boldsymbol{a}_{23})\right\}^2}$$

Finally, interchanging indices 1 and 3 in the original equation yields

$$\ln \boldsymbol{g}_3 = \frac{\left\{x_2^2\boldsymbol{b}_{23}(\boldsymbol{a}_{23}/\boldsymbol{b}_{23})^2 + x_1^2\boldsymbol{b}_{13}(\boldsymbol{a}_{13}/\boldsymbol{b}_{13})^2\right\} + x_1x_2(\boldsymbol{a}_{23}/\boldsymbol{b}_{23})(\boldsymbol{a}_{13}/\boldsymbol{b}_{13})[\boldsymbol{b}_{23} + \boldsymbol{b}_{13} - \boldsymbol{b}_{12}(\boldsymbol{b}_{23}/\boldsymbol{a}_{23})]}{\left\{x_3 + x_2(\boldsymbol{a}_{23}/\boldsymbol{b}_{23}) + x_1(\boldsymbol{a}_{13}/\boldsymbol{b}_{13})\right\}^2}$$

7.9   (also available as a Mathcad worksheet)

Using Eqns. (7.6-b) yields: $\boldsymbol{a} = \dfrac{b_1}{RT}\left[\dfrac{\sqrt{a_1}}{b_1} - \dfrac{\sqrt{a_2}}{b_2}\right]^2$ and $\boldsymbol{b} = \dfrac{b_2}{RT}\left[\dfrac{\sqrt{a_1}}{b_1} - \dfrac{\sqrt{a_2}}{b_2}\right]^2$. From Section 4.6,

we have three different expressions relating the a and b parameters to the critical properties:

1) $a = \dfrac{27R^2T_C^2}{64P_C}$ and $b = \dfrac{RT_C}{8P_C}$. Eqn. (4.6-4a)

2) $a = 3P_C\underline{V}_C^2$ and $b = \dfrac{\underline{V}_C}{3}$. Eqn. (4.6-4b)

3) $\quad a = \dfrac{9\underline{V}_C RT_C}{8}$ and $b = \dfrac{\underline{V}_C}{3}$. Eqn. (4.6-3a)

Since Z_C is not equal to 3/8 for the fluids under consideration, each set of relations will give a different pair of values for a and b. Generally, set 1 is used, since $\underline{V}_C$ is known with less accuracy than P_C and T_C. All three sets of parameters will be considered here.

		Benzene		2,2,4-trumethyl pentane
$V_C = MW/\mathbf{r}_C$		$0.2595 \ \text{m}^3/\text{kg}$		$0.4776 \ \text{m}^3/\text{kg}$
Set 1	a	$1.875\times10^6 \ \left(\text{m}^3\right)^2 \text{Pa}/\text{kmol}^2$		$3.609\times10^6 \ \left(\text{m}^3\right)^2 \text{Pa}/\text{kmol}^2$
	b	$0.119 \ \left(\text{m}^3\right)^2/\text{kmol}$		$0.232 \ \left(\text{m}^3\right)^2/\text{kmol}$
	a		0.480	
	b		0.937	
Set 2	a	$9.945\times10^5 \ \left(\text{m}^3\right)^2 \text{Pa}/\text{kmol}^2$		$1.698\times10^6 \ \left(\text{m}^3\right)^2 \text{Pa}/\text{kmol}^2$
	b	$0.0865 \ \text{m}^3/\text{kmol}$		$0.159 \ \text{m}^3/\text{kmol}$
	a		0.353	
	b		0.658	
Set 3	a	$1.3655\times10^6 \ \left(\text{m}^3\right)^2 \text{Pa}/\text{kmol}^2$		$2.476\times10^6 \ \left(\text{m}^3\right)^2 \text{Pa}/\text{kmol}^2$
	b	$0.0865 \ \text{m}^3/\text{kmol}$		$0.159 \ \text{m}^3/\text{kmol}$
	a		0.433	
	b		0.807	

Set 4

    Example 7.5-1 $\boldsymbol{a} = 0.415$

    Fitting the van Laar equation $\boldsymbol{b} = 0.706$

Set 5

    Example 7.6-1 $\boldsymbol{a} = \dfrac{\underline{V}_1}{RT}(\boldsymbol{d}_1 - \boldsymbol{d}_2)^2 = 0.703$

    Regular Solution Theory $\boldsymbol{b} = \dfrac{\underline{V}_2}{\underline{V}_1}\boldsymbol{a} = 1304$

The 5 sets of results are plotted below.

Numbers in circles denote parameter sets used.

    Parameter set ④, fitted to the experimental data, should be the most accurate. Parameter set ③, obtained using $\underline{V}_C$ and T_C data should be reasonably good, also.
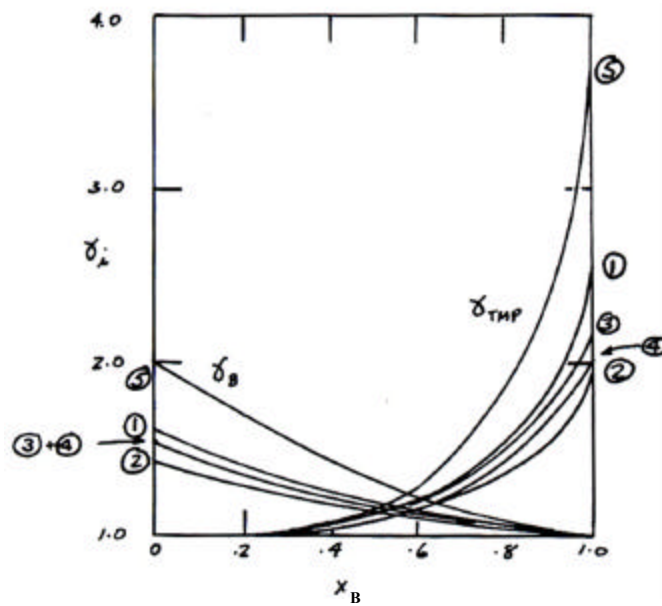
7.10 i) One-constant Margules equation

$$RT\ln \boldsymbol{g}_1 = Ax_2^2 \qquad\qquad RT\ln \boldsymbol{g}_1(x_1 = 0) = A$$

Thus

$$RT\ln \boldsymbol{g}_1^* = RT\ln \frac{\boldsymbol{g}_1(x_1)}{\boldsymbol{g}_1(x_1 = 0)} = Ax_2^2 - A = -A\left(1 - x_2^2\right)$$

or

$$\boldsymbol{g}_1^* = \exp\left[\frac{-A\left(1 - x_2^2\right)}{RT}\right] \quad \text{and} \quad \boldsymbol{g}_1^{\square} = \frac{x_1 \cdot 1000}{m_s M_1}\exp\left[\frac{-A\left(1 - x_2^2\right)}{RT}\right]$$

ii) Two-constant Margules equation

$$RT\ln \boldsymbol{g}_1(x_1) = \boldsymbol{a}_1 x_2^2 + \boldsymbol{b}_1 x_2^3$$

$$RT\ln \boldsymbol{g}_1(x_1 = 0) = \boldsymbol{a}_1 + \boldsymbol{b}_1$$

$$RT\ln \boldsymbol{g}_1^* = RT\ln \frac{\boldsymbol{g}_1(x_1)}{\boldsymbol{g}_1(x_1 = 0)} = -\boldsymbol{a}_1\left(1 - x_2^2\right) - \boldsymbol{b}_1\left(1 - x_2^3\right)$$

Thus

$$\boldsymbol{g}_1^* = \exp\left[\frac{-\boldsymbol{a}_1\left(1 - x_2^2\right) - \boldsymbol{b}_1\left(1 - x_2^3\right)}{RT}\right]$$

and

$$\boldsymbol{g}_1^{\square} = \frac{x_1 \cdot 1000}{m_s M_1}\exp\left[\frac{-\boldsymbol{a}_1\left(1 - x_2^2\right) - \boldsymbol{b}_1\left(1 - x_2^3\right)}{RT}\right]$$

iii) van Laar equation

$$\ln \boldsymbol{g}_1(x_1) = \frac{\boldsymbol{a}}{\left[1 + \left(\boldsymbol{a}x_1/\boldsymbol{b}x_2\right)\right]^2}\;; \quad \ln \boldsymbol{g}_1(x_1 = 0) = \boldsymbol{a}$$

$$\ln \boldsymbol{g}_1^*(x_1) = \ln \boldsymbol{g}_1(x_1) - \ln \boldsymbol{g}_1(x_1 = 0) = \frac{\boldsymbol{a}}{\left[1 + \left(\boldsymbol{a}x_1/\boldsymbol{b}x_2\right)\right]^2} - \boldsymbol{a}$$

or, upon rearrangement,

$$\boldsymbol{g}_1^* = \exp\left[\frac{-\boldsymbol{a}^2 x_1(2\boldsymbol{b}x_2 + \boldsymbol{a}x_1)}{\left(\boldsymbol{b}x_2 + \boldsymbol{a}x_1\right)^2}\right]$$

and

$$\boldsymbol{g}_1^{\square} = \frac{x_1 \cdot 1000}{m_s M_1}\exp\left[\frac{-\boldsymbol{a}^2 x_1(2\boldsymbol{b}x_2 + \boldsymbol{a}x_1)}{\left(\boldsymbol{b}x_2 + \boldsymbol{a}x_1\right)^2}\right]$$

iv) Regular Solution Theory

$$RT\ln \boldsymbol{g}_1(x_1) = \underline{V}_1 \boldsymbol{f}_2^2(\boldsymbol{d}_1 - \boldsymbol{d}_2)^2 \text{ and } RT\ln \boldsymbol{g}_1(x_1 = 0) = \underline{V}_1(\boldsymbol{d}_1 - \boldsymbol{d}_2)^2$$

$$\left(\text{since } \boldsymbol{f}_2 = \frac{x_2 \underline{V}_2}{x_1 \underline{V}_1 + x_2 \underline{V}_2} \Rightarrow 1 \text{ as } x_1 \to 0\right)$$

Thus

$$RT\ln \boldsymbol{g}_1^*(x_1) = RT\ln \boldsymbol{g}_1(x_1) - RT\ln \boldsymbol{g}_1(x_1 = 0) = \underline{V}_1\left(\boldsymbol{f}_2^2 - 1\right)(\boldsymbol{d}_1 - \boldsymbol{d}_2)^2$$

$$\boldsymbol{g}_1^* = \exp\left[\frac{\underline{V}_1\left(\boldsymbol{f}_2^2 - 1\right)(\boldsymbol{d}_1 - \boldsymbol{d}_2)^2}{RT}\right] \text{ and}$$

$$\boldsymbol{g}_1^{\square} = \frac{x_1 \cdot 1000}{m_s M_1}\exp\left[\frac{\underline{V}_1\left(\boldsymbol{f}_2^2 - 1\right)(\boldsymbol{d}_1 - \boldsymbol{d}_2)^2}{RT}\right]$$

v) UNIQUAC Model

$$\ln \boldsymbol{g}_i = \ln\frac{\boldsymbol{f}_i}{x_i} + \frac{z}{2}q_i\ln\frac{\boldsymbol{q}_i}{\boldsymbol{f}_i} + l_i - \frac{\boldsymbol{f}_i}{x_i}\sum x_j l_j - q_i\left[1 - \ln\sum_j\left(\boldsymbol{q}_j \boldsymbol{t}_{ij}\right) - \sum_j\frac{\boldsymbol{q}_j \boldsymbol{t}_{ij}}{\sum_k \boldsymbol{q}_k \boldsymbol{t}_{kj}}\right]$$

$$\ln \boldsymbol{g}_i(x_i \to 0) = \lim_{x_i \to 0}\left(\ln \boldsymbol{g}_i\right)$$

Now consider $x_i \to 0$, then $\boldsymbol{q}_j \to 1$ and $\boldsymbol{q}_i \to 0$

$$\frac{\boldsymbol{f}_i}{x_i} = \frac{x_i r_i}{x_1 r_1 + x_2 r_2}\cdot\frac{1}{x_i} = \frac{r_i}{x_1 r_1 + x_2 r_2}\,, \quad \frac{\boldsymbol{f}_i}{x_i} = \frac{r_i}{r_j}\,; \quad \frac{\boldsymbol{q}_i}{\boldsymbol{f}_i} = \frac{x_i q_i/(x_1 q_1 + x_2 q_2)}{x_i r_i/(x_1 r_1 + x_2 r_2)} = \frac{q_i}{r_i}\frac{r_j}{q_j}$$

$$\ln \boldsymbol{g}_i = \ln\left(\frac{r_i}{r_j}\right) + \frac{z}{2}q_i\ln\left(\frac{q_i}{q_j}\cdot\frac{r_j}{r_i}\right) + l_i - \frac{r_i}{r_j}l_j - q_i\left[1 - \ln\left(\boldsymbol{t}_{ij}\right) - \frac{\boldsymbol{t}_{ij}}{\boldsymbol{t}_{jj}}\right]$$

$$\ln\frac{\boldsymbol{g}_1}{\boldsymbol{g}_1(x_1 \to 0)} = \ln \boldsymbol{g}_1^* = \ln\left(\frac{\boldsymbol{f}_i r_j}{x_i r_i}\right) + \frac{z}{2}q_i\ln\left(\frac{\boldsymbol{q}_i}{\boldsymbol{f}_i}\cdot\frac{q_j r_i}{q_i r_j}\right) - \frac{\boldsymbol{f}_i}{x_i}\sum x_j l_j + \frac{r_i}{r_j}l_i$$

$$-q_i\left[-\ln\sum_j \boldsymbol{q}_j \boldsymbol{t}_{ij} - \sum_j\frac{\boldsymbol{q}_j \boldsymbol{t}_{ij}}{\sum_k \boldsymbol{q}_k \boldsymbol{t}_{kj}} + \ln \boldsymbol{t}_{ij} + \frac{\boldsymbol{t}_{ij}}{\boldsymbol{t}_{jj}}\right]$$

$$g_1^\square = \frac{x_1 \cdot 1000}{m_s M_1} g_1^* \quad \text{where } g_1^* \text{ is as given above.}$$

7.11   An ideal gas constrained to remain at constant volume and T, is also a system at constant internal energy and volume, since $\underline{U}$ is only a function of temperature for the ideal gas. Consequently, at equilibrium, the entropy should be a maximum.

Suppose there were N_1 molecules and N lattice sites. For any distribution of the N_1 molecules among the N lattice sites there will be N_1 lattice sites with molecules, and $N_2 = N - N_1$ empty lattice sites. Thus we can consider the "lattice gas" to be a mixture of N_1 molecules and N_2 holes, and the entropy of various configurations of this binary system can be computed. Following the analysis of Appendix 7.1, it is clear that the random mixture, or uniform distribution of gas molecules, is the state of maximum entropy. A completely ordered state (for example, the first N_1 lattice sites filled, and the next $N_2 = N - N_1$ lattice sites empty) is an especially low entropy configuration.

7.12   The principle of corresponding states, and the pseudo-critical constant concept will be used first, then the Peng-Robinson equation of state (program PR1)

(a) O_2: $T_C = 154.6$ K ; $P_C = 50.46$ bar ; $T_r = \dfrac{290}{154.6} = 1.876$; $P_r = \dfrac{800}{50.46} = 15.85$.

From Figure 5.4-1: $\dfrac{f}{P} = 1.025 \Rightarrow f = P\left(\dfrac{f}{P}\right) = 820$ bar .

Using the P-R e.o.s.. and the program PR1 $f_{O_2} = 735.1$ bar .

(b) N_2: $T_C = 126.2$ K ; $P_C = 33.94$ bar ; $T_r = \dfrac{290}{126.2} = 2.298$; $P_r = \dfrac{800}{33.94} = 23.57$; $\dfrac{f}{P} \cong 1.36$;

$f_{N_2} = 1088$ bar .

Using the P-R e.o.s. $f_{N_2} = 1043$ bar .

(c)   Lewis-Randall Rule

	Corresponding states	P-R e.o.s.
$\bar{f}_{O_2}$	$0.3 \times 820 = 246.0$ bar	$0.3 \times 735.1 = 220.5$ bar
$\bar{f}_{N_2}$	$0.7 \times 1088 = 761.6$ bar	$0.7 \times 1043 = 730.1$ bar

(d)   Kay's Rule

$T_{CM} = 0.3 \times 154.6 + 0.7 \times 126.2 = 134.72$ K

$P_{CM} = 0.3 \times 50.46 + 0.7 \times 38.94 = 38.90$ bar

$$y^{O_2} = -\frac{T}{T_{CM}^2}\left(T_{C,O_2} - T_{CM}\right) = -\frac{290}{134.72^2}(154.6 - 134.72) = -0.318$$

$$y^{N_2} = -\frac{290}{134.72^2}(126.2 - 134.72) = +0.136$$

$$y_2^{O_2} = -\frac{P\left(P_{C,O_2} - P_{CM}\right)}{P_{CM}^2} = -6.112$$

$$y_2^{N_2} = 2.622$$

$$T_{rM} = \frac{290}{134.72} = 2.1526 ; \quad P_{rM} = \frac{800}{38.90} = 20.565$$

$$\frac{f}{P} \sim 1.23 \; ; \; \frac{H - \underline{H}^{\mathrm{IG}}}{RT_{\mathrm{C}}} \cong -\frac{1.7}{1.987} = -0.856 \; ; \; Z_{\mathrm{M}} \sim 1.6$$

$$\ln \frac{\bar{f}_{\mathrm{N_2}}}{x_{\mathrm{N_2}} P} = \ln 1.23 - \frac{(0.136)(-0.856)}{(2.1526)^2} + \frac{(1.6-1)(2.622)}{20.565}$$

$$= 0.2070 + 0.0251 + 0.0765 = 0.3086$$

$$\Rightarrow \frac{\bar{f}_{\mathrm{N_2}}}{x_{\mathrm{N_2}} P} = 1.3615 \; ; \; \bar{f}_{\mathrm{N_2}} = 0.7 \times 800 \times 1.3615 = 762.4 \text{ bar}$$

$$\ln \frac{\bar{f}_{\mathrm{O_2}}}{x_{\mathrm{O_2}} P} = \ln 1.23 - \frac{(-0.318)(-0.856)}{(2.1526)^2} + \frac{(1.6-1)(-6.112)}{20.65} = -0.02929$$

$$\Rightarrow \frac{\bar{f}_{\mathrm{O_2}}}{x_{\mathrm{O_2}} P} = 0.97113 \; ; \; \bar{f}_{\mathrm{O_2}} = 0.97113 \times 0.3 \times 800 = 233.1 \text{ bar}$$

(e) Prausnitz-Gunn Rule

$$P_{\mathrm{CM}} = R \underbrace{\left(\sum_i x_i Z_{\mathrm{C},i} \right)}_{=Z_{\mathrm{CM}}} \underbrace{\left(\sum_i x_i T_{\mathrm{C},i} \right)}_{=T_{\mathrm{CM}}} / \underbrace{\left(\sum_i x_i \underline{V}_{\mathrm{C},i} \right)}_{=\underline{V}_{\mathrm{CM}}}$$

$$Z_{\mathrm{CM}} = 0.3 \times 0.288 + 0.7 \times 0.290 = 0.2894$$

$$T_{\mathrm{CM}} = 134.72 \text{ (see part d)}$$

$$\underline{V}_{\mathrm{CM}} = 0.3 \times 0.0732 + 0.72 \times 0.0895 = 0.08461$$

$$P_{\mathrm{CM}} = \frac{0.08314 \times 0.2894 \times 134.72}{0.08461} = 38.31 \text{ bar } \{\text{vs. } 38.90 \text{ bar in part d}\}$$

$T_{r\mathrm{M}}$ and $P_{r\mathrm{M}}$ are so close to results in (d) that Z_{M}, f/P; $\underline{H} - \overline{H}^{\mathrm{IG}}$ are all the same. Also, $\mathbf{y}$'s are the same.

$$\mathbf{y}_2^{\mathrm{N_2}} = \frac{800}{38.31} \left\{ \left(\frac{0.0895 - 0.0846}{0.0846} \right) - \left(\frac{126.2 - 134.72}{134.72} \right) - \left(\frac{0.290 - 0.2894}{0.2894} \right) \right\}$$

$$= \frac{800}{38.31} \{ 0.05792 + 0.06324 - 0.00207 \} = 2.487$$

$$\mathbf{y}_2^{\mathrm{O_2}} = \frac{800}{38.31} \left\{ \left(\frac{0.0732 - 0.0846}{0.0846} \right) - \left(\frac{154.6 - 134.72}{134.72} \right) - \left(\frac{0.288 - 0.2894}{0.2894} \right) \right\}$$

$$= -5.794$$

$$\ln \frac{\bar{f}_{\mathrm{N_2}}}{x_{\mathrm{N_2}} P} = 0.2070 + 0.0251 + \frac{0.6 \times 2.487}{20.88} = 0.30357$$

$$\mathbf{f}_{\mathrm{N_2}} = \frac{\bar{f}_{\mathrm{N_2}}}{x_{\mathrm{N_2}} P} = 1.3547 \qquad \bar{f}_{\mathrm{N_2}} = 758.6 \text{ bar}$$

$$\ln \frac{\bar{f}_{\mathrm{O_2}}}{x_{\mathrm{O_2}} P} = -0.01819 \; ; \; \mathbf{f}_{\mathrm{O_2}} = \frac{\bar{f}_{\mathrm{O_2}}}{x_{\mathrm{O_2}} P} = 0.9820 \; ; \; \bar{f}_{\mathrm{O_2}} = 235.7 \text{ bar}$$

(f)   Using the program PR1 we find $\bar{f}_{O_2} = 224.9$ bar and $\bar{f}_{N_2} = 732.3$ bar .

<div align="center">

SUMMARY

	$\bar{f}_{N_2}$	$\bar{f}_{O_2}$
Lewis-Randall	761.6 bar	246.0 bar
with corresponding states		
with Peng-Robinson eos	730.1	220.5
Kay's Rule	762.4	233.1
Prousnitz-Gunn	758.6	235.7
Peng-Robinson e.o.s. directly	732.3	224.9
(program PR1)		

</div>

7.13

This problem was solved using the program UNIFAC. To present the extent of nonideality, two measures will be used. One is the infinite dilution activity coefficients, and the other is $\underline{G}^{ex}(max)$, that is, the maximum value of the excess Gibbs free energy. The results appear below for the case of $T = 50°C$

1	2	g_1^∞	g_2^∞	$\underline{G}^{ex}$ (J/mol)
water	ethanol	2.7469	7.2861	829.6
	benzene	304.0	1867.7	3507.9
	toluene	446.5	8776.2	3765.4
ethanol	benzene	8.8774	4.5590	1162.0
	toluene	8.1422	5.4686	1177.7
benzene	toluene	0.9650	0.9582	−26.1

These results were obtained treating toluene as 5 ACH groups + 1 ACCH$_3$ group.

An alternative is to consider toluene to be 5 ACH groups, 1 AC group and 1 CH$_3$ group. We do this just to demonstrate that there can be a number of possible group assignments, each of which will result in somewhat different activity coefficients.

1	2	g_1^∞	g_2^∞	$\underline{G}^{ex}$ (J/mol)
water	toluene	340.1	6162.0	3685.0
ethanol	toluene	9.928	5.966	1269.2
benzene	toluene	1.0058	1.0080	4.5

We see, from the results (independent of which group assignment is used for toluene) that the benzene-toluene mixture, which contains chemically similar species, is virtually an ideal solution. The water-toluene and water-benzene mixtures consist of very dissimilar species and, therefore, the mixtures are very nonideal.   Ethanol contains a hydrocarbon end and a polar -OH end. Consequently, it is almost equally compatible (or incompatible) with both water and hydrocarbon solvents and forms only moderately nonideal mixtures with both this behavior is predicted above.

7.14 Regular solution theory should not be used with hydrogen-bonded solvents such as water and ethanol. However, merely for demonstration, we will use R.S.T. for these compounds.   The "Handbook of Chemistry and Physics" reports $d_{EtOH} = 10.0$ and $d_{H_2O} = 9.9$.   Also, $\underline{V}_{H_2O} = 18$ cc/mol   and $\underline{V}_{EtOH} = 58.4$ cc/mol .

In regular solution theory

$$RT\ln g_i = \underline{V}_i f_j^2 (d_1 - d_2)^2 \quad \text{so} \quad g_i^\infty = \exp\left[\frac{\underline{V}_i (d_1 - d_2)^2}{RT}\right]$$

so

1	2	g_1^∞	g_2^∞	
Water	ethanol	1.000	1.001	$d_{EtOH} = 10.0$
	benzene	1.014	1.070	$d_{benz} = 9.2$
	toluene	1.028	1.181	$d_{tol} = 8.9$
Ethanol	benzene	1.060	1.093	
	toluene	1.116	1.223	
Benzene	toluene	1.013	1.015	

Since the solubility parameters of all the components are similar, regular solution theory predicts essentially ideal solution behavior, even though, for example, the water-aromatic hydrocarbon mixtures are highly nonideal. This is an example of how bad the regular solution theory predictions can be when used for mixtures for which it is not appropriate.

This example should serve as a warning about the improper use of thermodynamic models.

7.15 Start from $\dfrac{G(T,P,\underline{x}) - G^{IGM}(T,P,\underline{x})}{T_{CM}} = \left[\dfrac{H - \underline{H}^{IG}}{T_c}\right] - T_{r,M}\left[\underline{S} - \underline{S}^{IG}\right]$.

$$\frac{\partial}{\partial T_r}\left[\frac{G - G^{IGM}}{RT}\right] = \frac{T_{CM}}{R}\frac{\partial}{\partial T}\left[\frac{G - G^{IGM}}{RT}\right]$$

In general $\dfrac{\partial}{\partial T}\left(\dfrac{\underline{G}}{T}\right) = -\dfrac{\underline{H}}{T^2}$; using this above yields

$$\frac{\partial}{\partial T_r}\left[\frac{G - G^{IGM}}{RT}\right] = -\frac{T_{CM}}{RT^2}\left[\underline{H} - \underline{H}^{IGM}\right] = -\frac{1}{RT_{rm}^2}\left[\frac{H - \underline{H}^{IGM}}{T_{CM}}\right] \quad \textbf{(7.7-12)}$$

Also

$$\frac{\partial}{\partial P_r}\left[\frac{G - G^{IGM}}{RT}\right] = \frac{P_{CM}}{RT}\frac{\partial}{\partial P}\left(\underline{G} - \underline{G}^{IGM}\right) = \frac{P_{CM}}{RT}\left(\underline{V} - \underline{V}^{IGM}\right)$$

$$= \frac{P_{CM}}{P}\left(\frac{PV}{RT} - \frac{P\underline{V}^{IGM}}{RT}\right) = \frac{1}{P_r}\left(Z_M - 1\right) \quad \textbf{(7.7-13)}$$

Using these equations in Eqns. (7.7-9 and 11) gives

$$\ln\frac{\bar{f}_j}{x_j P} = \ln\left(\frac{\bar{f}}{P}\right) - \frac{T_{CM}\left(\underline{H}-\underline{H}^{IGM}\right)}{RT^2} N\left(\frac{\partial T_{rm}}{\partial N_j}\right)_{T,\,P,\,N_{i\neq j}}$$

$$+ \frac{1}{P_r}(Z_M - 1)N\left(\frac{\partial P_{r,M}}{\partial N_j}\right)_{T,P,N_{i\neq j}}$$

$$= \ln\left(\frac{\bar{f}}{P}\right) - \frac{\left(\underline{H}-\underline{H}^{IGM}\right)}{RT_{r,M}^2 T_{CM}}\mathbf{y}_1^j + \frac{(Z_M - 1)}{P_r}\mathbf{y}_2^j \qquad (7.7\text{-}14)$$

For Kay's rules, $T_{CM} = \sum x_i T_{C,i}$ and $P_{CM} = \sum x_i P_{C,i}$, we have

$$\mathbf{y}_1^j(\text{K}) = N\left(\frac{\partial T_r}{\partial N_j}\right) = N\frac{\partial}{\partial N_j}\left\{\frac{T}{T_{CM}}\right\} = -\frac{NT}{T_{CM}^2}\frac{\partial T_{CM}}{\partial N_j} = -\frac{NT}{T_{CM}^2}\frac{\partial}{\partial N_j}\left\{\frac{\sum N_i T_{C,i}}{N}\right\}$$

$$= -\frac{NT}{T_{CM}^2}\left\{\frac{T_{C,j}}{N} - \frac{\sum N_i T_{C,i}}{N^2}\right\} = -\frac{T}{T_{CM}^2}\left\{T_{C,j} - T_{CM}\right\}$$

Since the "combining rule" for P_{CM} is the same as for T_{CM} (for Kay's rule), it follows that

$$\mathbf{y}_2^j(\text{K}) = -\frac{P}{P_{CM}^2}\left\{P_{C,j} - P_{CM}\right\}$$

For the Prausnitz-Gunn rule, $T_{CM} = T_{CM}(\text{Kay})$, so $\mathbf{y}_1^j(\text{PG}) = \mathbf{y}_1^j(\text{K})$. However

$$P_{CM} = \frac{R\left(\sum_i x_i Z_{C,i}\right)\left(\sum_i x_i T_{C,i}\right)}{\sum_i x_i \underline{V}_{C,i}}$$

Thus,

$$\mathbf{y}_2^j(\text{PG}) = N\left(\frac{\partial P_r}{\partial N_j}\right)_{T,P,N_{i\neq j}} = -\frac{NP}{P_{CM}^2}\frac{\partial}{\partial N_j}\left\{P_{CM}\right\}$$

$$= -\frac{NP}{P_{CM}^2}\frac{\partial}{\partial N_j}\left\{\frac{R\sum N_i Z_{C,i}\sum N_i T_{C,i}}{\sum N_i \sum N_i \underline{V}_{C,i}}\right\}$$

$$= -\frac{NP}{P_{CM}^2}\left\{\frac{RZ_{C,j}\sum N_i T_{C,i}}{\sum N_i \sum N_i \underline{V}_{C,i}} + \frac{RT_{C,j}\sum N_i Z_{C,i}}{\sum N_i \sum N_i \underline{V}_{C,i}} - P_{CM}\left[\frac{1}{\sum N_i} - \frac{\underline{V}_{C,j}}{\sum N_i \underline{V}_{C,i}}\right]\right\}$$

$$= -\frac{NP}{P_{CM}}\left\{\frac{Z_{C,j}}{\sum N_i Z_{C,i}} + \frac{T_{C,j}}{\sum N_i T_{C,i}} - \frac{1}{N} - \frac{\underline{V}_{C,j}}{\sum N_i \underline{V}_{C,i}}\right\}$$

$$= \frac{P}{P_{CM}}\left\{1 + \frac{\underline{V}_{C,j}}{\underline{V}_{CM}} - \frac{T_{C,j}}{T_{CM}} - \frac{Z_{C,j}}{Z_{CM}}\right\}$$

Thus

$$\mathbf{y}_2^j(\text{PG}) = \frac{P}{P_{CM}}\left[\left(\frac{\underline{V}_{C,j} - \underline{V}_{CM}}{\underline{V}_{CM}}\right) - \left(\frac{T_{C,j} - T_{CM}}{T_{CM}}\right) - \left(\frac{Z_{C,j} - Z_{CM}}{Z_{CM}}\right)\right]$$

7.16
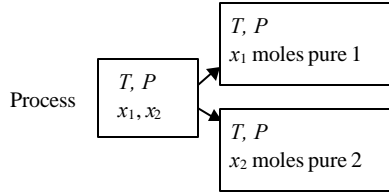
System: 1 mole of initial mixture

system is closed, isothermal and isobaric

Mass balance: $x_1 + x_2 = 1$

Energy balance: $\dfrac{dU}{dt} = \dot{Q} - P\dfrac{dV}{dt} + \dot{W}_s$

Entropy balance: $\dfrac{dS}{dt} = \dfrac{\dot{Q}}{T} + \dot{S}_{gen}$

Thus

$$\dot{W}_s = \frac{dU}{dt} - \dot{Q} + P\frac{dV}{dT}$$

$$\dot{Q} = T\frac{dS}{dt} - T\dot{S}_{gen}$$

$$\Rightarrow \dot{W}_s = \frac{dU}{dt} - T\frac{dS}{dt} + T\dot{S}_{gen} + P\frac{dV}{dt}$$

a) Since both P and T are constant, we can write

$$\dot{W}_s = \frac{dU}{dt} + \frac{d}{dt}(PV) - \frac{d}{dt}(TS) + T\dot{S}_{gen}$$

$$= \frac{d}{dt}(U + PV - TS) + T\dot{S}_{gen} = \frac{dG}{dt} + T\dot{S}_{gen}$$

Clearly, for $\dot{W}_s$ to be a minimum, $\dot{S}_{gen} = 0$, and $\dot{W}_s^{min} = \dfrac{dG}{dt}$.

$$W_s^{min}\left(\begin{array}{c}\text{per mole of}\\\text{initial mixture}\end{array}\right) = \underline{G}_f - \underline{G}_i = x_1\underline{G}_1 + x_2\underline{G}_2 - x_1\overline{G}_1 - x_2\overline{G}_2$$

$$= x_1(\underline{G}_1 - \overline{G}_1) + x_2(\underline{G}_2 - \overline{G}_2)$$

$$= x_1 RT\ln\frac{f_1(T,P)}{\overline{f}_1(T,P,\underline{x})} + x_2 RT\ln\frac{f_2(T,P)}{\overline{f}_2(T,P,\underline{x})}$$

b) Now for either ideal mixtures or Lewis-Randall mixtures, $\dfrac{\overline{f}_i(T,P,\underline{x})}{f_i(T,P)} = x_i$.

Therefore,

$$W_s^{min} = RT[-x_1\ln x_1 - x_2\ln x_2] \ge 0 \text{, so work must be added!}$$

[Note: $\dot{Q} = T\dfrac{dS}{dt} - T\dot{S}_{gen}$; thus $\dot{Q}^{max} = T\dfrac{dS}{dt}$, which occurs when $W_s = W_s^{min}$.

Following same analysis as above leads to

$$Q^{max} = T\{x_1[\underline{S}_1(T,P) - \overline{S}_1(T,P,\underline{x})] + x_2[\underline{S}_2(T,P) - \overline{S}_2(T,P,\underline{x})]\}$$

c) Using the ideal gas or ideal mixture assumption, since isomers can be expected to form ideal mixtures, and the result above

$$W_s^{min} = RT[-x_1 \ln x_1 - x_2 \ln x_2] = 8.314 \,\frac{J}{mol \cdot K} \times 300 \text{ K} \times [-0.5\ln 0.5 - 0.5\ln 0.5]$$

$$= -8.314 \,\frac{J}{mol \cdot K} \times 300 \text{ K} \times \ln 0.5 = -1728.8 \,\frac{J}{mol \text{ of feed}}$$

7.17 $N\underline{G} = \dfrac{N_1 N_2}{N_1 + N_2}\left[A + \dfrac{C(N_1 - N_2)^2}{(N_1 + N_2)^2}\right]$

$\overline{G}_1 = \dfrac{\partial(N\underline{G})}{\partial N_1}\bigg|_{T,P,N_2} = x_2\left[A + C(x_1 - x_2)^2\right] - x_1 x_2\left[A + C(x_1 - x_2)^2\right]$

$+x_1 N_2\left[2C\dfrac{(N_1 - N_2)}{(N_1 + N_2)^2} - \dfrac{2C(N_1 - N_2)^2}{(N_1 + N_2)^3}\right]$

$= x_2(1 - x_1)\left[A + C(x_1 - x_2)^2\right] + x_1 x_2\left[2C(x_1 - x_2) - 2C(x_1 - x_2)^2\right]$

$= x_2^2\left[A + C(x_1 - x_2)^2\right] + 2Cx_1 x_2(x_1 - x_2)[1 - x_1 + x_2]$

$= x_2^2\left[A + C(x_1 - x_2)^2\right] + 4Cx_1 x_2^2(x_1 - x_2) = RT \ln\boldsymbol{g}_1$

$\overline{G}_2 = \dfrac{\partial(N\underline{G})}{\partial N_2}\bigg|_{T,P,N_1} = x_1\left[A + C(x_1 - x_2)^2\right] - x_1 x_2\left[A + C(x_1 - x_2)^2\right]$

$+x_1 x_2(N_1 + N_2)\left[\dfrac{-2(N_1 - N_2)}{(N_1 + N_2)^2} - \dfrac{2C(N_1 - N_2)^2}{(N_1 + N_2)^3}\right]$

$= x_1(1 - x_2)\left[A + C(x_1 - x_2)^2\right] - 2x_1 x_2 C(x_1 - x_2)[1 + x_1 - x_2]$

$= x_1^2\left[A + C(x_1 - x_2)^2\right] - 4Cx_2 x_1^2(x_1 - x_2) = RT \ln\boldsymbol{g}_2$

or

$RT \ln\boldsymbol{g}_1 = x_2^2\left[A + C(x_1 - x_2)^2 + 4Cx_1(x_1 - x_2)\right]$

$RT \ln\boldsymbol{g}_2 = x_1^2\left[A + C(x_1 - x_2)^2 - 4Cx_2(x_1 - x_2)\right]$

7.18   (a) i) One constant Margules equation.

$$RT \ln\boldsymbol{g}_1 = A(1 - x_1)^2 \;;\; RT \,\frac{\partial \ln\boldsymbol{g}_1}{\partial x_1} = -2A(1 - x_1)$$

$$\frac{\partial \ln g_1}{\partial x_1} = \frac{-2 A(1-x_1)}{RT}$$

or

$$\lim_{x_1 \to 1} \frac{\partial \ln g_1}{\partial x_1} = \lim_{x_1 \to 1} \frac{2 A(1-x_1)}{RT} = 0$$

ii) Two constant Margules equations

$$RT \ln g_1 = a_1(1-x_1)^2 + b_1(1-x_1)^3$$

$$\frac{\partial \ln g_1}{\partial x_1} = \frac{1}{RT}\left\{-2a_1(1-x_1) - 3b_1(1-x_1)^2\right\} \to 0 \text{ as } x_1 \to 1$$

iii) van Laar Equation

$$\ln g_1 = \frac{a}{\left[1 + (ax_1/bx_2)\right]^2}$$

Thus

$$\frac{\partial \ln g_1}{\partial x_1} = \frac{2a^2 b^2(1-x_1)}{\left[b(1-x_1) + ax_1\right]^3} \to 0 \text{ as } x_1 \to 1$$

iv) Regular Solution Theory expression
R.S.T. has the same form as the van Laar Equation, so that proof follows from (iii) above.

(b) Starting from the Gibbs-Duhem Equation, Eqn. (7.3-16)

$$0 = \sum_{i=1}^{C} x_i \left(\frac{\partial \ln g_i}{\partial x_j}\right)_{T,P}$$

we obtain

$$0 = x_1 \left(\frac{\partial \ln g_1}{\partial x_1}\right)_{T,P} + x_2 \left(\frac{\partial \ln g_2}{\partial x_1}\right)_{T,P}$$

Alternatively, since $dx_2 = -dx_1$, we have

$$x_1 \left(\frac{\partial \ln g_1}{\partial x_1}\right)_{T,P} = x_2 \left(\frac{\partial \ln g_2}{\partial x_2}\right)_{T,P} \qquad (*)$$

Now $\lim_{x_1 \to 1} x_1 = 1$ and $\lim_{x_1 \to 1} \left(\frac{\partial \ln g_1}{\partial x_1}\right)_{T,P} = 0$

$$\Rightarrow \lim_{x_1 \to 1} x_1 \left(\frac{\partial \ln g_1}{\partial x_1}\right)_{T,P} = 0 \quad \Rightarrow \quad \lim_{x_1 \to 1} x_2 \left(\frac{\partial \ln g_2}{\partial x_2}\right)_{T,P} = 0$$

which also implies that $\lim\limits_{x_2 \to 0} x_2 \left(\dfrac{\partial \ln \boldsymbol{g}_2}{\partial x_2} \right)_{T,P} = 0$ or, more generally

$$\lim\limits_{x_i \to 0} x_i \left(\frac{\partial \ln \boldsymbol{g}_i}{\partial x_i} \right)_{T,P} = 0$$

Thus we have

$$\lim\limits_{x_i \to 1} \left(\frac{\partial \ln \boldsymbol{g}_i}{\partial x_i} \right)_{T,P} = 0 \Rightarrow \begin{array}{l} \ln \boldsymbol{g}_1 \text{ departs, with} \\ \text{zero slope, from its} \\ \text{value of } 0 \text{ at } x_i = 1 \end{array}$$

and

$$\lim\limits_{x_i \to 0} x_i \left(\frac{\partial \ln \boldsymbol{g}_i}{\partial x_i} \right)_{T,P} = 0 \Rightarrow \begin{array}{l} \ln \boldsymbol{g}_1 \text{ rises less rapidly} \\ \text{than } \dfrac{1}{x_i} \text{ as } x_i \to 0. \text{ Thus} \\ x_i \ln \boldsymbol{g}_i \text{ is bounded!!!} \end{array}$$

7.19 Let $M =$ molality of salt in solution.

i)   For KCl: $z_+ = 1$, $z_- = 1$, $M_K = M$, $M_{Cl} = M$;

$$I = \frac{1}{2} \sum z_i^2 M_i = \frac{1}{2}(1 \times M + 1 \times M) = M$$

ii)   For $CrCl_3$: $\left.\begin{array}{ll} z_+ = 3 & z_- = -1 \\ M_+ = M & M_- = 3M \end{array}\right\}$ $I = \frac{1}{2}\{3^2 \times M + 1 \times 3M\} = 6M$

iii)   For $Cr_2(SO_4)_3$: $\left.\begin{array}{ll} z_+ = 3 & z_- = -2 \\ M_+ = 2M & M_- = 3M \end{array}\right\}$ $I = \frac{1}{2}\{3^2 \times 2M + 4 \times 3M\} = 15M$

Now, the Debye-Hückel expression is $\ln \boldsymbol{g}_\pm = -a|z_+ z_-|\sqrt{I}$

and Equation (7.11-18)

$$\ln \boldsymbol{g}_\pm = \frac{-a|z_+ z_-|\sqrt{I}}{1+\sqrt{I}} + 0.1|z_+ z_-|I ; \qquad a = 1.178\left(\frac{\text{mol}}{\text{lit}}\right)^{1/2} \text{ at } 25°C$$

i)   KCl

M	$\ln \boldsymbol{g}_\pm$ experiment	Debye-Hückel $\ln \boldsymbol{g}_\pm = -1.178\sqrt{M}$	Eqn. (7.11-18) $\ln \boldsymbol{g}_\pm = \dfrac{-1.178\sqrt{M}}{1+\sqrt{M}} + 0.1M$
0.1	0.770	0.689	0.761
0.2	0.718	0.590	0.709
0.3	0.688	0.525	0.679
0.5	0.649	0.435	0.645
0.6	0.637	0.402	0.635
0.8	0.618	0.349	0.621
1.0	0.604	0.308	0.613

ii) $CrCl_3$

M	$\ln g_\pm$	$\ln g_\pm = -8.657\sqrt{M}$	$\ln g_\pm = \dfrac{-8.657\sqrt{M}}{1+2.449\sqrt{M}} + 1.8M$
0.1	0.331	0.065	0.256
0.2	0.298	0.021	0.226
0.3	0.294	8.7×10^{-3}	0.227
0.5	0.314	2.2×10^{-3}	0.262
0.6	0.335	1.2×10^{-3}	0.291
0.8	0.397	4.3×10^{-4}	0.373
1.0	0.481	1.7×10^{-4}	0.492

iii) $Cr_2(SO_4)_3$

M	$\ln g_\pm$	$\ln g_\pm = -27.374\sqrt{M}$	$\ln g_\pm = \dfrac{-27.374\sqrt{M}}{1+3.873\sqrt{M}} + 9M$
0.1	0.0458	1.74×10^{-4}	0.0502
0.2	0.0300	4.82×10^{-6}	0.0113
0.3	0.0238	3.08×10^{-7}	0.122
0.5	0.0190	3.92×10^{-9}	0.508
0.6	0.0182	6.18×10^{-10}	1.104
0.8	0.0185	2.33×10^{-11}	5.559
1.0	0.0208	1.29×10^{-12}	29.44

Thus the Debye-Hückel and extended Debye-Hückel (with a fixed value of the δ parameter) theories are not very accurate. However, if the δ parameter is adjusted, much better agreement with experimental data can be achieved. This is left to the student to prove.

7.20   (also available as a Mathcad worksheet)

7.20

$M_0 := 0.001$	$Gam_0 := 0.967$	$M_1 := 0.005$	$Gam_1 := 0.934$	$M_2 := 0.01$	$Gam_2 := 0.891$
$M_3 := 0.05$	$Gam_3 := 0.847$	$M_4 := 0.1$	$Gam_4 := 0.790$	$M_5 := 0.5$	$Gam_5 := 0.739$
$M_6 := 1.0$	$Gam_6 := 0.774$	$M_7 := 3.0$	$Gam_7 := 1.156$	$M_8 := 5.0$	$Gam_8 := 2.74$
$M_9 := 8.0$	$Gam_9 := 8.61$	$M_{10} := 10$	$Gam_{10} := 19.92$	$M_{11} := 12.0$	$Gam_{11} := 46.3$
$M_{12} := 14.0$	$Gam_{12} := 104.7$	$M_{13} := 16.0$	$Gam_{13} := 198$	$M_{14} := 20$	$Gam_{14} := 485$

$i := 0 .. 14$

$$\ln gDH_i := -1.178 \cdot (M_i)^{0.5}$$

$$\ln gDH1_i := \frac{-1.178 \cdot (M_i)^{0.5}}{1 + (M_i)^{0.5}}$$
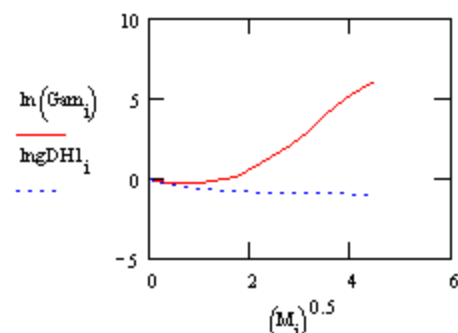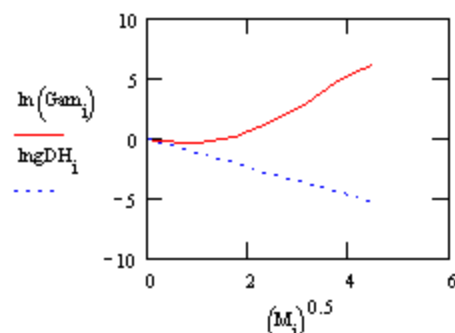
$$\ln gDH2_i := \frac{-1.178 \cdot \left(M_i\right)^{0.5}}{1 + \left(M_i\right)^{0.5}} + 0.1 \cdot M_i \qquad \ln gDH3_i := \frac{-1.178 \cdot \left(M_i\right)^{0.5}}{1 + \left(M_i\right)^{0.5}} + 0.30 \cdot M_i$$
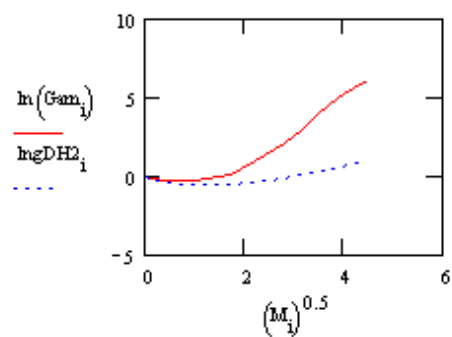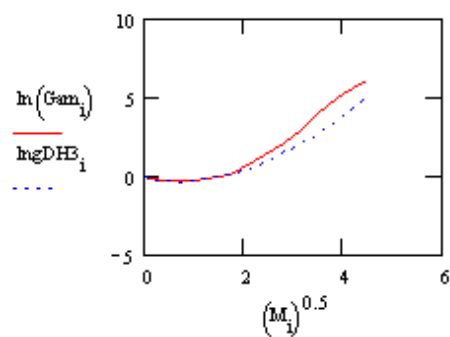
$$\ln gDH4_i := \frac{-1.178 \cdot \left(M_i\right)^{0.5}}{1 + \left(M_i\right)^{0.5}} + 0.33 \cdot M_i \qquad \ln gDH5_i := \frac{-1.178 \cdot \left(M_i\right)^{0.5}}{1 + \left(M_i\right)^{0.5}} + 0.37 \cdot M_i$$
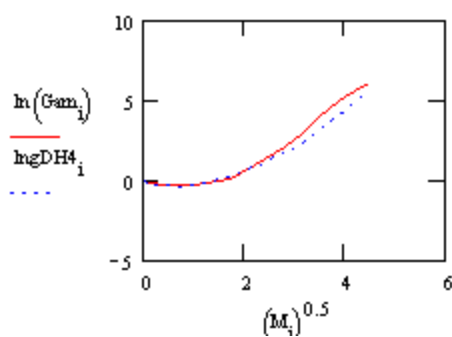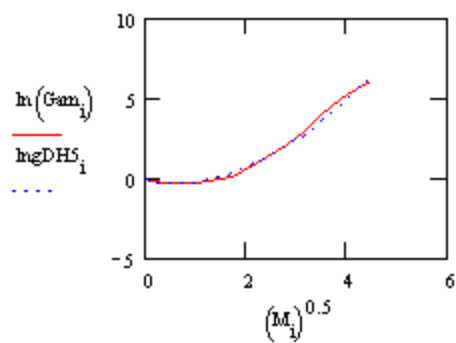
7.21   The Gibbs-Duhem equation, written in terms of molalities and using the mean ionic activity coefficient is as follows:

$$M_S d\overline{G}_S + M_E d\overline{G}_E = 0 \text{ where S is solvent and E is electrolyte}$$

but

$$\overline{G}_E = \underline{G}_E^o + RT \ln\left(\boldsymbol{g}_{\pm}^{\boldsymbol{n}} M_+^{\boldsymbol{n}_+} M_-^{\boldsymbol{n}_-}\right)$$

$$\overline{G}_S = \underline{G}_S^o + RT \ln(x_S \boldsymbol{g}_S)$$

So that

$$M_S d\overline{G}_S + M_E d\overline{G}_E = 0$$

$$M_S d \ln(x_S \boldsymbol{g}_S) + M_E d \ln\left(\boldsymbol{g}_{\pm}^{\boldsymbol{n}} M_+^{\boldsymbol{n}_+} M_-^{\boldsymbol{n}_-}\right) = 0$$

$$M_S d \ln(x_S \boldsymbol{g}_S) + M_E d \ln\left(\boldsymbol{g}_{\pm}^{\boldsymbol{n}} M_{\pm}^{\boldsymbol{n}}\right) = 0 = M_S d \ln(x_S \boldsymbol{g}_S) + M_E \boldsymbol{n} d \ln\left(\boldsymbol{g}_{\pm} M_{\pm}\right)$$

This is the Gibbs-Duhem equation for the solute-electrolyte system.

For HCl

$$M_+ = M_{HCl} \qquad\qquad \boldsymbol{n}_+ = 1$$

$$M_- = M_{HCl} \qquad\qquad \boldsymbol{n}_- = 1$$

$$M_{\pm}^2 = M_{HCl}^1 \cdot M_{HCl}^1 = M_{HCl}^2$$

$$M_S = \frac{1000}{18} = 5556$$

$$x_S = \frac{M_S}{M_S + M_E} = \frac{5556}{55.56 + M_E}$$

$$M_S d \ln \boldsymbol{g}_S x_S + M_{HCl}(1+1) d \ln(\boldsymbol{g}_{\pm} M_{HCl}) = 0$$

$$d \ln \boldsymbol{g}_S x_S = \frac{-2 M_{HCl} d \ln(\boldsymbol{g}_{\pm} M_{HCl})}{M_{H_2O}}$$

$$d \ln \boldsymbol{g}_S x_S = \frac{-2 M_{HCl} d \ln(\boldsymbol{g}_{\pm} M_{HCl})}{5556}$$

$$\Delta \ln \boldsymbol{g}_S x_S = \frac{-2 M_{HCl}}{5556} \Delta \ln(\boldsymbol{g}_{\pm} M_{HCl})$$

This can now be used as a basis for numerical integration with the activity coefficient expression from Illustration 7.11-1. Or proceeding further,

$$d \ln\boldsymbol{g}_S x_S = \frac{-2\,M_{HCl}d\,\ln(\boldsymbol{g}_\pm M_{HCl})}{M_{H_2O}}$$

$$d \ln\boldsymbol{g}_S + d \ln x_S = -\frac{2\,M_{HCl}d\,\ln(\boldsymbol{g}_\pm)}{5556} + \frac{-2\,M_{HCl}d\,\ln(M_{HCl})}{5556}$$

$$d \ln\boldsymbol{g}_S + d \ln\left(\frac{5556}{5556 + M_{HCl}}\right) = -\frac{2\,M_{HCl}d\,\ln(\boldsymbol{g}_\pm)}{5556} + \frac{-2\,M_{HCl}d\,\ln(M_{HCl})}{5556}$$

From Illustration 7.11-1

$$\ln(\boldsymbol{g}_\pm) = \frac{-1.178\sqrt{M_{HCl}}}{1 + \sqrt{M_{HCl}}} + 0.3 M_{HCl}$$

$$d \ln(\boldsymbol{g}_\pm) = \left(-\frac{1}{2\sqrt{M_{HCl}}}\frac{1.178}{1 + \sqrt{M_{HCl}}} + \frac{1}{2}\frac{1.178}{(1 + \sqrt{M_{HCl}})^2} + 0.3\right)dM_{HCl}$$

$$d \ln\boldsymbol{g}_S - \frac{dM_{HCl}}{5556 + M_{HCl}}$$

$$= -\frac{2\,M_{HCl}}{5556}\left(-\frac{1}{2\sqrt{M_{HCl}}}\frac{1.178}{1 + \sqrt{M_{HCl}}} + \frac{1}{2}\frac{1.178}{(1 + \sqrt{M_{HCl}})^2} + 0.3\right)dM_{HCl} - \frac{2}{55.56}dM_{HCl}$$

$$d \ln\boldsymbol{g}_S$$

$$= \left(\frac{1}{5556 + M_{HCl}} + \frac{1.178\sqrt{M_{HCl}}}{5556\cdot(1 + \sqrt{M_{HCl}})} - \frac{1.178\,M_{HCl}}{5556\cdot(1 + \sqrt{M_{HCl}})^2} - \frac{0.6\,M_{HCl}}{5556} - \frac{2}{5556}\right)dM_{HCl}$$

This can only be solved by numerical integration. (See MATHCAD file for this problem).
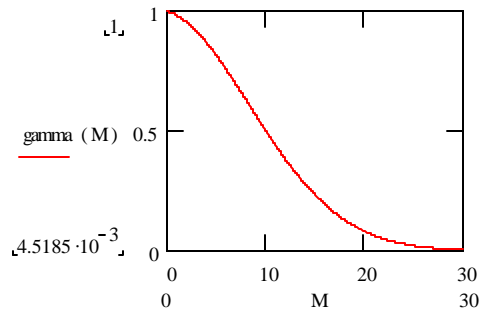
7.22   (a) The two-constant Redlich-Kister expansion, which leads to the two-constant Margules equation is

$$\underline{G}^{ex} = x_1 x_2 \{A + B(x_1 - x_2)\}$$

Thus

$$\frac{G^{ex}}{x_1 x_2} = A + B(2x_1 - 1) \tag{1}$$

Which is a linear function of x.
The form of the Wohl Equation which leads to the van Laar Equation is

$$\underline{G}^{ex} = \frac{2RTa_{12}x_1q_1x_2q_2}{x_1q_1 + x_2q_2}$$

which can be rearranged to

$$\frac{x_1 x_2}{\underline{G}^{ex}} = \frac{x_1 q_1 + (1 - x_1)q_2}{2RTa_{12}q_1q_2} \tag{2}$$

which is also a linear function of x. Equations (1) and (2) provide the justification for the procedure.

(b) The figure below is the required plot. Clearly, neither equation is an accurate fit of the data. [The 2-constant Wohl (or van Laar) equation plot of the data, i.e., the form of Eq. (2), is closest to being linear, and therefore should be the better of the two-constant fits of the data. The data can, however, be fit quite well with a 3-constant Redlich-Kister expansion—See Illustration 8.1-4]
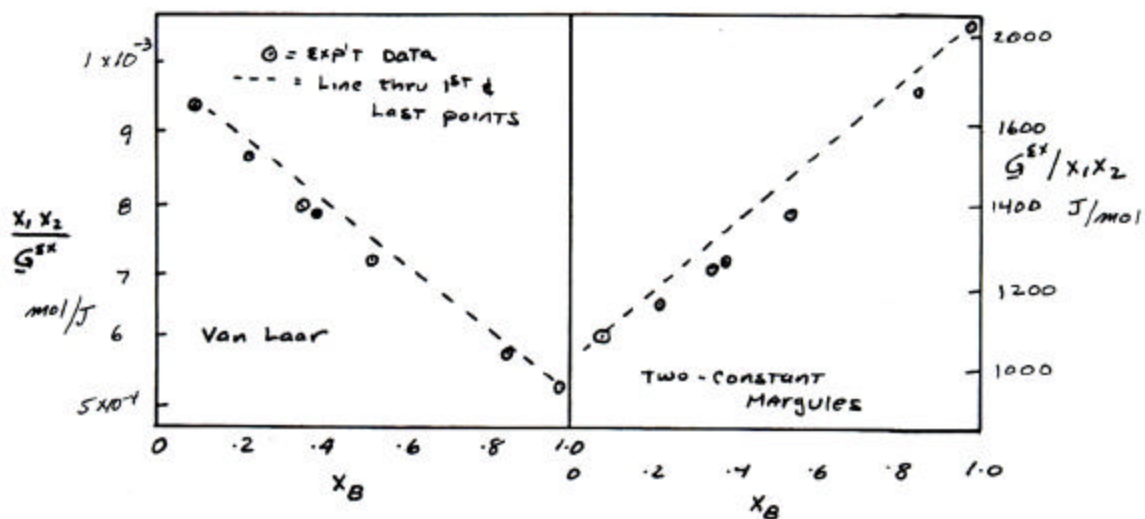
7.23   Expression for $\underline{G}^{ex}$ in this problem is the same as that of Eq. (7.6-6). If we recognize that A and B in Eq. (7.6-6) is replaced by ART and BRT here. Also, since $(1 - 2x_{Ar}) = (x_{CH_4} - x_{Ar})$, species 1 is methane and species 2 is argon.

(a)   Therefore

$$RT\ln \boldsymbol{g}_1 = (ART + 3BRT)x_2^2 - 4BRTx_2^3$$

and

$$RT\ln \boldsymbol{g}_2 = (ART - 3BRT)x_2^2 + 4BRTx_2^3$$

At $x_1 = x_2 = 0.5$

$$\ln \boldsymbol{g}_1 = \frac{1}{4}(A+B) = \frac{1}{4}(0.2944 + 0.0118) = 0.0766 ; \ \boldsymbol{g}_{CH_4} = 1.0796$$

$$\ln \boldsymbol{g}_2 = \frac{1}{4}(A-B) = \frac{1}{4}(0.2944 - 0.0118) = 0.0706 ; \ \boldsymbol{g}_{Ar} = 1.0732$$

(b) $\underline{G}^{ex} = RTx_{Ar}(1 - x_{Ar})\{A + B(1 - 2x_{Ar})\}$ at $x_{Ar} = 0.5$

$$\underline{G}^{ex}(x_{Ar} = 0.5) = \frac{ART}{A} \quad \text{and} \quad \frac{\underline{G}^{ex}(x_{Ar} = 0.5)}{R} = \frac{AT}{4}$$

Thus

$$\frac{\underline{G}^{ex}(x_{Ar} = 0.5)}{R}(\text{at } T = 109 \text{ K}) = 109 \times \frac{0.3036}{4} = 8.2731 \text{ K}$$

$$\frac{\underline{G}^{ex}(x_{Ar} = 0.5)}{R}(\text{at } T = 112 \text{ K}) = 112 \times \frac{0.2944}{4} = 8.2432 \text{ K}$$

$$\frac{\underline{G}^{ex}(x_{Ar} = 0.5)}{R}(\text{at } T = 115.74 \text{ K}) = 115.74 \times \frac{0.2804}{4} = 8.1134 \text{ K}$$

Now replacing differentials with finite differences

T	ΔT	$\dfrac{\underline{G}^{ex}}{R}$	$\Delta\left(\dfrac{\underline{G}^{ex}}{R}\right)$	$\dfrac{\underline{G}^{ex}}{RT}$	$\Delta\left(\dfrac{\underline{G}^{ex}}{RT}\right)$
109		8.2731		0.0759	
	3		–0.0299		–0.0023
112		8.2432		0.0736	
	3.74		–0.1298		–0.0035
115.74		8.1134		0.0701	

Next using

$$\frac{\P(\Delta \underline{G}/RT)}{\P T}\bigg|_P = \frac{-\Delta \underline{H}}{RT^2} \quad \text{and} \quad \left[\frac{\P(\Delta \underline{G}^{ex}/RT)}{\P T}\right]_P = \frac{-\underline{H}^{ex}}{RT^2} = \frac{-\Delta \underline{H}_{mix}}{RT^2}$$

Thus $\dfrac{\Delta(\underline{G}^{ex}/RT)}{\Delta T} \times (-R\overline{T}^2) = \Delta\underline{H}_{mix}$ where $\overline{T} =$ average temperature over ΔT.

$$\Rightarrow \Delta \underline{H}_{\text{mix}} \cong -8.314 \times (112 \text{ K})^2 \times \frac{1}{2} \left\{ \frac{-0.0023}{3} + \frac{-0.0035}{3.74} \right\} = 88.8 \text{ J/mol}$$

(c) From $\left(\frac{\partial \underline{G}}{\partial T} \right)_P = -\underline{S}$ we obtain $\frac{\partial}{\partial T} \left(\frac{G^{\text{ex}}}{R} \right)_P = -\frac{S^{\text{ex}}}{R}$. Therefore,

$$\underline{S}^{\text{ex}} = -\frac{R\Delta\left(\underline{G}^{\text{ex}} / R\right)}{\Delta T} = -8.314 \text{ J/mol K} \times \frac{1}{2} \left\{ \frac{-0.0299}{3} + \frac{-0.1298}{3} \right\}$$

$$= 0.2213 \text{ J/mol K}$$

Also

$$\Delta \underline{S}_{\text{mix}} = -R\sum x_i \ln x_i + \underline{S}^{\text{ex}} = -8.314 \times 2 \times (0.5 \ln 0.5) + 0.045$$

$$= 5.984 \text{ J/mol K}$$

7.24 We start with

$$\ln \frac{\bar{f}_i}{x_i P} = \frac{1}{RT} \int_0^P (\bar{V}_i - \bar{V}_i^{\text{IGM}}) dP = \frac{1}{RT} \int_0^P \left[\left(\frac{\partial V}{\partial N_i} \right)_{T,P,N_{j\neq i}} - \frac{RT}{P} \right] dP$$

<center>Eqn. (7.2-3a)</center>

Now

$$dP = \frac{1}{\underline{V}} d(P\underline{V}) - \frac{P}{\underline{V}} d\underline{V} = \frac{RT}{\underline{V}} dZ - \frac{P}{\underline{V}} d\underline{V} = \frac{P}{Z} dZ = -\frac{P}{\underline{V}} d\underline{V}$$

Also, by triple product rule

$$\left(\frac{\partial V}{\partial N_i} \right)_{T,P,N_{j\neq i}} \cdot \left(\frac{\partial P}{\partial \underline{V}} \right)_{T,N_j} \cdot \left(\frac{\partial N_i}{\partial P} \right)_{T,V,N_{j\neq i}} = -1$$

$$\Rightarrow \bar{V}_i = \left(\frac{\partial V}{\partial N_i} \right)_{P,T,N_{j\neq i}} = -\left(\frac{\partial P}{\partial N_i} \right)_{T,V,N_{j\neq i}} \left(\frac{\partial V}{\partial P} \right)_{T,N_j}$$

So

$$\ln\frac{\overline{f}_i}{x_i P} = \frac{1}{RT}\int -\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_{j\neq i}}\left(\frac{\partial V}{\partial P}\right)_{T,N_j} dP - \int\frac{1}{P}\left[\frac{P}{Z}dZ - \frac{P}{\underline{V}}d\underline{V}\right]$$

$$= -\frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}}\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_{j\neq i}} N d\underline{V} + \int_{\underline{V}=\infty}^{\underline{V}}\frac{1}{\underline{V}}d\underline{V} - \int_{\substack{P=0\\Z=1}}^{Z}\frac{1}{Z}dZ$$

$$= \frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}}\left[\frac{RT}{\underline{V}} - N\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_{j\neq i}}\right]d\underline{V} - \ln\frac{Z}{Z=1}$$

$$= \frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}}\left[\frac{RT}{\underline{V}} - N\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_{j\neq i}}\right]d\underline{V} - \ln Z$$

7.25

$$\frac{\underline{G}^{ex}}{RT} = -\sum_{i=1}^{C} x_i \ln\left[\sum_j x_j\Lambda_{ij}\right]$$

$$\frac{G^{ex}}{RT} = \frac{N\underline{G}^{ex}}{RT} = -\sum_{i=1}^{C} N_i \ln\left[\frac{\sum_j x_j\Lambda_{ij}}{N}\right]$$

$$\Rightarrow \frac{\overline{G}_1^{ex}}{RT} = \frac{\partial}{\partial N_1}\left(\frac{G^{ex}}{RT}\right)_{T,P,N_{j\neq i}}$$

$$= -\ln\left[\frac{\sum_j x_j\Lambda_{ij}}{N}\right] - \sum_{i=1}^{C} N_i \frac{N}{\sum_j N_j\Lambda_{ij}}\left[\frac{\Lambda_{i1}}{N} - \frac{\sum_j N_j\Lambda_{ij}}{N^2}\frac{dN}{dN_1}\right]$$

$$\ln\boldsymbol{g}_1 = \frac{\overline{G}_1^{ex}}{RT} = -\ln\left[\sum_{j=1}^{C} x_j\Lambda_{ij}\right] - \sum_{i=1}^{C}\frac{x_i\Lambda_{i1}}{\sum_j x_j\Lambda_{ij}} + \sum_{i=1}^{C}\frac{x_i\sum_j x_j\Lambda_{ij}}{\sum_j x_j\Lambda_{ij}}$$

$$= 1 - \ln\left[\sum_{j=1}^{C} x_j\Lambda_{ij}\right] - \sum_{i=1}^{C}\frac{x_i\Lambda_{i1}}{\sum_j x_j\Lambda_{ij}}$$

Which is the answer to part b... To obtain the result of part a, we restrict i and j to the values 1 and 2, and note that $\Lambda_{ii} = 1$. Thus

$$\ln\boldsymbol{g}_1 = 1 - \ln[x_1 + x_2\Lambda_{12}] - \frac{x_1}{x_1 + x_2\Lambda_{12}} - \frac{x_2\Lambda_{21}}{x_1\Lambda_{21} + x_2}$$
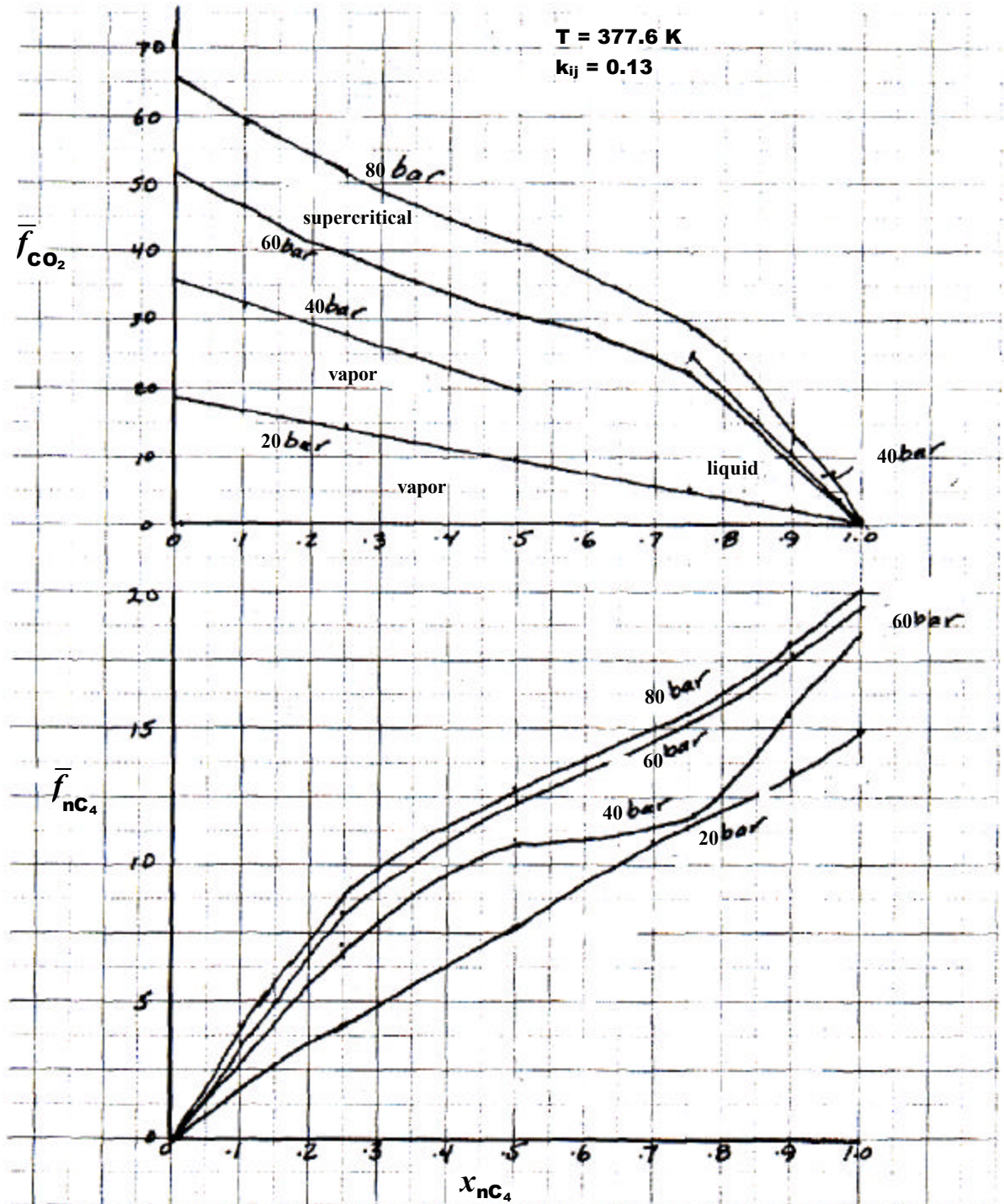
but

$$1 - \frac{x_1}{x_1 + x_2\Lambda_{12}} = \frac{x_1 + x_2\Lambda_{12} - x_1}{x_1 + x_2\Lambda_{12}} = \frac{x_2\Lambda_{12}}{x_1 + x_2\Lambda_{12}}$$
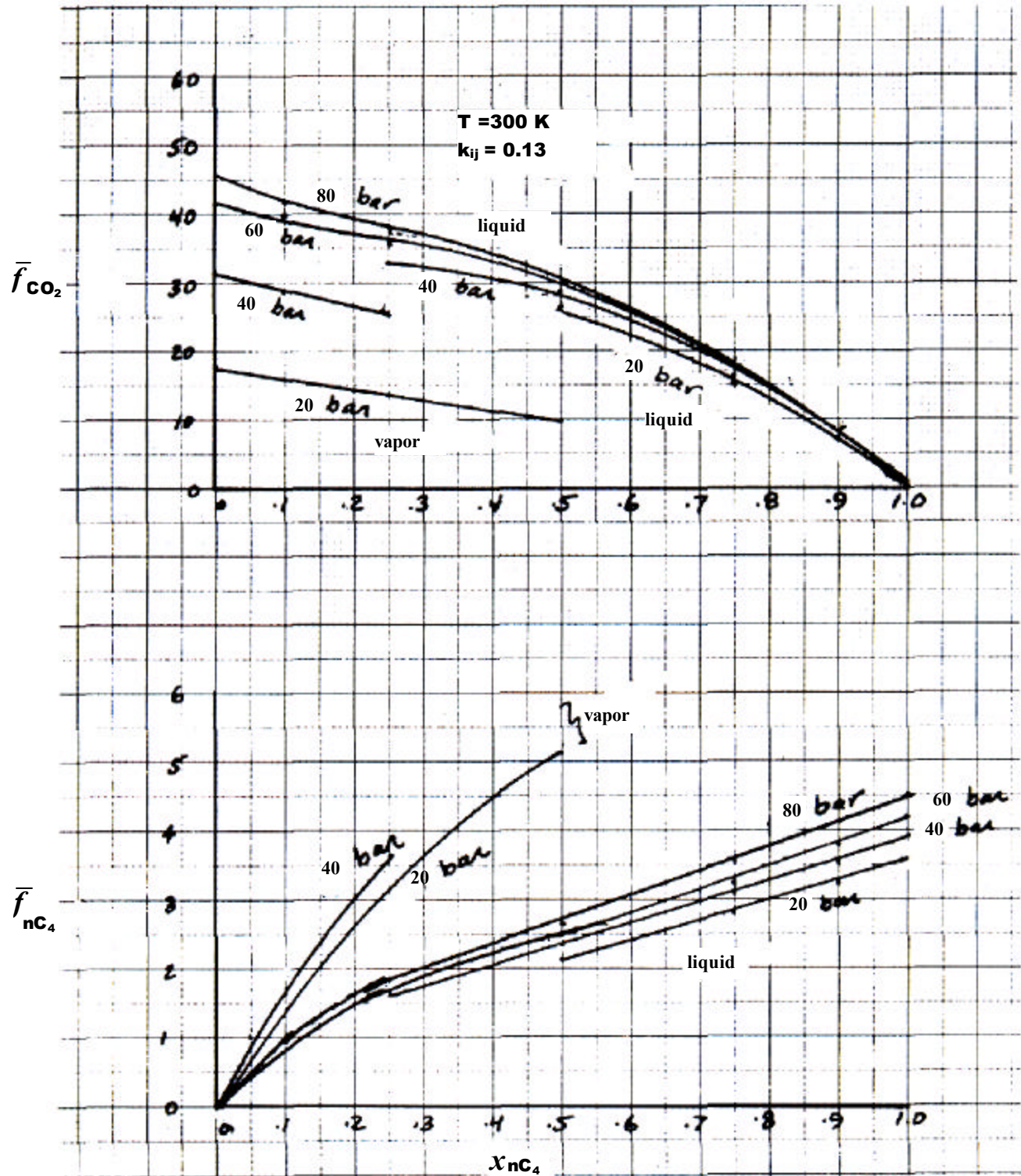
so that

$$\ln\boldsymbol{g}_1 = -\ln[x_1 + x_2\Lambda_{12}] + x_2\left[\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_1\Lambda_{21} + x_2}\right]$$

7.26 All the calculations for this problem were done using the program VLMU with the binary interaction parameter for $CO_2 - nC_4$ equal to 0.13 as given in Table 7.4-1.

The results are only given in graphical form here.

T = 300 K
k_{ij} = 0.13

$\overline{f}_{CO_2}$

80 bar
60 bar
liquid
40 bar
40 bar
20 bar
liquid
20 bar
vapor

$\overline{f}_{nC_4}$

vapor
80 bar
60 bar
40 bar
40 bar
20 bar
20 bar
liquid

x_{nC_4}

7.27

$$\underline{G}^{ex} = ax_1x_2(x_1 - x_2)$$

$$N\underline{G}^{ex} = \frac{AN_1N_2(N_1 - N_2)}{(N_1 + N_2)^2} = A\left[\frac{N_1^2N_2 - N_1N_2^2}{(N_1 + N_2)^2}\right]$$

$$\left.\frac{\P N\underline{G}^{ex}}{\P N_1}\right|_{N_2,T,P} = A\left[\frac{2N_1N_2 - N_2^2}{(N_1 + N_2)^2} - \frac{2(N_1^2N_2 - N_1N_2^2)}{(N_1 + N_2)^3}\right]$$

$$= A\left[2x_1x_2 - x_2^2 - 2x_1^2x_2 + 2x_1x_2^2\right]$$

$$= Ax_2\left[2x_1 - x_2 - 2x_1^2 + 2x_1x_2\right] = Ax_2\left[2x_1(1 - x_1) - x_2 + 2x_1x_2\right]$$

$$= Ax_2\left[2x_1x_2 - x_2 + 2x_1x_2\right] = Ax_2^2\left[4x_1 - 1\right] = Ax_2^2(4 - 4x_2 - 1)$$

$$= Ax_2^2(3 - 4x_2) = RT\ln\boldsymbol{g}_1$$

$$\left.\frac{\P N\underline{G}^{ex}}{\P N_2}\right|_{N_1,T,P} = A\left[\frac{N_1^2 - 2N_1N_2}{(N_1 + N_2)^2} - \frac{2(N_1^2N_2 - N_1N_2^2)}{(N_1 + N_2)^3}\right]$$

$$= A\left[x_1^2 - 2x_1x_2 - 2x_1^2x_2 + 2x_1x_2^2\right]$$

$$= Ax_1\left[x_1 - 2x_2 - 2x_1x_2 + 2x_2^2\right] = Ax_1\left[x_1 + 2x_2(x_2 - 1) - 2x_1x_2\right]$$

$$= Ax_1\left[x_1 - 2x_1x_2 - 2x_1x_2\right] = Ax_1^2\left[1 - 4x_2\right] = Ax_1^2\left[1 - 4(1 - x_1)\right]$$

$$= Ax_1^2(-3 + 4x_1) = RT\ln\boldsymbol{g}_2$$

(This is just a check since by symmetry of original equation $1 \leftrightarrow 2$ gives minus sign. Therefore $1 \leftrightarrow 2$ on $\ln\boldsymbol{g}$ must give minus sign!)

Does this expression satisfy the Gibbs-Duhem Equation?

$$x_1\frac{d\ln\boldsymbol{g}_1}{dx_1} + x_2\frac{d\ln\boldsymbol{g}_1}{dx_1} = 0 \text{ or } -x_1\frac{d\ln\boldsymbol{g}_1}{dx_2} + x_2\frac{d\ln\boldsymbol{g}_1}{dx_1} = 0$$

$$\frac{d\ln\boldsymbol{g}_2}{dx_1} = \frac{A}{RT}\frac{d}{dx_1}\left[x_1^2(-3 + 4x_1)\right] = \frac{A}{RT}\frac{d}{dx_1}\left(-3x_1^2 + 4x_1^3\right)$$

$$= \frac{A}{RT}\left(-6x_1 + 12x_1^2\right)$$

$$\frac{d\ln\boldsymbol{g}_1}{dx_2} = \frac{A}{RT}\frac{d}{dx_2}\left[x_2^2(3 - 4x_2)\right] = \frac{A}{RT}\frac{d}{dx_2}\left(3x_2^2 - 4x_2^3\right)$$

$$= \frac{A}{RT}\left(6x_2 - 12x_2^2\right)$$

Gibbs-Duhem Equation

$$-x_1\frac{A}{RT}\left(6x_2 - 12x_2^2\right) + x_2\frac{A}{RT}\left(-6x_1 + 12x_1^2\right)$$

$$= \frac{A}{RT}\left[-6x_2x_1 + 12x_1x_2^2 - 6x_2x_1 + 12x_1^2x_2\right]$$

$$= \frac{A}{RT}x_1x_2\left(-12x_1x_2 + 12x_1x_2^2 + 12x_1^2x_2\right) = \frac{12A}{RT}x_1^2x_2^2(x_1 + x_2 - 1)$$

$$= \frac{12A}{RT}x_1^2x_2^2(0) = 0$$

$\Rightarrow$ Satisfies Gibbs-Duhem Equation

7.28   To check the utility of these models we will use the Gibbs-Duhem equation in the form

$$x_1\left(\frac{\partial \ln g_1}{\partial x_1}\right)_{T,P} + x_2\left(\frac{\partial \ln g_2}{\partial x_1}\right)_{T,P} = 0$$

For the model

$$\ln g_1 = Ax_2^2 = A(1-x_1)^2$$
$$\ln g_2 = Bx_1^2$$

Gives

$$x_1\left(\frac{\partial \ln g_1}{\partial x_1}\right)_{T,P} + x_2\left(\frac{\partial \ln g_2}{\partial x_1}\right)_{T,P} = 0 = x_1 \cdot 2 \cdot A(1-x_1)(-1) + x_2 B \cdot 2x_1$$

$$= 2x_1 x_2 (B-A) = 0$$

The only way this equation can be satisfied is if $A = B$; if not the Gibbs-Duhem equation is violated.

For the model $\ln g_1 = Ax_2^n$; $\ln g_2 = Ax_1^n$

$$x_1\left(\frac{\partial \ln g_1}{\partial x_1}\right)_{T,P} + x_2\left(\frac{\partial \ln g_2}{\partial x_1}\right)_{T,P} = x_1 \cdot n \cdot A(1-x_1)^{n-1}(-1) + x_2 \cdot n \cdot Ax_1^{n-1} = 0$$

$$= nAx_1 x_2\left[-x_2^{n-2} + x_1^{n-2}\right] = 0$$

The only way the Gibbs-Duhem equation can be satisfied for all values of x_1 and x_2 (with $x_1 + x_2 = 1$) is if $n = 2$ in which case the term in brackets is always zero.

For the model $\ln g_1 = Ax_2^n$; $\ln g_2 = Bx_1^n$. We have

$$x_1\left(\frac{\partial \ln g_1}{\partial x_1}\right)_{T,P} + x_2\left(\frac{\partial \ln g_2}{\partial x_1}\right)_{T,P} = x_1 \cdot n \cdot A(1-x_1)^{n-1}(-1) + x_2 \cdot n \cdot Bx_1^{n-1} = 0$$

$$= nx_1 x_2\left[-Ax_2^{n-2} + Bx_1^{n-2}\right] = 0$$

For this equation to be satisfied, the term in the brackets must be zero. This can only be in $n = 2$ and $A = B$.

7.29   We will write the Flory-Huggins expression as

$$\left.\frac{G^{\text{ex}}}{RT}\right|_{\text{res}} = c(x_1 + mx_2)\phi_1\phi_2 = \frac{cx_1x_2m}{x_1 + mx_2}$$

$$\left.\frac{G^{\text{ex}}}{RT}\right|_{\text{comb}} = N_1 \ln\frac{\phi_1}{x_1} + N_2 \ln\frac{\phi_2}{x_2} \text{ with } \phi_1 = \frac{x_1}{x_1 + mx_2}, \ \phi_2 = \frac{mx_2}{x_1 + mx_2}$$

$$\left.\frac{G^{\text{ex}}}{RT}\right|_{\text{res}} = \left.\frac{N\underline{G}^{\text{ex}}}{RT}\right|_{\text{res}} = \frac{cN_1N_2m}{N_1 + mN_2}$$

$$\frac{\partial}{\partial N_1}\left(\left.\frac{G^{\text{ex}}}{RT}\right|_{\text{res}}\right) = \frac{cN_2m}{N_1 + mN_2} - \frac{cN_1N_2m}{(N_1 + mN_2)^2} = c(\phi_2 - \phi_1\phi_2) = c\phi_2(1 - \phi_1) = c\phi_2^2$$

Similarly

$$\frac{\partial}{\partial N_2}\left(\left.\frac{G^{\text{ex}}}{RT}\right|_{\text{res}}\right) = \frac{cN_1m}{N_1 + mN_2} - \frac{cN_1N_2m}{N_1 + mN_2} = cm(\phi_1 - \phi_1\phi_2) = xm\phi_1^2$$

$$\left.\frac{G^{\text{ex}}}{RT}\right|_{\text{comb}} = N_1 \ln\frac{\phi_1}{x_1} + N_2 \ln\frac{\phi_2}{x_2}$$

$$\frac{\partial}{\partial N_1}\left(\left.\frac{G^{\text{ex}}}{RT}\right|_{\text{comb}}\right) = \ln\frac{\phi_1}{x_1} + N_1\frac{\partial}{\partial N_1}\ln\frac{\phi_1}{x_1} + N_2\frac{\partial}{\partial N_1}\ln\frac{\phi_2}{x_2}$$

$$\frac{\phi_1}{x_1} = \frac{1}{x_1 + mx_2} = \frac{N}{N_1 + mN_2}$$

and

$$\frac{\partial}{\partial N_1}\ln\frac{\phi_1}{x_1} = \frac{N_1 + mN_2}{N}\left[\frac{1}{N_1 + mN_2} - \frac{N}{(N_1 + mN_2)^2}\right]; \ N_1\frac{\partial}{\partial N_1}\ln\frac{\phi_1}{x_1} = x_1 - \phi_1$$

$$\frac{\phi_2}{x_2} = \frac{m}{x_1 + mx_2} = \frac{Nm}{N_1 + mN_2}$$

$$\frac{\partial}{\partial N_1}\ln\frac{\phi_2}{x_2} = \left[\frac{m}{Nm} - \frac{1}{N_1 + mN_2}\right]; \ N_2\frac{\partial}{\partial N_1}\ln\frac{\phi_2}{x_2} = x_2 - \frac{\phi_2}{m}$$

Therefore

$$\ln\gamma_1 = \frac{\partial}{\partial N_1}\left(\left.\frac{G^{\text{ex}}}{RT}\right|_{\text{comb}}\right) + \frac{\partial}{\partial N_1}\left(\left.\frac{G^{\text{ex}}}{RT}\right|_{\text{res}}\right)$$

$$= \ln\frac{\phi_1}{x_1} + (x_1 - \phi_1) + \left(x_2 - \frac{\phi_2}{m}\right) + c\phi_2^2$$

$$= \ln\frac{\phi_1}{x_1} + 1 - \phi_1 - \frac{\phi_2}{m} + x\phi_2^2 = \ln\frac{\phi_1}{x_1} + \phi_2\left(1 - \frac{1}{m}\right) + c\phi_2^2$$

Also

$$\frac{\partial}{\partial N_2}\left(\frac{G^{ex}}{RT}\bigg|_{conf}\right) = \frac{\partial}{\partial N_2}\left[N_1 \ln\frac{f_1}{x_1} + N_2 \ln\frac{f_2}{x_2}\right]$$

$$= \ln\frac{f_2}{x_2} + \underbrace{N_1\frac{x_1}{f_1}\frac{\partial}{\partial N_2}\frac{f_1}{x_1}}_{x_1 - mf_1} + \underbrace{N_2\frac{x_2}{f_2}\frac{\partial}{\partial N_2}\frac{f_2}{x_2}}_{x_2 - f_2}$$

$$\ln g_2 = \ln\frac{f_2}{x_2} + (x_1 - mf_1) + (x_2 - f_2) + cf_1^2$$

$$= \ln\frac{f_2}{x_2} + f_1 - mf_1 + xf_1^2 = \ln\frac{f_2}{x_2} + (1-m)f_1 + cf_1^2$$

$$= \ln\frac{f_2}{x_2} - (m-1)f_1 + cf_1^2$$

7.30   (also available as a Mathcad worksheet)

7.30

$$i := 0, 1 .. 10 \qquad x_i := 0.1 \cdot i$$

$$fma_i := x_i \cdot \exp\left[1.06 \cdot (1 - x_i)^2\right] \cdot 1.126$$

$$fm_i := (1 - x_i) \cdot \exp\left[1.06 \cdot (x_i)^2\right] \cdot 0.847$$

x =	0
0	0
1	0.1
2	0.2
3	0.3
4	0.4
5	0.5
6	0.6
7	0.7
8	0.8
9	0.9
10	1

fma =	0
0	0
1	0.266
2	0.444
3	0.568
4	0.66
5	0.734
6	0.8
7	0.867
8	0.94
9	1.024
10	1.126

fm =	0
0	0.847
1	0.77
2	0.707
3	0.652
4	0.602
5	0.552
6	0.496
7	0.427
8	0.334
9	0.2
10	0

$$Hma := 1.126 \cdot \exp(1.06) \qquad\qquad Hma = 3.25$$

$$Hm := 0.847 \cdot \exp(1.06) \qquad\qquad Hm = 2.445$$
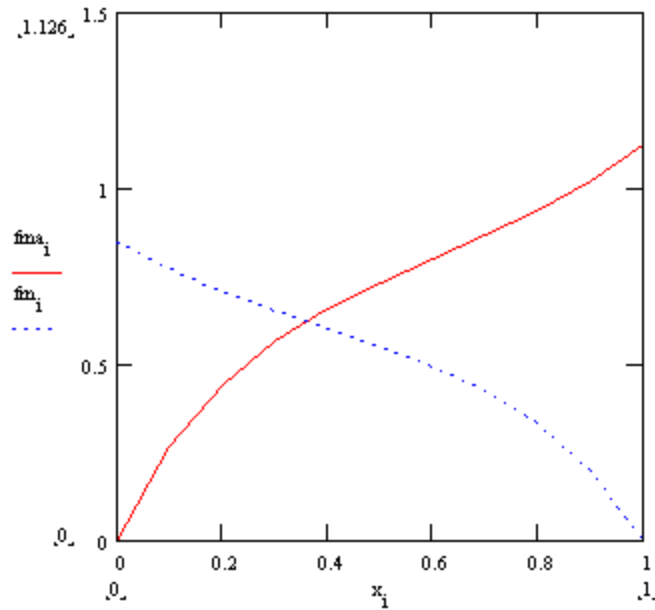
7.31 Show $\underline{A}_{\text{EOS}}(P \to \infty) = C\left[\dfrac{a_{\text{mix}}}{b_{\text{mix}}} - \sum x_i \dfrac{a_i}{b_i}\right]$

start $-P = \dfrac{\P \underline{A}}{\P \underline{V}}\bigg|_T \;\to\; \underline{A}\big|_{\underline{V}} - \underline{A}\big|_{\underline{V}\to\infty} = -\int\limits_{\infty}^{\underline{V}} P\,d\underline{V}$

($\underline{V} \to \infty$ is convenient since we have ideal gas and ideal gas mixtures)

<u>P-R</u>

$P = \dfrac{RT}{\underline{V} - b} - \dfrac{a}{\underline{V}(\underline{V}+b) + b(\underline{V}-b)}$ $\leftarrow$ pure component

$\underline{A}\big|_{\underline{V}} - \underline{A}\big|_{\underline{V}\to\infty} = -\int\limits_{\infty}^{\underline{V}} \dfrac{RT}{\underline{V}-b} + \int\limits_{\infty}^{\underline{V}} \dfrac{a}{\underline{V}(\underline{V}+b) + b(\underline{V}-b)}\,d\underline{V}$

$\qquad\qquad = -RT\big[\ln(\underline{V}-b) - \ln\infty\big] + \underbrace{\int\limits_{\infty}^{\underline{V}} \dfrac{a}{\underline{V}^2 + 2b\underline{V} - b^2}\,d\underline{V}}_{\text{Need to integrate}}$

From Problem 4.2 we have that

$\int\limits_{\infty}^{\underline{V}} \dfrac{1}{\underline{V}^2 + 2b\underline{V} - b^2}\,d\underline{V} = \dfrac{1}{2\sqrt{2}b}\ln\left(\dfrac{\underline{V} + \left(1 - \sqrt{2}\right)b}{\underline{V} + \left(1 + \sqrt{2}\right)b}\right)$

$\Rightarrow \underline{A}\big|_{\underline{V}} - \underline{A}\big|_{\underline{V}\to\infty} = -RT\big[\ln(\underline{V}-b) - \ln\infty\big] + \dfrac{a}{2\sqrt{2}b}\ln\left(\dfrac{\underline{V} + \left(1 - \sqrt{2}\right)b}{\underline{V} + \left(1 + \sqrt{2}\right)b}\right)$

So for pure component:

$$\underline{A}_i\big|_{\underline{V}} - \underline{A}_i\big|_{\underline{V}\to\infty} = -RT\{\ln(\underline{V}-b_i) - \ln\infty\} + \frac{a_i}{2\sqrt{2}b_i}\ln\left(\frac{\underline{V}+b_i(1-\sqrt{2})}{\underline{V}+b_i(1+\sqrt{2})}\right)$$

By exact analogy for mixture

$$\underline{A}\big|_{\underline{V}} - \underline{A}\big|_{\underline{V}\to\infty} = -RT\{\ln(\underline{V}_{\text{mix}}-b_{\text{mix}}) - \ln\infty\} + \frac{a_{\text{mix}}}{2\sqrt{2}b_{\text{mix}}}\ln\left(\frac{\underline{V}_{\text{mix}}+b_{\text{mix}}(1-\sqrt{2})}{\underline{V}_{\text{mix}}+b_{\text{mix}}(1+\sqrt{2})}\right)$$

Now when $\underline{V}\to\infty$ get ideal gas or ideal gas mixture:

$$\underline{A}\big|_{\underline{V}} - \underline{A}\big|^{\text{IG}} = -RT\{\ln(\underline{V}-b) - \ln\infty\} + \frac{a}{2\sqrt{2}b}\ln\left(\frac{\underline{V}+b(1-\sqrt{2})}{\underline{V}+b(1+\sqrt{2})}\right)$$

$$\underline{A}\big|_{\underline{V}} - \underline{A}\big|^{\text{IGM}} = -RT\{\ln(\underline{V}_{\text{mix}}-b_{\text{mix}}) - \ln\infty\}$$

$$+ \frac{a_{\text{mix}}}{2\sqrt{2}b_{\text{mix}}}\ln\left(\frac{\underline{V}_{\text{mix}}+b_{\text{mix}}(1-\sqrt{2})}{\underline{V}_{\text{mix}}+b_{\text{mix}}(1+\sqrt{2})}\right)$$

and by definition $\underline{A}^{\text{ex}} = \underline{A} - \underline{A}^{\text{IM}}$ (i.e., $\underline{A} = \underline{A}^{\text{IM}} + \underline{A}^{\text{ex}}$) so; have $\underline{A} - \underline{A}^{\text{IGM}}$ so

$$\underline{A}^{\text{ex}} = \left(\underline{A} - \underline{A}^{\text{IGM}}\right) - \underline{A}^{\text{IM}} + \underline{A}^{\text{IGM}} \quad \text{and}$$

$$\underline{A}^{\text{IGM}} = \sum x_i \underline{A}_i^{\text{IG}} + RT\sum x_i \ln x_i \ ; \ \underline{A}^{\text{IM}} = \sum x_i \underline{A}_i + RT\sum x_i \ln x_i$$

$$\underline{A}^{\text{ex}} = \underline{A} - \underline{A}^{\text{IGM}} - \sum x_i \underline{A}_i - RT\sum x_i \ln x_i + \sum x_i \underline{A}_i^{\text{IG}} + RT\sum x_i \ln x_i$$

$$\underline{A}^{\text{ex}} = \left(\underline{A} - \underline{A}^{\text{IGM}}\right) - \sum x_i\left(\underline{A}_i - \underline{A}_i^{\text{IG}}\right)$$

this is why we found $\Delta\underline{A}$ for pure component

So putting in results for $\underline{A}\big|_{\underline{V}} - \underline{A}\big|_\infty = -\int_\infty^{\underline{V}} P\,dV$ for pure i and mixture.

$$\underline{A}^{\text{ex}} = -RT\left[\ln(\underline{V}_{\text{mix}}-b_{\text{mix}}) - \ln\infty\right] + \frac{a_{\text{mix}}}{2\sqrt{2}b_{\text{mix}}}\ln\left(\frac{\underline{V}_{\text{mix}}+b_{\text{mix}}(1-\sqrt{2})}{\underline{V}_{\text{mix}}+b_{\text{mix}}(1+\sqrt{2})}\right)$$

$$- \sum_i x_i\left\{\left[-RT\ln(\underline{V}_i-b_i) + RT\ln\infty\right] + \frac{a_i}{2\sqrt{2}b_i}\ln\left(\frac{\underline{V}_i+b_i(1-\sqrt{2})}{\underline{V}_i+b_i(1+\sqrt{2})}\right)\right\}$$

Need to collect some terms.

$$\underline{A}^{\text{ex}} = -RT\left[\ln(\underline{V}_{\text{mix}}-b_{\text{mix}}) - \ln\infty - \sum_i x_i\left[\ln(\underline{V}_i-b_i) - \ln\infty\right]\right]$$

$$+ \frac{a_{\text{mix}}}{2\sqrt{2}b_{\text{mix}}} - \ln\left(\frac{\underline{V}_{\text{mix}}+b_{\text{mix}}(1-\sqrt{2})}{\underline{V}_{\text{mix}}+b_{\text{mix}}(1+\sqrt{2})}\right) - \sum_i x_i \frac{a_i}{2\sqrt{2}b_i}\ln\left(\frac{\underline{V}_i+b_i(1-\sqrt{2})}{\underline{V}_i+b_i(1+\sqrt{2})}\right)$$

Now let $P\to\infty$ which is the same as $\underline{V}_i\to b_i$ and $\underline{V}_{\text{mix}}\to b_{\text{mix}}$

$$= -RT\ \big[\ \ln\underset{\boxed{1}}{(b_{\text{mix}}-b_{\text{mix}})}\ \ln\underset{\boxed{3}}{\infty} - \sum x_i[\ \ln\underset{\boxed{2}}{(b_i-b_i)} - \ln\underset{\boxed{4}}{\infty}]$$

$$+ \frac{a_{\text{mix}}}{2\sqrt{2}b_{\text{mix}}}\ \ln\left(\frac{(2-\sqrt{2})b_{\text{mix}}}{(2+\sqrt{2})b_{\text{mix}}}\right) - \sum x_i \frac{a_i}{2\sqrt{2}b_i}\ \ln\left(\frac{(2-\sqrt{2})b_i}{(2+\sqrt{2})b_i}\right)$$

Now $\boxed{1}$ and $\boxed{2}$ cancel $\ln 0 - \sum x_i \ln 0 = 0$

and $\boxed{3}$ and $\boxed{4}$ cancel $-\ln\infty + \sum x_i \ln\infty = 0$. i.e., $-\infty + 3 \cdot \infty = 0$

So

$$\underline{A}^{ex}_{\substack{P\text{-}R \\ P\to\infty}} = \frac{1}{2\sqrt{2}} \cdot \frac{a_{mix}}{b_{mix}} \ln\left(\frac{2-\sqrt{2}}{2+\sqrt{2}}\right) - \sum x_i \frac{a_i}{2\sqrt{2}b_i} \ln\left(\frac{2-\sqrt{2}}{2+\sqrt{2}}\right)$$

$$= \ln\left(\frac{2-\sqrt{2}}{2+\sqrt{2}}\right) \cdot \frac{1}{2\sqrt{2}}\left[\frac{a_{mix}}{b_{mix}} - \sum x_i \frac{a_i}{b_i}\right]$$

$$\boxed{\underline{A}^{ex}_{\substack{P\text{-}R \\ P\to\infty}} = -0.6232\left[\frac{a_{mix}}{b_{mix}} - \sum x_i \frac{a_i}{b_i}\right]}$$

where $\ln\left(\dfrac{2-\sqrt{2}}{2+\sqrt{2}}\right)\dfrac{1}{2\sqrt{2}} = -0.6232 = C^*$ for P-R

Now for van der Waals $\Rightarrow$ same process though solution is briefer.

$$-P = \left.\frac{\P\underline{A}}{\P\underline{V}}\right|_T \Rightarrow \underline{A}|_{\underline{V}} - \underline{A}|_{\underline{V}\to\infty} = -\int_\infty^{\underline{V}} \frac{RT}{\underline{V}-b}d\underline{V} + \int_\infty^{\underline{V}} \frac{a}{\underline{V}^2}d\underline{V}$$

Pure component

$$\underline{A}|_{\underline{V}} - \underline{A}\Big|^{IG} = -RT\ln(\underline{V}_i - b_i) + RT\ln\infty - \frac{a_i}{\underline{V}_i}$$

and for the mixture

$$\underline{A}|_{\underline{V}} - \underline{A}\Big|^{IGM} = -RT\ln(\underline{V}_M - b_M) + RT\ln\infty - \frac{a_M}{\underline{V}_M}$$

and $\underline{A}^{ex} \equiv \underline{A} - \underline{A}^{IM} = \left(\underline{A} - \underline{A}^{IGM}\right) = \sum x_i\left(\underline{A}_i - \underline{A}^{IG}\right) \leftarrow$ same as above

Putting in results for $\underline{A}|_{\underline{V}} - \underline{A}|_\infty = -\int_\infty^{\underline{V}} PdV$ for pure i and for the mixture.

$$\underline{A}^{ex} = -RT\left[\ln(\underline{V}_M - b_M) - RT\ln\infty\right] - \frac{a_M}{\underline{V}_M}$$

$$-\sum x_i\left\{-RT\left[\ln(\underline{V}_i - b_i) - RT\ln\infty\right] - \frac{a_i}{\underline{V}_i}\right\}$$

$$= -RT\left[\ln(\underline{V}_M - b_M) + \sum x_i\ln(\underline{V}_i - b_i) + \ln\infty - \sum x_i\ln\infty\right] - \frac{a_M}{\underline{V}_M} + \sum x_i\frac{a_i}{\underline{V}_i}$$

Take limit $P\to\infty$, $\underline{V}_i \to b_i$; $\underline{V}_M \to b_M$.

First 4 terms cancel!

$$\underline{A}^{ex}_{\substack{VDW \\ P\to\infty}} = -1\left[\frac{a_M}{b_M} - \sum x_i \frac{a_i}{b_i}\right]$$

7.32 Starting from

$$b_M - \frac{a_M}{RT} = \sum_i\sum_j x_i x_j\left(b_{ij} - \frac{a_{ij}}{RT}\right) \equiv Q \quad \text{and}$$

$$\underline{G}^{ex} = C^*\left[\frac{a_M}{b_M} - \sum_i x_i\frac{a_i}{b_i}\right]$$

or

$$\frac{a_M}{b_M} = \frac{G^{ex}}{C^*} + \sum_i x_i \frac{a_i}{b_i} \equiv DRT \quad \text{and} \quad b_M = \frac{a_M}{DRT}$$

Substituting, we then obtain

$$\frac{a_M}{DRT} - \frac{a_M}{RT} = Q \quad \text{so that} \quad \frac{a_M}{RT} = Q\frac{D}{1-D}$$

and

$$b_M = \frac{a_M}{RT} + Q = Q\frac{D}{1-D} + Q = \frac{Q}{1-D}$$

7.33   Equation (7.10-11) is easily derived, is generic, and applies to any mixing rule.
This will be used as the starting point. With the Wong-Sandler mixing rule
Note that derivatives must be taken with respect to mole numbers.

Therefore

$$Q = \sum_i \sum_j x_i x_j \left(b_{ij} - \frac{a_{ij}}{RT} \right) \quad \text{needs to be in the form of}$$

$$N^2 Q = \sum_i \sum_j N_i N_j \left(b_{ij} - \frac{a_{ij}}{RT} \right)$$

Similarly

$$D = \sum_i x_i \frac{a_i}{b_i RT} + \frac{G^{ex}}{C^* RT} \quad \text{needs to be in the form of}$$

$$ND = \sum_i N_i \frac{a_i}{b_i RT} + \frac{N\underline{G}^{ex}}{C^* RT}$$

From this starting point, eqns. (7.10 -12 and 13) are easily derived.

7.34   Starting from eqn. (7.2-13)

$$\ln \frac{\overline{f}_k}{x_k P} = \frac{1}{RT} \int\limits_{\underline{V}=\infty}^{\underline{V}=ZRT/P} \left[\frac{RT}{\underline{V}} - N\left(\frac{\partial P}{\partial N_k} \right)_{T,V,N_{j\neq k}} \right] dV - \ln Z$$

The Soave-Redlich-Kwong equation of state is

$$P = \frac{RT}{\underline{V} - b} - \frac{a(T)}{\underline{V}(\underline{V} + b)} = \frac{NRT}{V - Nb} - \frac{N^2 a(T)}{V(V + Nb)}$$

with

$$Nb = \sum_i N_i b_i \quad \text{and} \quad N^2 a = \sum_i \sum_j N_i N_j a_{ij}$$

Now taking the derivative, we obtain

$$N\left(\frac{\partial P}{\partial N_k} \right)_{T,V,N_{j\neq k}} = \frac{RT}{\underline{V}-b} + \frac{RTb_k}{(\underline{V}-b)^2} - \frac{2\sum_i x_i a_{ik}}{\underline{V}(\underline{V}+b)} + \frac{ab_k}{\underline{V}(\underline{V}+b)^2}$$

$$\frac{RT}{\underline{V}} - N\left(\frac{\partial P}{\partial N_k} \right)_{T,V,N_{j\neq k}} = \frac{RT}{\underline{V}} - \frac{RT}{\underline{V}-b} - \frac{RTb_k}{(\underline{V}-b)^2} + \frac{2\sum_i x_i a_{ik}}{\underline{V}(\underline{V}+b)} - \frac{ab_k}{\underline{V}(\underline{V}+b)^2}$$

and then

$$\ln\frac{\overline{f}_k}{x_k P} = \frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}=ZRT/P}\left[\frac{RT}{\underline{V}} - N\left(\frac{\partial P}{\partial N_k}\right)_{T,V,N_{j\neq k}}\right]dV - \ln Z$$

$$= \frac{1}{RT}\left[\begin{array}{l} RT\ln\dfrac{ZRT/P}{ZRT/P - b} + \dfrac{RTb_k}{ZRT/P - b} + \left\{\dfrac{2\sum_i x_i a_{ik}}{b} - \dfrac{ab_k}{b^2}\right\}\ln\dfrac{ZRT/P}{ZRT/P + b} \\ \\ - \dfrac{ab_k}{b(ZRT/P + b)} \end{array}\right] - \ln Z$$

Now using $B=Pb/RT$ and $A = Pa/(RT)^2$ we obtain

$$\ln\frac{\overline{f}_k}{x_k P} = \ln\frac{Z}{Z-B} + \frac{B_k}{Z-B} + \frac{A}{B}\left\{\frac{2\sum_i x_i A_{ik}}{A} - \frac{B_k}{B}\right\}\ln\frac{Z}{Z+B} - \frac{A}{B}\frac{B_k}{Z+B} - \ln Z$$

However, the Soave-Redlich-Kwong equation of state can be rewritten as follows

$$P = \frac{RT}{\underline{V}-b} - \frac{a}{\underline{V}(\underline{V}+b)}$$

$$\frac{P\underline{V}}{RT} = Z = \frac{\underline{V}}{\underline{V}-b} - \frac{a}{RT(\underline{V}+b)} = \frac{Z}{Z-B} - \frac{A}{Z+B}$$

$$Z-1 = \frac{B}{Z-B} - \frac{A}{Z+B}$$

Using this expression in the 2nd and 4th terms on the right-hand side of the fugacity expression yields the desired result

$$\ln\frac{\overline{f}_k}{x_k P} = -\ln Z - B\frac{Z}{Z-B} + \frac{A}{B}\left\{\frac{2\sum_i x_i A_{ik}}{A} - \frac{B_k}{B}\right\}\ln\frac{Z}{Z+B} + \frac{B_k}{B}(Z-1)$$

Note that in this derivation, we have used the following

$$\int\frac{dx}{x(x+b)} = \frac{1}{b}\ln\left(\frac{x}{x+b}\right)$$

$$\int\frac{dx}{x(x+b)^2} = \frac{1}{b^2}\ln\left(\frac{x}{x+b}\right) + \frac{1}{b(x+b)}$$

$$\int\frac{dx}{(x-b)} = \ln(x-b)$$

7.35 See Mathcad worksheet.
a and b) See Mathcad file 7-35.MCD and figures contained there

c) Clearly

$$\underline{H}^{\text{ex}} = \mathbf{c}RT(x_1 + mx_2)\mathbf{f}_1\mathbf{f}_2 = \frac{Ax_2RT}{T}(x_1 + mx_2)\frac{x_1}{(x_1 + mx_2)}\frac{mx_2}{(x_1 + mx_2)}$$

$$= \frac{Ax_2^2 x_1 Rm}{x_1 + mx_2}$$

$$\frac{G^{\text{ex}}}{RT} = x_1 \ln\frac{\mathbf{f}_1}{x_1} + x_2 \ln\frac{\mathbf{f}_2}{x_2} + \frac{Ax_2}{T}(x_1 + mx_2)\mathbf{f}_1\mathbf{f}_2$$

$$\ln\mathbf{g}_1 = \frac{1}{RT}\left(\frac{\partial N\underline{G}^{\text{ex}}}{\partial N_1}\right)_{T,P,N_2} = \ln\frac{\mathbf{f}_1}{x_1} + \left(1 - \frac{1}{m}\right)\mathbf{f}_2 + \left(\frac{\partial\left(N\frac{Ax_2}{T}(x_1 + mx_2)\mathbf{f}_1\mathbf{f}_2\right)}{\partial N_1}\right)_{T,P,N_2}$$

$$\left(\frac{\partial\left(N\frac{Ax_2}{T}(x_1 + mx_2)\mathbf{f}_1\mathbf{f}_2\right)}{\partial N_1}\right)_{T,P,N_2} = \frac{A}{T}\frac{\partial}{\partial N_1}\left[\frac{Nx_2(x_1 + mx_2)x_1 mx_2}{(x_1 + mx_2)^2}\right] = \frac{A}{T}\frac{\partial}{\partial N_1}\left[\frac{N_2 N_1 mN_2}{(N_1 + mN_2)(N_1 + N_2)}\right]$$

$$= \frac{A}{T}\left[\frac{N_2 mN_2}{(N_1 + mN_2)(N_1 + N_2)} - \frac{N_2 N_1 mN_2}{(N_1 + mN_2)^2(N_1 + N_2)} - \frac{N_2 N_1 mN_2}{(N_1 + mN_2)(N_1 + N_2)^2}\right]$$

$$= \frac{A}{T}[x_2\mathbf{f}_2 - x_2\mathbf{f}_2\mathbf{f}_1 - x_1 x_2\mathbf{f}_2] = \frac{Ax_2\mathbf{f}_2}{T}[1 - \mathbf{f}_1 - x_1] = \frac{Ax_2\mathbf{f}_2}{T}[\mathbf{f}_2 - x_1]$$

$$\ln\mathbf{g}_1 = \ln\frac{\mathbf{f}_1}{x_1} + \left(1 - \frac{1}{m}\right)\mathbf{f}_2 + \frac{Ax_2\mathbf{f}_2}{T}[\mathbf{f}_2 - x_1]$$

$$\ln\mathbf{g}_2 = \frac{1}{RT}\left(\frac{\partial N\underline{G}^{\text{ex}}}{\partial N_2}\right)_{T,P,N_1} = \ln\frac{\mathbf{f}_2}{x_2} + (1 - m)\mathbf{f}_1 + \left(\frac{\partial\left(N\frac{Ax_2}{T}(x_1 + mx_2)\mathbf{f}_1\mathbf{f}_2\right)}{\partial N_2}\right)_{T,P,N_1}$$

$$\left(\frac{\partial\left(N\frac{Ax_2}{T}(x_1 + mx_2)\mathbf{f}_1\mathbf{f}_2\right)}{\partial N_2}\right)_{T,P,N_1} = \frac{A}{T}\frac{\partial}{\partial N_2}\left[\frac{Nx_2(x_1 + mx_2)x_1 mx_2}{(x_1 + mx_2)^2}\right] = \frac{A}{T}\frac{\partial}{\partial N_2}\left[\frac{N_2^2 N_1 m}{(N_1 + mN_2)(N_1 + N_2)}\right]$$

$$= \frac{A}{T}\left[\frac{2N_2 mN_1}{(N_1 + mN_2)(N_1 + N_2)} - \frac{N_2^2 N_1 m^2}{(N_1 + mN_2)^2(N_1 + N_2)} - \frac{N_2^2 N_1 m}{(N_1 + mN_2)(N_1 + N_2)^2}\right]$$

$$= \frac{A}{T}\left[2x_1\mathbf{f}_2 - x_1\mathbf{f}_2^2 - x_1 x_2\mathbf{f}_2\right] = \frac{Ax_1\mathbf{f}_2}{T}[2 - \mathbf{f}_2 - x_2] = \frac{Ax_2\mathbf{f}_2}{T}[\mathbf{f}_1 + x_1]$$

$$\ln\mathbf{g}_2 = \ln\frac{\mathbf{f}_2}{x_2} + (1 - m)\mathbf{f}_2 + \frac{Ax_2\mathbf{f}_2}{T}[\mathbf{f}_1 + x_1]$$

d) and e) See figures in Mathcad worksheet 7-35.mcd.

7.35

$i := 1, 2 .. 1999$

$$x_i := 0.0005 \cdot i$$

$VPS := 1000$ $VT := 1$ $m := \dfrac{VPS}{VT}$ $T := 298$ $\chi := 0.6$

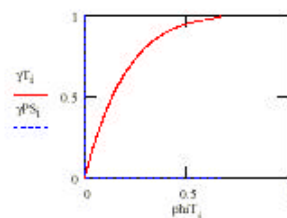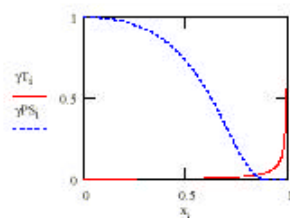$$phiT_i := \dfrac{x_i \cdot VT}{x_i \cdot VT + (1-x_i) \cdot VPS}$$ $phiPS_i := 1 - phiT_i$

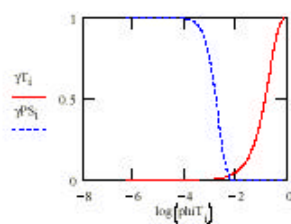$$\gamma T_i := \dfrac{VT \cdot \exp\left[\left(1 - \dfrac{1}{m}\right) \cdot phiPS_i + \chi \cdot (phiPS_i)^2\right]}{x_i \cdot VT + (1-x_i) \cdot VPS}$$ $$\gamma PS_i := \dfrac{VPS \cdot \exp\left[(1-m) \cdot phiT_i + \chi \cdot (phiT_i)^2\right]}{x_i \cdot VT + (1-x_i) \cdot VPS}$$

Graph of activity coefficients versus mole fraction

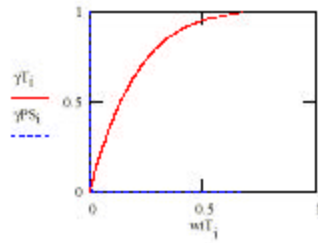Graph of activity coefficients versus volume fraction of toluene.

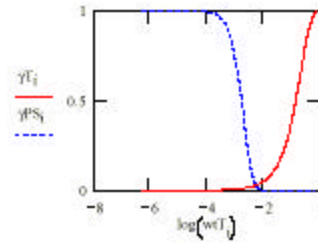Graph of activity coefficients versus log of the volume fraction of toluene.

$$wtT_i := \dfrac{(92 \cdot x_i)}{92 \cdot x_i + 90000 \cdot (1-x_i)}$$

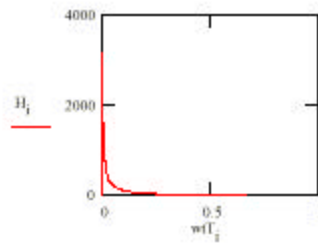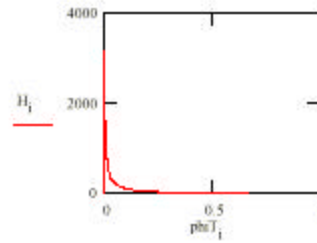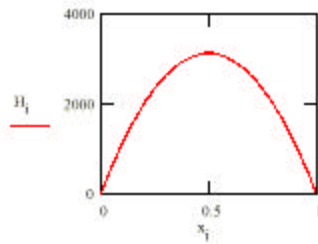Graph of activity coefficients versus weight fraction of toluene.

Graph of activity coefficients versus log of the weight fraction of toluene.

The heat of mixing is computed as follows:

$$H_i := \frac{\left[1500 \cdot 8.314 \cdot m \cdot x_i \cdot \left(1 - x_i\right)^2\right]}{x_i + m \cdot \left(1 - x_i\right)}$$

With new axticity coefficient model

$$\gamma T_i := \frac{VT \cdot exp\left[\left(1 - \frac{1}{m}\right) \cdot phiPS_i + \frac{\left[1500 \cdot \left(1 - x_i\right) \cdot phiPS_i\right] \cdot \left(phiPS_i - x_i\right)}{298.15}\right]}{x_i \cdot VT + \left(1 - x_i\right) \cdot VPS}$$

$$\gamma PS_i := \frac{VPS \cdot exp\left[\left(1 - m\right) \cdot phiT_i + \frac{\left[1500 \cdot \left(1 - x_i\right) \cdot phiPS_i\right] \cdot \left(phiT_i + x_i\right)}{298.15}\right]}{x_i \cdot VT + \left(1 - x_i\right) \cdot VPS}$$

Graph of activity coefficients versus mole fraction

Graph of activity coefficients versus volume fraction of toluene.

γT_i
———
γPS_i
- - - -

γT_i
———
γPS_i
- - - -

Graph of activity coefficients versus log of the volume fraction of toluene.

γT_i
———
γPS_i
- - - -
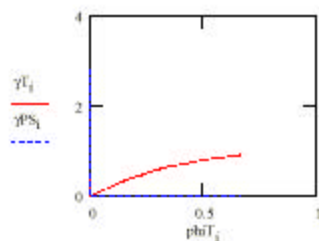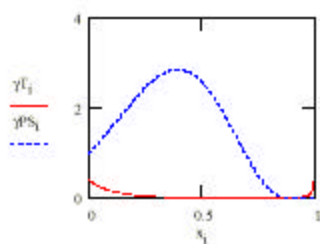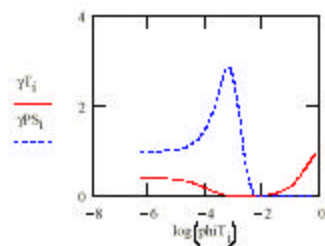
I would say this is not physically correct behavior!

Graph of activity coefficients versus weight fraction of toluene.

Graph of activity coefficients versus log of the weight fraction of toluene.

γT_i
———
γPS_i
- - - -

γT_i
———
γPS_i
- - - -
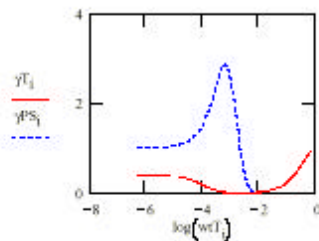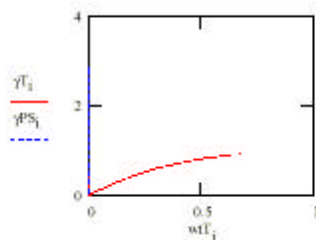
8

8.1-1 $\bar{f}_i^V = \bar{f}_i^L \Rightarrow x_i P_i^{\text{vap}} \boldsymbol{g}_i = y_i P$, since the pressure is low enough that fugacity coefficient corrections will be small.

(a) For the ideal solution, $\boldsymbol{g}_i = 1$ for all species; $1 = \text{EB}$, $2 = \text{nH}$; $y_i = x_i P_i^{\text{vap}} / P$. Thus,

$$y_1 = 0.4723 \times 0.7569 / 0.4537 = 0.7879$$

and

$$y_2 = 0.5277 \times 0.0773 / 0.4537 = 0.0899 ;$$

$\sum y_i = 0.8778$ which indicates that the ideal solution assumption is invalid!

(b) Regular solution behavior:

$$\underline{V}_1 = 75 \text{ cm}^3 \qquad \underline{V}_2 = 148 \text{ cm}^3$$
$$\boldsymbol{d}_1 = 8.9 (\text{cal/cc})^{1/2} \quad \boldsymbol{d}_2 = 7.4 (\text{cal/cc})^{1/2}$$

$\boldsymbol{f}_1 = x_1 \underline{V}_1 / (x_1 \underline{V}_1 + x_2 \underline{V}_2) = 0.4723 \times 75 / (0.4723 \times 75 + 0.5277 \times 148) = 0.312$
$\boldsymbol{f}_2 = 0.688$

$\ln \boldsymbol{g}_1 = \dfrac{\underline{V}_1 \boldsymbol{f}_2^2 [\boldsymbol{d}_1 - \boldsymbol{d}_2]}{RT} = 0.133 ; \qquad \boldsymbol{g}_1 = 1.142$.   Similarly $\boldsymbol{g}_2 = 1.055$.   Therefore,

$y_1 = 1.142 \times 0.7879 = 0.8998$; $y_2 = 1.055 \times 0.0899 = 0.0948$; and $\sum y_i = 0.9946$ which is much closer to unity.

(c) UNIFAC: using   the   program   UNIFAC   we   have $\boldsymbol{g}_1 = 1.173$ and $\boldsymbol{g}_2 = 1.118$; $\Rightarrow y_1 = 1.173 \times 0.7879 = 0.9242$; $y_2 = 1.118 \times 0.0899 = 0.1005$; $\sum y_i = 1.0247$ which is too high.

(d) First the expression $\boldsymbol{g}_i = y_i P / x_i P_1^{\text{vap}}$ and the given vapor-liquid equilibrium data will be used to compute the species activity coefficients in the given solution:

$$\boldsymbol{g}_1 = \dfrac{0.8152 \times 0.3197}{0.2843 \times 0.7569} = 1.211 ; \text{ similarly, } \boldsymbol{g}_2 = 1.069$$

Using eqns. (7.5-10) we obtain $\boldsymbol{b} = 0.3055$ and $\boldsymbol{a} = 0.6747$. Thus, using the van Laar eqn.

$$\ln \boldsymbol{g}_1 = \dfrac{0.6747}{\left[1 + 2.2085 x_1 / x_2\right]^2} \text{ and } \ln \boldsymbol{g}_2 = \dfrac{0.3055}{\left[1 + 0.4528 x_2 / x_1\right]^2}$$

at $x_1 = 0.4723$, $\boldsymbol{g}_1 = 1.079$, $\boldsymbol{g}_2 = 1.144$, so that $y_1 = 0.8504$, $y_2 = 0.1029$ and $\sum y_i = 0.953$.

Since none of the models yields $\sum y_i = 1.0$, none of the solution models is completely correct.

Since the regular solution model comes closest to meeting this criteria, it presumably leads to the best predictions—however, this is merely a hypothesis.

8.1-2   The van Laar equation will be used to fit the data given. Starting from

$$\boldsymbol{g}_i = y_i P / x_i P_i^{\text{vap}} \qquad \begin{array}{l} 1 = \text{H}_2\text{O} \\ 2 = \text{FURF} \end{array}$$

we obtain, at 10 mole % water, $\boldsymbol{g}_1 = 5.826$ and $\boldsymbol{g}_2 = 1.266$. Using eqn. (7.5-10) we get $\boldsymbol{a} = 8.5648$ and $\boldsymbol{b} = 0.7901$. Thus,

$$\ln \boldsymbol{g}_1 = \frac{8.5648}{\left(1 + 10.841 \, x_1 / x_2\right)^2} \text{ and } \ln \boldsymbol{g}_2 = \frac{0.7901}{\left(1 + 0.0922 \, x_2 / x_1\right)^2}$$

which we will assume is valid at all temperatures.

At the new temperature we have $x_i \boldsymbol{g}_i P_1^{\text{vap}} = y_i P$ or $x_1 \boldsymbol{g}_1 \times 1.0352 = y_1 \times 1.013$ and $x_2 \boldsymbol{g}_2 \times 0.1193 = y_2 \times 1.013$ which must be solved together with the activity coefficient expressions above, and the criteria that $x_1 + x_2 = 1$ and $y_1 + y_2 = 1$. Solution procedure I used was to guess a value of x_1, compute x_2 from $x_2 = 1 - x_1$, compute $\boldsymbol{g}_1$ and $\boldsymbol{g}_2$ from the expression above, y_i from $y_i = x_i \boldsymbol{g}_i P_i^{\text{vap}} / P$ for $i = 1$ and 2, and then check to see if $\sum y_i = 1$. Proceeding this way, the following results were obtained

	calculated	measured
x_1	0.075	0.20
x_2	0.925	0.80
y_1	0.867	0.89
y_2	0.129	0.11

Note $\sum y_i = 0.996$ which is not quite equal to 1. The discrepancy between the calculated and experimental results indicates the dangers of using approximate solution models.

8.1-3   The desired result may be proved a number of different ways.

Simplest proof: We have show that at an azeotropic point $\left(\dfrac{\partial P}{\partial x_1}\right)_T = 0$ using the triple product rule in the form

$$\left(\frac{\partial P}{\partial x_1}\right)_T \left(\frac{\partial T}{\partial P}\right)_{x_1} \left(\frac{\partial x_1}{\partial T}\right)_P = -1$$

yields

$$\left(\frac{\partial P}{\partial x_1}\right)_T = -\left(\frac{\partial T}{\partial x_1}\right)_P \left(\frac{\partial P}{\partial T}\right)_{x_1} = 0$$

Since there is no reason to believe $\left(\dfrac{\partial P}{\partial T}\right)_{x_1} = 0$ $\left\{\text{in fact, } \left(\dfrac{\partial P}{\partial T}\right)_{x_1} = \dfrac{P \Delta \underline{H}^{\text{vap}}}{RT^2}\right\}$

We then have $\left(\dfrac{\partial T}{\partial x_1}\right)_P = 0$.

Alternate proof: $P = x_1 \boldsymbol{g}_1 P_1^{\text{vap}} + x_2 \boldsymbol{g}_2 P_2^{\text{vap}} = RT/V$ for an ideal gas phase. Thus

$$\left(\frac{\partial T}{\partial x_1}\right)_P = \frac{V}{R}\left\{ \boldsymbol{g}_1 P_1^{\text{vap}} + x_1 \boldsymbol{g}_1 P_1^{\text{vap}}\left[\frac{\partial \ln \boldsymbol{g}_1}{\partial x_1} + \frac{\partial \ln P_1^{\text{vap}}}{\partial x_1}\right] - \boldsymbol{g}_2 P_2^{\text{vap}} \right.$$

$$\left. + x_2 \boldsymbol{g}_2 P_2^{\text{vap}}\left[\frac{\partial \ln \boldsymbol{g}_2}{\partial x_1} + \frac{\partial \ln P_2^{\text{vap}}}{\partial x_1}\right]_P \right\} = 0$$

Now:

i) $\left(\dfrac{\partial \ln P_1^{\text{vap}}}{\partial x_1}\right)_P = 0$ Since the pure component vapor pressure does not depend on the mixture

   composition at fixed P and T since $\left(\dfrac{\partial T}{\partial x_1}\right)_P = 0$

ii)   Gibbs-Duhem eqn. is

$$\frac{\underline{H}^{ex}}{T}\underbrace{\left(\frac{\partial T}{\partial x_1}\right)_P}_{\to 0} - \underline{V}^{ex}\underbrace{\left(\frac{\partial P_1}{\partial x_1}\right)_P}_{\to 0} + x_1\left(\frac{\partial \ln \boldsymbol{g}_1}{\partial x_1}\right)_P + x_2\left(\frac{\partial \ln \boldsymbol{g}_2}{\partial x_1}\right)_P = 0$$

$$\Rightarrow \left(\boldsymbol{g}_1 P_1^{\text{vap}} - \boldsymbol{g}_2 P_2^{\text{vap}}\right)\left[1 + x_1\left(\frac{\partial \ln \boldsymbol{g}_1}{\partial x_1}\right)_P\right] = 0$$

or $\boldsymbol{g}_1 P_1^{\text{vap}} = \boldsymbol{g}_2 P_2^{\text{vap}}$. From here on it is the same argument as in the text.

Alternative to proof above: start with $P = x_1 \boldsymbol{g}_1 P_1^{\text{vap}} + x_2 \boldsymbol{g}_2 P_2^{\text{vap}}$

$$\left(\frac{\partial P_1}{\partial x_1}\right)_P \equiv 0 = \boldsymbol{g}_1 P_1^{\text{vap}} + x_1 \boldsymbol{g}_1 P_1^{\text{vap}}\left\{\left(\frac{\partial \ln \boldsymbol{g}_1}{\partial x_1}\right)_P + \left(\frac{\partial \ln P_1^{\text{vap}}}{\partial x_1}\right)_P\right\} - \boldsymbol{g}_2 P_2^{\text{vap}}$$

$$+ x_2 \boldsymbol{g}_2 P_2^{\text{vap}}\left\{\left(\frac{\partial \ln \boldsymbol{g}_2}{\partial x_1}\right)_P + \left(\frac{\partial \ln P_2^{\text{vap}}}{\partial x_1}\right)_P\right\}$$

Now using an argument similar to (i) above, and also using (ii), gives $\boldsymbol{g}_1 P_1^{\text{vap}} = \boldsymbol{g}_2 P_2^{\text{vap}}$

8.1-4   In general, we have $x_i \boldsymbol{g}_i P_i^{\text{vap}} = y_i P$ and $\sum x_i \boldsymbol{g}_i P_i^{\text{vap}} = P$. Also, from the experimental data, we

know $P_{\text{ET}}^{\text{vap}} = 0.2321$ bar and $P_B^{\text{vap}} = 0.2939$ bar.

(a)   Ideal   solution: $x_i P_i^{\text{vap}} = y_i P$ and $\sum x_i P_i^{\text{vap}} = P$.   Thus $y_{\text{ET}} = \dfrac{x_{\text{ET}} \times 0.2321}{P}$ and

   $P = x_{\text{ET}} \times 0.2321 + x_E = 0.2939$ or $P = 0.2321 - 0.0617 x_{\text{ET}}$. Consequently $x - y$ and $P - x$

   diagrams are given on following page.

(b)   Regular solution model:

$$
\begin{array}{ccc}
 & \boldsymbol{d}_i & \underline{V}_i^{\mathrm{L}} \\
\text{ethanol} & 12.5 & 58.4 \\
\text{benzene} & 9.2 & 89.0
\end{array}
$$

Ethanol solubility parameters at $25°\mathrm{C}$ was computed using $\Delta\underline{H}_{\mathrm{ET}}^{\mathrm{vap}} = 9674$ cal/mol

$\Delta\underline{U}_{\mathrm{ET}}^{\mathrm{vap}} = \Delta\underline{H}_{\mathrm{ET}}^{\mathrm{vap}} - RT$ and $\boldsymbol{d}_{\mathrm{ET}} = \left(\Delta\underline{U}_{\mathrm{ET}}^{\mathrm{vap}}\big/\underline{V}_{\mathrm{ET}}^{\mathrm{L}}\right)^{1/2}$

Thus $\ln\boldsymbol{g}_{\mathrm{ET}} = \dfrac{\boldsymbol{f}_{\mathrm{B}}^2 \underline{V}_{\mathrm{ET}}^2 [\boldsymbol{d}_{\mathrm{ET}} - \boldsymbol{d}_{\mathrm{B}}]^2}{RT} = 1.0059\boldsymbol{f}_{\mathrm{B}}^2$ and $\ln\boldsymbol{g}_{\mathrm{B}} = 15329\boldsymbol{f}_{\mathrm{ET}}^2$. These activity coefficient expressions are used with the general equations above to obtain the solution. The results are given below.

(c)   The program UNIFAC was used to obtain the predictions shown in the figures below.

(d)   First we evaluate the activity coefficients at the given data point using $\boldsymbol{g}_i = y_i P\big/x_i P_i^{\mathrm{vap}}$ to obtain $\boldsymbol{g}_{\mathrm{ET}} = 1.2244$ and $\boldsymbol{g}_{\mathrm{B}} = 2.0166$. Next using eqns. (7.5-10) we obtain $\boldsymbol{a} = 2.0271$ and $\boldsymbol{b} = 1.4993$. {This is to be compared with $\boldsymbol{a} = 1.95$ and $\boldsymbol{b} = 1.16$ in Table 7.5-1]. Thus we obtain

$$
\boldsymbol{g}_{\mathrm{ET}} = \exp\left\{\frac{2.0271}{\left[1 + 1.3520 x_{\mathrm{ET}}\big/(1 - x_{\mathrm{ET}})\right]^2}\right\}
$$

and

$$
\boldsymbol{g}_{\mathrm{B}} = \exp\left\{\frac{1.4993}{\left[1 + 0.7396(1 - x_{\mathrm{ET}})\big/x_{\mathrm{ET}}\right]^2}\right\}
$$

Using these expressions in the general equations we obtain the results plotted below.
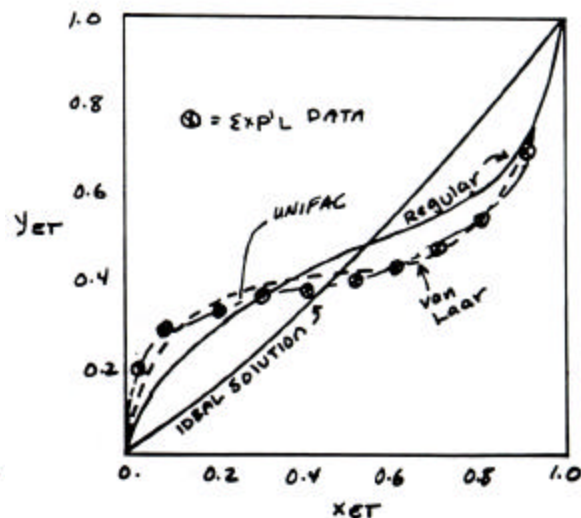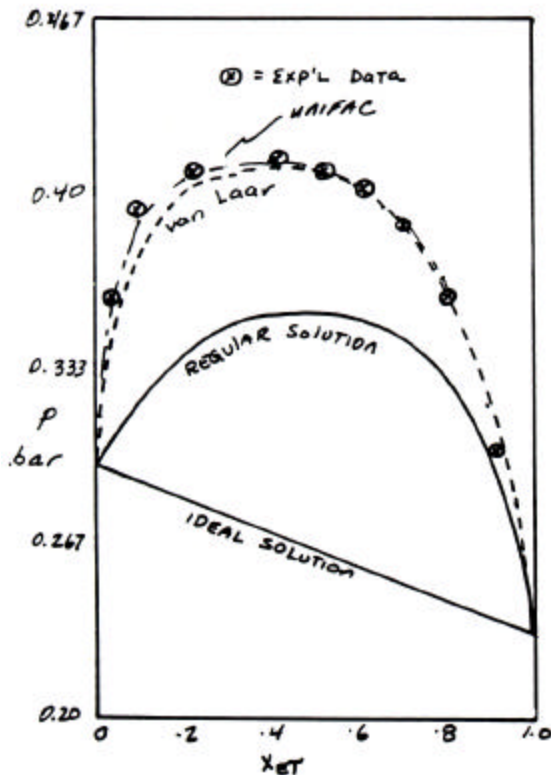
8.1-5 (a) Using the vapor pressure data (Plotting $\ln P^{vap}$ vs $1/T$), I find that at $T = 105.4°C$, $P_{AC}^{vap} \approx 0.6665$ bar and $P_{T}^{vap} \approx 0.8793$ bar. Thus $g_{AC} = (1.013/0.6665) = 1.520$ and $g_{T} = 1.013/0.8793 = 1.152$ at the azeotropic composition of $x_T = 0.627$. Next, using eqns. (7.5-10) and treating toluene as species 1, I find $a = 1.075$ and $b = 1.029$. Thus,

$$\ln g_T = \frac{1.075}{\left[1 + 1.045\,\frac{x_T}{x_M}\right]^2} \quad \text{and} \quad \ln g_{AC} = \frac{1.029}{\left[1 + 0.957\,\frac{x_{AC}}{x_T}\right]^2}.$$

These expressions have been used to obtain the results plotted below.

(b) $\bar{f}_i^L = \bar{f}_i^V \Rightarrow x_i g_i P_i^{vap} = y_i P$. Thus, $g_i = x_i g_i P_i^{vap}/P$ and $\sum y_i = 1$. Procedure I used was, for each value of x_T, to

i) Guess an equilibrium temperature T

ii) Compute y_T and y_{AC}, and check to see if $\sum y_i = 1$

iii) If not, guess a new value of T and repeat the calculation

A simpler procedure is to use Mathcad or another computer algebra program

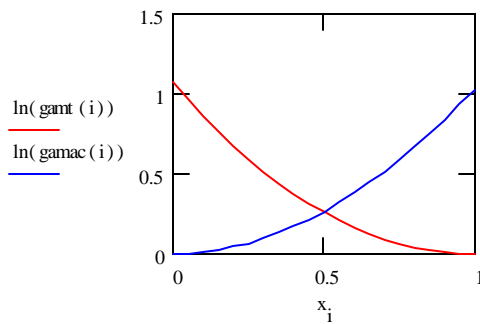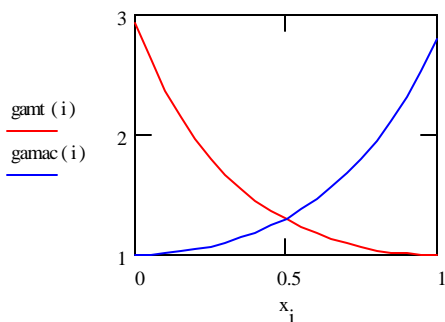| Results	Experiment			van Laar			Ideal		
x_T	0.25	0.50	0.75	0.25	0.50	0.75	0.25	0.50	0.75
y_T	0.43	0.57	0.69	0.43	0.57	0.70	0.30	0.56	0.80
$T(°C)$	104.5	100.8	100.6	107.5	105.8	105.8	116.5	114	111

Ideal solution results were obtained in a similar matter, except that all activity coefficients were set equal to unity.

$$i := 0, 1 .. 20 \qquad x_i := 0.05 \cdot i$$

Write van Laar model this way to avoid division by zero.

$$\text{gamt}(i) := \exp\left[\frac{1.075 \cdot \left(1 - x_i\right)^2}{\left[\left(1 - x_i\right) + 1.045 \cdot x_i\right]^2}\right] \qquad \text{gamac}(i) := \exp\left[\frac{1.029 \cdot \left(x_i\right)^2}{\left[x_i + 0.957 \cdot \left(1 - x_i\right)\right]^2}\right]$$
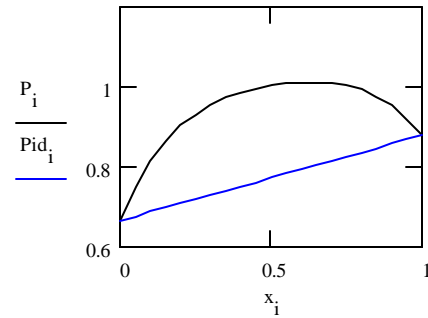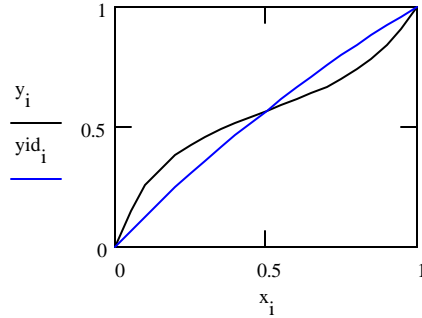
$$P_i := x_i \cdot \text{gamt}(i) \cdot 0.8793 + \left(1 - x_i\right) \cdot \text{gamac}(i) \cdot 0.6665 \qquad\qquad y_i := x_i \cdot \text{gamt}(i) \cdot \frac{0.8793}{P_i}$$

$$\text{Pid}_i := x_i \cdot 0.8793 + \left(1 - x_i\right) \cdot 0.6665$$

$$\text{yid}_i := x_i \cdot \frac{0.8793}{\text{Pid}_i}$$

8.1-6 (a) We start with eqn. (6.2-12b): $\sum x_i d\overline{G_i} + \underline{S}dT - \underline{V}dP = 0$. And note that at constant temperature $\underline{S}dT = 0$ and

$$d\overline{G_i} = RTd\ln \overline{f_i} = RTd\ln(x_i \boldsymbol{g}_i f_i(T_i P)),$$

so that

$$RT\sum x_i d\ln x_i + RT\sum x_i d\ln \boldsymbol{g}_i + RT\sum x_i d\ln f_i - \underline{V}dP = 0$$

However, for the pure fluid fugacity, we have, from eqn. (7.2-8a)

$$RTd\ln f_i = d\underline{G_i} = \underline{V_i}dP$$

Thus

$$RT\sum x_i d\ln x_i + RT\sum x_i d\ln \boldsymbol{g}_i + \left(\sum x_i \underline{V_i} - \underline{V}\right)dP = 0$$

Also

$$\sum x_i \underline{V_i} - \underline{V} = \sum x_i \underline{V_i} - \sum x_i \overline{V_i} = -\sum x_i \overline{V}_i^{\text{ex}}$$
$$= -\underline{V}^{\text{ex}} \Rightarrow RT\sum x_i d\ln(x_i \boldsymbol{g}_i) - \underline{V}^{\text{ex}}dP = 0$$

Now assuming

i) Ideal gas-phase behavior: $x_i \boldsymbol{g}_i P_i^{\text{vap}} = y_i P$ or $x_i \boldsymbol{g}_i = y_i P / P_i^{\text{vap}}$ and

ii) That $P\underline{V}^{\text{ex}} / RT \ll 1$ we obtain

$$\sum x_i d\ln(x_i \boldsymbol{g}_i) = \sum x_i d\ln\left(y_i P / P_i^{\text{vap}}\right) = \frac{P\underline{V}^{\text{ex}}}{RT}d\ln P$$

or

$$\sum x_i d\ln y_i + \sum x_i d\ln P - \sum x_i d\ln P_i^{\text{vap}} = \left(P\underline{V}^{\text{ex}}/RT\right)d\ln P$$

Now noting that $\sum x_i d \ln P_i^{\text{vap}} = 0$, since P_i^{vap} is a function of temperature only and

$$\sum x_i d \ln P = d \ln P\left(\sum x_i\right) = d \ln P, \text{ yields } \sum x_i d \ln y_i = \left(\frac{P\underline{V}^{\text{ex}}}{RT} - 1\right) d \ln P \text{ or}$$

$$\frac{x_1}{y_1} dy_1 + \frac{x_2}{y_2} dy_2 = \left(\frac{x_1}{y_1} - \frac{x_2}{y_2}\right) dy_1 = \left(\frac{P\underline{V}^{\text{ex}}}{RT} - 1\right) d \ln P \approx -d \ln P$$

Since $\quad y_1 + y_2 = 1, \qquad dy_2 = -dy_1.\qquad$ Also $\qquad y_2 = 1 - y, \qquad$ and $\qquad x_2 = 1 - x_1,$

$$\frac{x_1}{y_1} - \frac{(1-x_1)}{1-y_1} = \frac{x_1(1-y_1) - y_1(1-x_1)}{y_1(1-y_1)} = \frac{x_1 - y_1}{y_1(1-y_1)} \qquad\qquad \text{so}$$

$$\frac{(y_1 - x_1)}{y_1(1-y_1)} \frac{dy_1}{dx_1} = \frac{d \ln P}{dx_1}$$

To obtain the $x - y$ diagram, I used the equation above in a finite difference form. Using the argument i to denote the ith data point, the equation above becomes

$$\frac{y_1(i) - x_1(i)}{y_1(i)(1 - y_1(i))} \cdot [y_1(i) - y_1(i-1)] = \ln P(i) - \ln P(i-1)$$

$y_1(i)$ is unknown, however, $P_1(i)$, $P_1(i-1)$, $x_1(i)$ are known. Also $y_1(1)$ is either 0 or 1 depending on which end of the data one starts with. In fact, I started at both ends, in two separate calculations, to check the results. I solved this problem using the equation above rewritten as

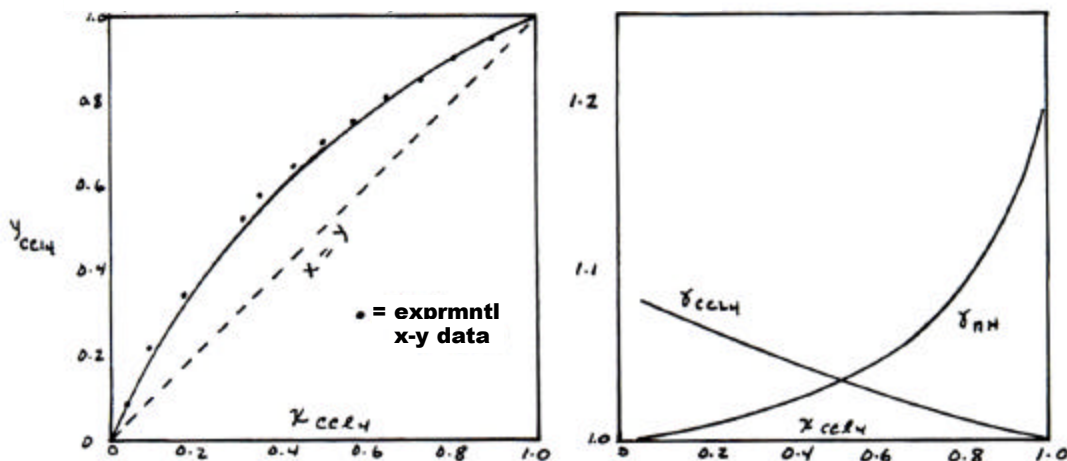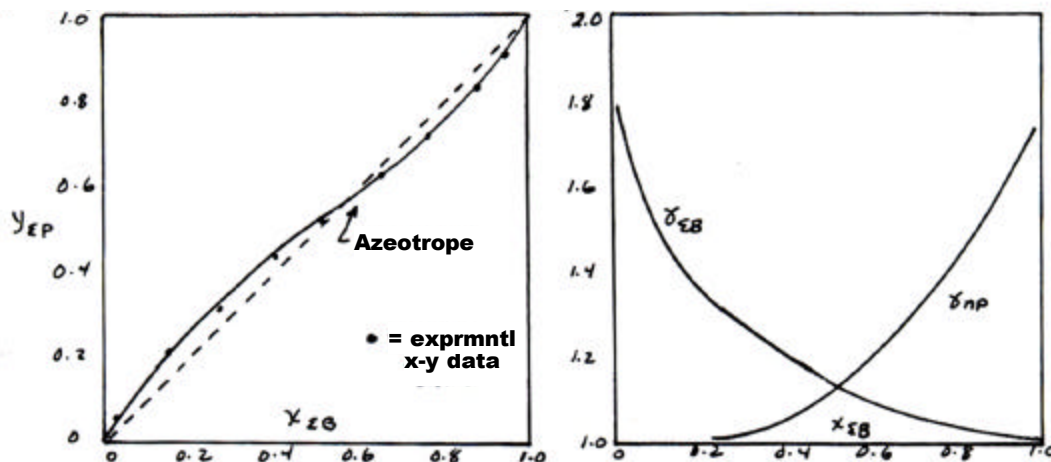$$y_1(i) = \frac{B \pm \sqrt{B^2 - 4C}}{2}$$

where

$$B = \frac{x_1(i) + y_1(i-1) + \Delta \ln P}{1 + \Delta \ln P} \text{ and } C = \frac{x_1(i)y_1(i-1)}{1 + \Delta \ln P}$$

and averaged the results from starting at the $x_1 = 0$ and $x_1 = 1$ ends.

Once x_1 and y_1, were known, the activity coefficients were calculated from $g_1 = y_1 P / x_1 P_1^{\text{vap}}$ and $g_2 = y_2 P / x_2 P_2^{\text{vap}}$. Results are given below.

b.   **CCl$_4$ + n-Heptane System**

c.   **Ethylene bromide + 1-nitropentane System**

8.1-7   A simpler solution using Mathcad is available as a Mathcad worksheet.
  (a) At the bubble point we have

$$y_i = x_i P_i^{\text{vap}}/P \quad \text{where} \quad P = 5 \text{ bar}$$

$x_{\text{ET}} = 0.05$; $x_{\text{P}} = 0.10$, $x_{\text{NB}} = 0.40$ and $x_{\text{MP}} = 0.45$. Procedure used was
  i)   Guess T,
  ii)   Compute each y_i, and the sum $\sum y_i$. If $\sum y_i = 1$, guessed T is correct; if $\sum y_i > 1$,
        guessed T is too high; if $\sum y_i < 1$, guessed T is too low. If $\sum y_i \neq 1$, we correct T and
        recalculate.   Solution: $T = 293.66$ K (bubble point) $y_{\text{ET}} = 0.4167$, $y_{\text{P}} = 0.1730$,
        $y_{\text{NB}} = 0.1601$ and $y_{\text{MP}} = 0.2502$.
  (b) The dew point calculation is similar. Here, $y_{\text{ET}} = 0.05$, $y_{\text{P}} = 0.10$, $y_{\text{NB}} = 0.40$ and $y_{\text{MP}} = 0.45$.
       $P = 5$ bar, and T and the x_i's are the unknowns. Thus, here we guess the dew point
       temperature, compute each of the x_i's from $x_i = P y_i / P_i^{\text{vap}}$ and evaluate $\sum x_i$. If $\sum x_i = 1$, the
       guessed temperature is the dew point temperature; if $\sum x_i > 1$, guessed T is too low; if
       $\sum x_i < 1$, guessed T is too high. Solution (obtained using the computer) $T = 314.23$ K (dew
       point) $x_{\text{ET}} = 0.0039$, $x_{\text{P}} = 0.0337$, $x_{\text{NB}} = 0.5215$ and $x_{\text{MP}} = 0.4409$.
  (c) The advantage of the Mathcad worksheet for the isothermal flash calculation is that one can use
       the initial flash equations directly, rather than having to make the substitutions below.

       For the isothermal flash vaporization calculation, we proceed as in Illustration 8.1-3. First, we
       calculate the K factors, i.e.
$$K_{\text{ET}} = \frac{10 + (-817.08/303.15 + 4.402229)}{5} = 10.185.$$
       and, similarly $K_{\text{P}} = 2.238$, $K_{\text{NB}} = 0.546$ and $K_{\text{MP}} = 0.743$. Thus, the equations to be solved
       are:
$$x_{\text{ET}} + x_{\text{P}} + x_{\text{NB}} + x_{\text{MP}} = 1 \tag{1}$$
$$y_{\text{ET}} + y_{\text{P}} + y_{\text{NB}} + y_{\text{MP}} = 1 \Rightarrow 10.185 x_{\text{ET}} + 2.238 x_{\text{P}} + 0.546 x_{\text{NB}} + 0.743 x_{\text{MP}} = 1 \tag{2}$$
       Also,
$$x_{\text{ET}}[L(1 - K_{\text{ET}}) + K_{\text{ET}}] = 0.05 \Rightarrow x_{\text{ET}}(10.185 - 9.185 L) = 0.05 \tag{3}$$
   and, similarly

$$x_P(2.238 - 1.238L) = 0.10 \qquad (4)$$

$$x_{NB}(0.546 + 0.454L) = 0.40 \qquad (5)$$

$$x_{MP}(0.743 + 0.257L) = 0.45 \qquad \textbf{(6)}$$

Solution procedure I used was to guess L, compute the x_i's from eqns. (3 to 6), and then ascertain whether eqns. (1) and (2) were satisfied. After a number of iterations, I obtained the following solution:

$$L = 0.86667 \qquad V = 0.13333$$
$$x_{ET} = 0.0225 \qquad y_{ET} = 0.2289$$
$$x_P = 0.0858 \qquad y_P = 0.1921$$
$$x_{NB} = 0.4258 \qquad y_{NB} = 0.2326$$
$$\underline{x_{MP} = 0.4659} \qquad \underline{y_{MP} = 0.3464}$$
$$\sum x_i = 1.000 \qquad \sum y_i = 1.000$$

(d) For an adiabatic flush vaporization, shown below, the energy balance must also be satisfied
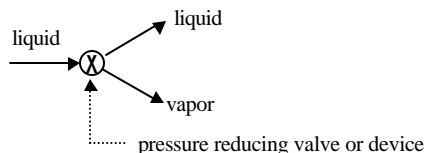
This is a (two-phase) Joule-Thomson expansion, so that the energy balance yields $\underline{H}_{in} = \underline{H}_{out}$, or

$$\left[\sum x_i \overline{H}_i^L(T,P,\underline{x})\right]_{inlet\ conditions} = L\left[\sum x_i \overline{H}_i^L(T,P,\underline{x})\right]_{outlet\ liquid\ conditions} +$$
$$V\left[\sum y_i \overline{H}_i^V(T,P,\underline{y})\right]_{outlet\ vapor\ conditions}$$

This equation must be satisfied, together with the mass balances and phase equilibrium equations of part c. Thus, we have one new unknown here, the outlet temperature, and an additional equation from which to find that unknown.

8.1-8 (a) Starting from $x_i g_i P_i^{vap} = y_i P$, we obtain $g_i = y_i P / x_i P_i^{vap}$, and using the data in the problem statement, we can compute each g_i, and then $\ln(g_P/g_A)$ and $\underline{G}^{ex}/RT = x_P \ln g_P + x_A \ln g_A$. These results, together with $\left[\underline{G}^{ex}/RT\right]/x_P x_A$ and its inverse are tabulated on the following page. Also, there is a plot of $\ln(g_P/g_A)$ vs. x_A. This plot indicates that the data appears to be thermodynamically consistent (i.e. $\int \ln(g_P/g_A)dx_A \approx 0$), though the points at the composition extremes ($x_A = 0.021$ and $x_A = 0.953$) look suspect

(b) See Problem 7.22 the plots of $\left[\underline{G}^{ex}/RT\right]/x_P x_A$ and $x_P x_A/\left[\underline{G}^{ex}/RT\right]$ appear on the following page. The fact that neither is linear indicates that neither the two-constant Margules, nor the van Laar equation will accurately fit the data. Hence, one will have to use at least a 3-constant Redlich-Kister expansion for the Gibbs free energy to obtain a good fit of the experimental data for this system!

x_A	x_P	g_P	g_A	$\ln\left(\dfrac{g_P}{g_A}\right)$	$\dfrac{G^{ex}}{RT}$	$\dfrac{G^{es}}{RTx_Ax_P}$	$\dfrac{x_Ax_PRT}{G^{ex}}$
0.021	0.979	3.3407	1.3140	0.9331	0.2927	14.237	0.0702
0.061	0.939	3.6497	1.0643	1.2323	0.1367	2.3866	0.4190
0.134	0.866	3.1326	1.1142	1.0337	0.2467	2.1259	0.4704
0.210	0.790	2.5617	1.1700	0.7837	0.3216	1.9385	0.5159
0.292	0.708	2.2196	1.2187	0.5995	0.3729	1.8037	0.5544
0.405	0.595	1.8190	1.3475	0.3000	0.4198	1.7421	0.5740
0.503	0.497	1.5132	1.5582	−0.0293	0.4288	1.7153	0.5830
0.611	0.389	1.3299	1.8214	−0.3145	0.4074	1.7141	0.5834
0.728	0.272	1.1689	2.3716	−0.7075	0.3485	1.7600	0.5682
0.869	0.131	1.0542	3.1505	−1.0948	0.1962	1.7235	0.5802
0.953	0.047	1.0191	4.5509	−1.4964	0.0893	1.9937	0.5016
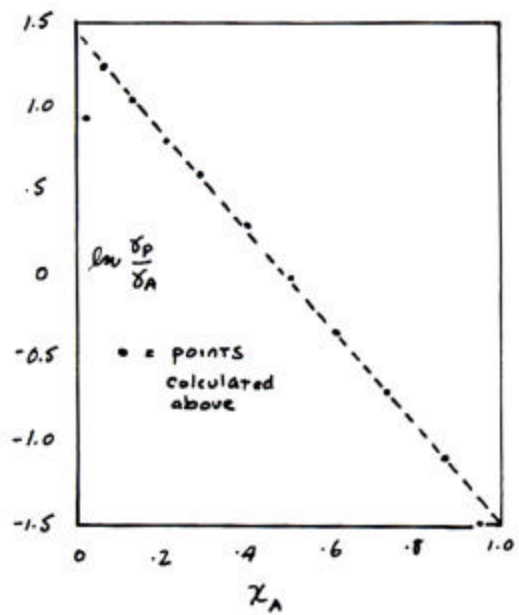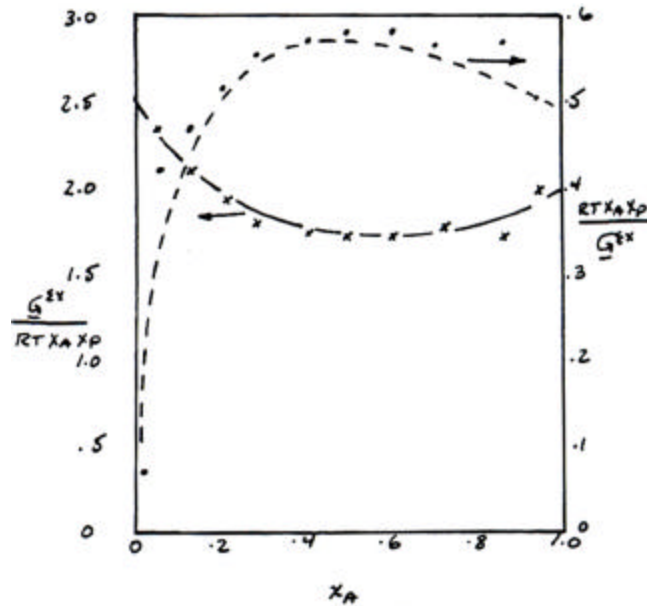
The next step is to fit parameters in the Gibbs free energy models to the experimental data. I have done this assuming small errors in all the variables (T, P, x and y) and using the maximum likelihood method. The results of the different models are given below:

Wilson model $\Lambda_{12} = 347.82$ $\Lambda_{21} = 1075.23$

P_{meas} (hPa)	P_{calc} (hPa)	T_{meas} (°C)	T_{calc} (°C)	$x_{1,meas}$	$x_{1,calc}$	$y_{1,meas}$	$y_{1,calc}$
1013.00	1008.46	49.15	49.17	.0210	.0317	.1080	.2353
1013.00	1012.01	45.76	45.76	.0610	.0556	· 3070	.3404
1013.00	1012.35	39.58	39.58	.1340	.1273	.4750	.5048
1013.00	1012.89	36.67	36.67	.2100	.1942	.5500	.5761
1013.00	1012.21	34.35	34.35	.2920	.2958	.6140	.6330
1013.00	1008.83	32.85	32.87	.4050	.4290	.6640	.6731
1013.00	1024.86	33.35	33.31	.5030	.4291	.6780	.6725
1013.00	1007.84	31.97	31.99	.6110	.6224	.7110	.7128
1013.00	1011.79	31.93	31.93	.7280	.7287	.7390	.7380
1013.00	1010.94	32.27	32.28	.8690	.8640	.8100	.7957
1013.00	1012.31	33.89	33.89	.9530	.9554	.9060	.8933

$1013 \text{ hPa} = 1.013 \text{ bar} = 1.013 \times 10^5 \text{ Pa}$

The sum of squares of weighted residuals for this model is 1298, the mean deviation in y_1 is 2.55%, and in P is 0.29%

NRTL model $t_{12} = 777.95$ $t_{21} = 432.53$

P_{meas} (hPa)	P_{calc} (hPa)	T_{meas} (°C)	T_{calc} (°C)	$x_{1,meas}$	$x_{1,calc}$	$y_{1,meas}$	$y_{1,calc}$
1013.00	1008.14	49.15	49.17	.0210	.0379	.1080	.2400
1013.00	1011.69	45.76	45.76	.0610	.0650	.3070	.3469
1013.00	1011.87	39.58	39.58	.1340	.1399	.4750	.5131
1013.00	1012.35	36.67	36.67	.2100	.2034	.5500	.5843
1013.00	1012.18	34.35	34.35	.2920	.2939	.6140	.6403
1013.00	1010.35	32.85	32.86	·4050	.4186	.6640	.6793
1013.00	1025.99	33.35	33.30	.5030	.4173	.6780	.6784
1013.00	1007.37	31.97	31.99	.6110	.6208	·7110	.7131
1013.00	1010.33	31.93	31.94	.7280	.7296	.7390	.7348
1013.00	1009.50	32.27	32.28	.8690	.8581	.8100	.7896
1013.00	1011.83	33.89	33.89	.9530	.9505	.9060	.8890

Sum of squares of weighted residuals $=1547$
Mean deviation in y_1 is 3.00%; in $P = 0.34\%$

UNIQUAC Model   The parameters are $t_{12} = 572.61$ and $t_{21} = -72.84$
Mean deviation in y_1 is 3.0790; in P is 0.34%

P_{meas} (hPa)	P_{calc} (hPa)	T_{meas} (°C)	T_{calc} (°C)	$x_{1,meas}$	$x_{1,calc}$	$y_{1,meas}$	$y_{1,calc}$
1013.00	1008.12	49.15	49.17	.0210	.0381	.1080	.2402
1013.00	1011.66	45.76	45.76	.0610	.0655	.3070	.3474
1013.00	1011.82	39.58	39.58	·1340	.1412	.4750	.5141
1013.00	1012.26	36.67	36.67	.2100	.2048	.5500	.5855
1013.00	1012.10	34.35	34.35	·2920	.2946	.6140	.6417
1013.00	1010.40	32.85	32.86	.4050	.4180	.6640	.6807
1013.00	1026.29	33.35	33.30	.5030	.4177	.6780	.6800
1013.00	1007.25	31-97	31.99	·6110	.6206	.7110	.7139
1013.00	1010.16	31.93	31.94	.7280	.7295	.7390	.7351
1013.00	1009.43	32.27	32.28	.8690	.8579	.8100	.7895
1013.00	1011.80	33.89	33.89	.9530	.9503	.9060	.8888

van Laar model $a = 1.5032$ $b = 1.8534$
Mean % $P = 0.34$; $y = 3.18\%$ sum of squares of wt. residuals $=1625$

P_{meas} (hPa)	P_{calc} (hPa)	T_{meas} (°C)	T_{calc} (°C)	$x_{1,meas}$	$x_{1,calc}$	$y_{1,meas}$	$y_{1,calc}$
1013.00	1008.13	49.15	49.17	.0210	.0380	.1080	.2403
1013.00	1011.66	45.76	45.76	.0610	.0656	.3070	.3478
1013.00	1011.78	39.58	39.58	.1340	.1419	.4750	.5154
1013.00	1012.19	36.67	36.67	.2100	.2057	.5500	.5874
1013.00	1012.06	34.35	34.35	.2920	.2947	.6140	.6441
1013.00	1010.66	32.85	32.86	.4050	.4164	.6640	.6837
1013.00	1025.98	33.35	33.30	.5030	.4121	.6780	.6822
1013.00	1007.14	31.97	31.99	.6110	.6202	.7110	.7162
1013.00	1009.92	31.93	31.94	.7280	.7293	.7390	.7362
1013.00	1009.57	32.27	32.28	.8690	.8585	.8100	.7897
1013.00	1011.89	33.89	33.89	.9530	.9512	.9060	.8894

2-Constant Margules Model $A = 1.7737$ $B = 1.9259$
Mean % deviation in $P = 0.33\%$ and in $y = 2.90\%$, and sum of squares of weighted residuals $= 1401$

P_{meas} (hPa)	P_{calc} (hPa)	T_{meas} (°C)	T_{calc} (°C)	$x_{1,\text{meas}}$	$x_{1,\text{calc}}$	$y_{1,\text{meas}}$	$y_{1,\text{calc}}$
1013.00	1008.60	49.15	49.17	.0210	.0287	.1080	.2337
1013.00	1012.14	45.76	45.76	.0610	.0502	.3070	.3382
1013.00	1012.66	39.58	39.58	.1340	.1135	.4750	.5022
1013.00	1013.56	36.67	36.67	.2100	.1731	.5500	.5736
1013.00	1013.81	34.35	34.35	.2920	.2764	.6140	.6314
1013.00	1004.67	32.85	32.88	.4050	.4396	.6640	.6653
1013.00	1023.95	33.35	33.31	.5030	.4598	.6780	.6670
1013.00	1005.18	31.97	32.00	.6110	.6465	.7110	.6899
1013.00	1014.78	31.93	31.92	.7280	.7317	.7390	.7082
1013.00	1013.07	32.27	32.27	.8690	.8863	.8100	.7932
1013.00	1012.36	33.89	33.89	.9530	.9578	.9060	.8928

So, of the models considered here, the Wilson model provides the best description (of the two-constant models) for this data set.

8.1-9   Using the program UNIFAC taking T and x_P as known, and computing $\mathbf{g}_P$, $\mathbf{g}_A$ and P as well as y_P we obtain

x_P	$T(°C)$	$\mathbf{g}_P^{\text{calc}}$	$\mathbf{g}_A^{\text{calc}}$	$P^{\text{calc}} = \sum\limits_{(\text{bar})} x_i \mathbf{g}_i P_i^{\text{vap}}$	y_P^{calc}	y_P^{exp}
0.021	49.15	4.1390	1.006	0.922	0.147	0.108
0.061	45.76	3.7515	1.0053	0.983	0.325	0.307
0.134	39.58	3.1680	1.0258	0.976	0.498	0.475
0.210	36.67	2.6687	1.0649	0.995	0.583	0.550
0.292	34.35	2.2487	1.1302	0.993	0.635	0.614
0.405	32.85	1.8162	1.2697	0.993	0.677	0.664
0.503	33.35	1.5416	1.4540	1.004	0.697	0.678
0.611	31.97	1.3247	1.7663	1.002	0.717	0.711
0.728	31.93	1.1592	2.3176	1.001	0.742	0.739
0.869	32.27	1.0388	3.5893	1.005	0.804	0.810
0.953	33.89	1.0053	4.9909	1.018	0.897	0.906

$\uparrow$

measured
value $= 1.013$ bar

While the prediction is not perfect, it is relatively good.
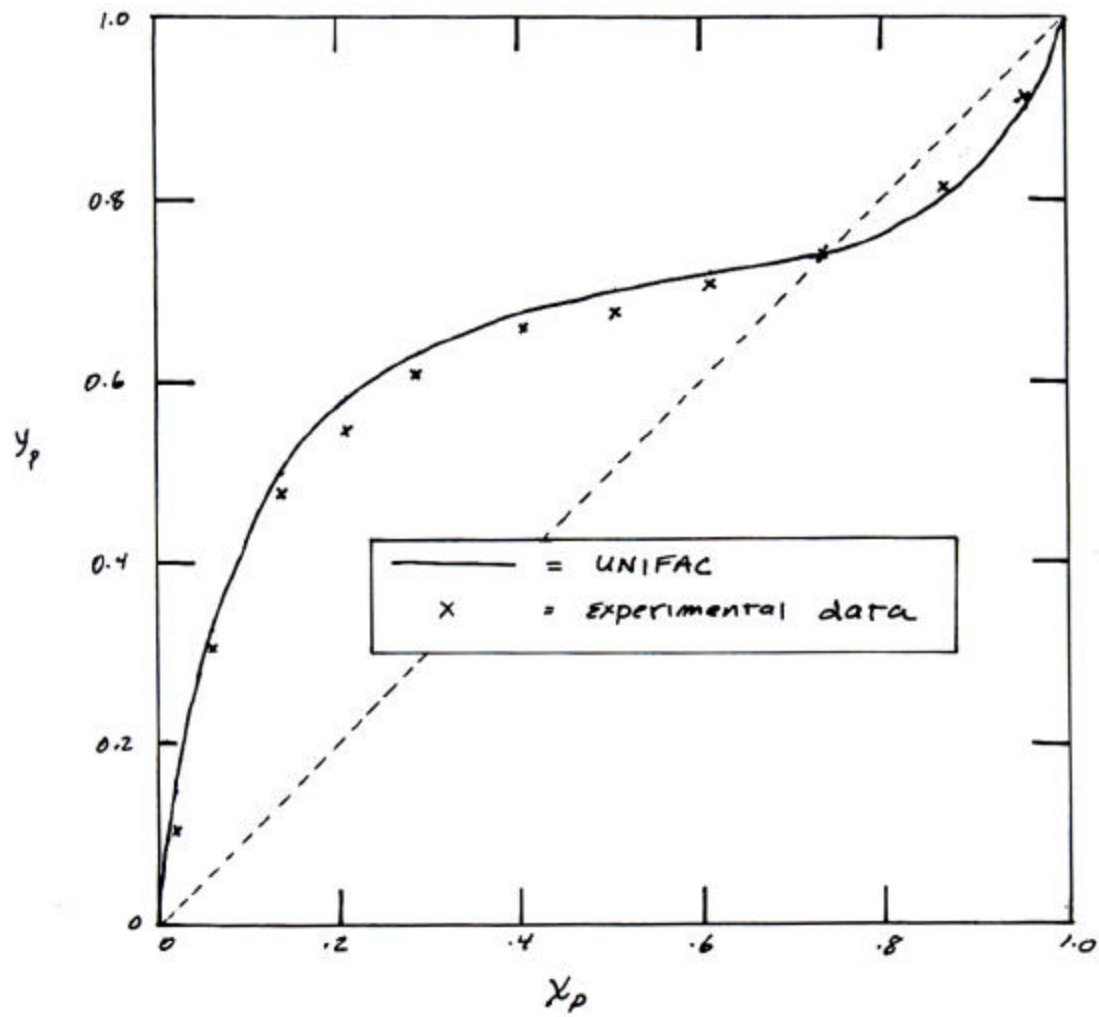
8.1-10   First we should check to see if this problem is soluble (i.e.., well-posed in the sense of the Gibbs phase rule). The Gibbs phase rule, eqn. (6.9-6) is $F = C - M - P + 2$. Thus here we have $F = 3 - 0 - 2 + 2 = 3$ degrees of freedom. Since the temperature, and two independent liquid-phase mole fractions are specified, the problem is well posed.

For the solution of this problem, the following subscripts will be used: $1 = \text{ethanol}$, $2 = \text{benzene}$ and $3 = \text{ethyl acetate}$. As the first step, compute the pure component vapor pressures. This is done by using the vapor pressure data in the "*Chemical Engineers' Handbook*", making plots of $\ln P_i^{\text{vap}}$ vs $1/T$, and then determining $\ln P_i^{\text{vap}}$ (and hence P_i^{vap}) at $T = 78°\text{C}$ $\left(1/T = 2.847 \times 10^{-3}\ \text{K}\right)$ we find

$$P_1^{\text{vap}} \cong 1.0\ \text{bar};\ P_2^{\text{vap}} \cong 0.9666\ \text{bar and}\ P_3^{\text{vap}} \cong 1.053\ \text{bar}$$

Next, we need compute the liquid phase activity coefficients. This will be done using the ternary van Laar eqn. (eqn. (A7.3-2)). [See also Problem 7.8c], together with the entries in Table 7.6-1. Here one has to be careful about the order in which the species appear in the table. I obtained the following:

$$a_{12} = 1.946 \quad b_{12} = 1.610 \quad \Rightarrow \quad a_{21} = b_{12} = 1.610 \quad b_{21} = a_{12} = 1.946$$
$$a_{32} = 1.15 \quad b_{32} = 0.92 \quad \Rightarrow \quad a_{23} = b_{32} = 0.92 \quad b_{23} = a_{32} = 1.15$$
$$a_{31} = 0.896 \quad b_{31} = 0.896 \quad \Rightarrow \quad a_{13} = b_{31} = 0.896 \quad b_{13} = a_{31} = 0.896$$

Now from eqn. (A7.3-2)

$$\ln g_1 = \frac{\left\{ x_2^2 a_{12}\left(\frac{b_{12}}{a_{12}}\right)^2 + x_3^2 a_{13}\left(\frac{b_{13}}{a_{13}}\right)^2 + x_2 x_3 \frac{b_{12}}{a_{12}}\frac{b_{13}}{a_{13}}\left(a_{12} + a_{13} - a_{23}\frac{a_{12}}{b_{12}}\right) \right\}}{\left[x_1 + x_2\left(\frac{b_{12}}{a_{12}}\right) + x_3\left(\frac{b_{13}}{a_{13}}\right) \right]^2}$$

$$= \frac{\left\{ 1.3320 x_2^2 + 0.896 x_3^2 + 1.730 x_2 x_3 \right\}}{\left[x_1 + 0.8273 x_2 + x_3 \right]^2}\Bigg|_{\substack{x_2 = x_3 = 0.4 \\ x_1 = 0.2}} = \frac{0.6333}{0.8666} = 0.7308$$

$$\Rightarrow g_1 = 2.0767$$

To obtain an expression for g_2, we interchange subscripts 1 and 2 in eqn. (A7.3-2) to obtain [see solution to prob. 7.8c]

$$\ln g_2 = \frac{\left\{ x_1^2 b_{12}\left(\frac{a_{12}}{b_{12}}\right)^2 + x_3^2 a_{23}\left(\frac{b_{23}}{a_{23}}\right)^2 + x_1 x_3 \left(\frac{a_{12}}{b_{12}}\right)\left(\frac{b_{23}}{a_{23}}\right)\left(b_{12} + a_{23} - a_{13}\frac{b_{12}}{a_{12}}\right) \right\}}{\left[x_2 + x_1\left(\frac{a_{12}}{b_{12}}\right) + x_3\left(\frac{b_{23}}{a_{23}}\right) \right]^2}$$

$$= \frac{\left\{ 2.3521 x_1^2 + 1.4375 x_3^2 + 2.7025 x_1 x_3 \right\}}{\left[x_2 + 1.2087 x_1 + 1.250 x_3 \right]^2}\Bigg|_{\substack{x_2 = x_3 = 0.4 \\ x_1 = 0.2}} = \frac{0.5403}{1.3036} = 0.4145$$

$$\Rightarrow g_2 = 1.5136$$

An expression for g_3 is obtained by interchanging indices 1 and 3 in eqn. (A7.3-2) to obtain [see solution to Problem 7.8c]

$$\ln \boldsymbol{g}_3 = \frac{\left\{ x_2^2 \boldsymbol{b}_{23}\left(\frac{\boldsymbol{a}_{23}}{\boldsymbol{b}_{23}}\right)^2 + x_1^2 \boldsymbol{b}_{13}\left(\frac{\boldsymbol{a}_{13}}{\boldsymbol{b}_{13}}\right)^2 + x_1 x_2 \left(\frac{\boldsymbol{a}_{23}}{\boldsymbol{b}_{23}}\right)\left(\frac{\boldsymbol{a}_{13}}{\boldsymbol{b}_{13}}\right)\left(\boldsymbol{b}_{23} + \boldsymbol{b}_{13} - \boldsymbol{b}_{12}\frac{\boldsymbol{b}_{23}}{\boldsymbol{a}_{23}}\right) \right\}}{\left[x_3 + x_2\left(\frac{\boldsymbol{a}_{23}}{\boldsymbol{b}_{23}}\right) + x_1\left(\frac{\boldsymbol{a}_{13}}{\boldsymbol{b}_{13}}\right) \right]^2}$$

$$= \frac{\left\{ 0.7360 x_2^2 + 0.896 x_1^2 + 0.0268 x_1 x_2 \right\}}{\left[x_3 + 0.80 x_2 + x_1 \right]^2}\Bigg|_{\substack{x_2 = x_3 = 0.4 \\ x_1 = 0.2}} = \frac{0.1557}{0.8464}$$

$$\Rightarrow \ln \boldsymbol{g}_3 = 0.1840 \text{ and } \boldsymbol{g}_3 = 1.2020$$

With these "preliminaries" taken care of, we can now proceed on to the solution. The equilibrium equations are

$$x_i \boldsymbol{g}_i P_i^{\text{vap}} = y_i P \text{ and } \sum x_i \boldsymbol{g}_i P_i^{\text{vap}} = P$$

Therefore

$$x_1 \boldsymbol{g}_1 P_1^{\text{vap}} = 0.2 \times 2.0767 \times 1.000 = 0.41534 \text{ bar}$$

$$x_2 \boldsymbol{g}_2 P_2^{\text{vap}} = 0.4 \times 1.5136 \times 0.9666 = 0.58522$$

$$x_3 \boldsymbol{g}_3 P_3^{\text{vap}} = 0.4 \times 1.2020 \times 1.053 = \underline{0.50620}$$

$$P = 1.50684 \text{ bar}$$

and

$$y_1 = 0.2756 \quad y_2 = 0.3884 \quad y_3 = 0.3360$$

Note that the vapor composition is only very slightly different than the liquid composition. (This is because the vapor pressures and activity coefficients of the species are all quite similar).

An alternative is to use the program UNIFAC to estimate the activity coefficients. Using the program with ethanol $(1- CH_3,\ 1- CH_2,\ 1- OH)$, benzene (6–ACH) and ethyl acetate $(1- CH_3,\ 1- CH_2,\ 1- CH_3COO)$ we obtain, at 20 mole % ethanol, 40 mole % benzene and 40 mole % ethyl acetate at $78°C$) that

$$\boldsymbol{g}_1 = 2.2062 ; \ \boldsymbol{g}_2 = 1.1931 \text{ and } \boldsymbol{g}_3 = 1.0038$$

The solution is $P = 1.2965$ bar and

$$y_1 = 0.3181; \ y_2 = 0.3558 \text{ and } y_3 = 0.3261$$

Clearly this result is different from the ternary van Laar prediction. In the absence of experimental data for this ternary mixture, it is difficult to say which model is better.

8.1-11 For the simpler models, it is possible to show by simple mathematics that the model either does or does not permit a double azeotrope. For example, the van Laar model is

$$\frac{G^{\text{ex}}}{RT} = \frac{2 a_{12} x_1 q_1 x_2 q_2}{x_1 q_1 + x_2 q_2} \times \frac{2 a_{12}}{2 a_{12}} = \frac{\boldsymbol{a}\boldsymbol{b} x_1 x_2}{\boldsymbol{a} x_1 + \boldsymbol{b} x_2} = \frac{\boldsymbol{a}\boldsymbol{b} x_1 (1 - x_1)}{\boldsymbol{a} x_1 + \boldsymbol{b}(1 - x_1)}$$

Now for the benzene-hexafluorobenzene system G^{ex} has an interior maximum and an interior minimum. That is, $d\underline{G}^{\text{ex}}/dx_1$ is zero twice in the region $0 \le x_1 \le 1$. To see if the van Laar model permits this we examine

$$\frac{d}{dx}\left(\frac{G^{ex}}{RT}\right) = \frac{ab(1-x_1)}{(ax_1 + b(1-x_1))} + \frac{abx_1(-1)}{ax_1 + b(1-x_1)} - \frac{abx_1(1-x_1)}{[ax_1 + b(1-x_1)]^2}(a-b) = 0$$

or

$$\frac{ab(1-2x_1)}{ax_1 + b(1-x_1)} - \frac{abx_1(1-x_1)(a-b)}{[dx_1 + b(1-x_1)]^2} = 0$$

$$\Rightarrow (x_2 - x_1)(ax_1 + bx_2) - x_1 x_2 (a-b) = 0$$

$$ax_1 x_2 - ax_1^2 - bx_1 x_2 + bx_2^2 - ax_1 x_2 + bx_1 x_2 = 0$$

or

$$ax_1^2 = bx_2^2 \Rightarrow \frac{a}{b} = \left(\frac{x_2}{x_1}\right)^2 \text{ or } \frac{x_2}{x_1} = \pm\sqrt{\frac{a}{b}}$$

Now a and b must be of same sign (otherwise we get the square root of a negative number). Also, since $0 \le x_1 \le 1$ and $0 \le x_2 \le 1$, only positive sign is allowed. Thus $x_2/x_1 = \sqrt{a/b}$ when $d\underline{G}^{ex}/dx_1 = 0$. And only an interior maximum (if $a>0$ and $b>0$) or an interior minimum (if $a<0$ and $b<0$) can occur, but not both! Therefore, van Laar model can not describe the observed behavior.

Similarly, obviously the one-constant Margules model $\underline{G}^{ex} = Ax_1 x_2$ can not give both an interior minimum & maximum, so it can not describe observed behavior.

Instead of continuing this extreme argument, we will look at the results of merely fitting the experimental data.

Two-constant-Margules model

P_{meas} (hPa)	P_{calc} (hPa)	$x_{1,meas}$	$x_{1,calc}$	$y_{1,meas}$	$y_{1,calc}$
521.60	521.60	.0000	.0000	.0000	.0000
525.70	518.42	.0941	.0940	.0970	.0880
525.68	517.53	.1849	.1849	.1788	.1777
522.87	517.19	.2741	.2741	.2567	.2679
518.18	516.24	.3648	.3648	.3383	.3605
509.89	514.09	.4538	.4539	.4237	.4522
507.73	511.32	.5266	.5268	.4982	.5275
503.50	507.72	.6013	.6015	.5783	.6051
499.74	503.06	.6894	.6896	.6760	.6970
497.57	498.70	.7852	.7852	.7824	.7960
497.94	496.96	.8960	.8960	.8996	.9063
501.55	501.55	1.0000	1.0000	1.0000	1.0000

- only 1 azeotrope at $x_1 \ge 0.9$

Wilson model

P_{meas} (hPa)	P_{calc} (hPa)	$y_{1,meas}$	$y_{1,calc}$
521.60	521.60	.0000	.0000
525.70	510.55	.0970	.0757
525.68	500.76	.1788	.1556
522.87	492.21	.2567	.2407
518.18	484.89	.3383	.3335
509.89	479.35	.4237	.4300
507.73	476.28	.4982	.5118
503.50	474.74	.5783	.5974
499.74	475.30	.6760	.6982
497.57	479.24	.7824	.8038
497.94	488.48	.8996	.9145
501.55	501.55	1.0000	1.0000

Only a single azeotrope predicted to occur.

NRTL model

P_{meas} (hPa)	P_{calc} (hPa)	$x_{1,meas}$	$y_{1,meas}$	$y_{1,calc}$
521.60	521.60	.0000	.0000	.0000
525.70	518.93	.0941	.0970	.0896
525.68	516.49	.1849	.1788	.1773
522.87	514.23	.2741	.2567	.2647
518.18	512.08	.3648	.3383	.3545
509.89	510.11	.4538	.4237	.4436
507.73	508.62	.5266	.4982	.5170
503.50	507.19	.6013	.5783	.5927
499.74	505.66	.6894	.6760	.6825
497.57	504.17	.7852	.7824	.7804
497.94	502.69	.8960	.8996	.8938
501.55	501.55	1.0000	1.0000	1.0000

No azeotrope results form the least squares fitting of parameters

UNIQUAC model

P_{meas} (hPa)	P_{calc} (hPa)	$x_{1,meas}$	$y_{1,meas}$	$y_{1,calc}$	
521.60	521.60	.0000	.0000	.0000	
525.70	528.19	.0941	.0970	.0953	
525.68	526.27	.1849	.1788	.1717	
522.87	521.58	.2741	.2567	.2503	
518.18	515.87	.3648	.3383	.3368	←
509.89	510.44	.4538	.4237	.4276	
507.73	506.61	.5266	.4982	.5046	
503 50	503.46	.6013	.5783	.5852	
499.74	500.91	.6894	.6760	.6807	
497.57	499.57	.7852	.7824	.7832	
497.94	499.80	.8960	.8996	.8978	←
501.55	501.55	1.0000	1.0000	1.0000	

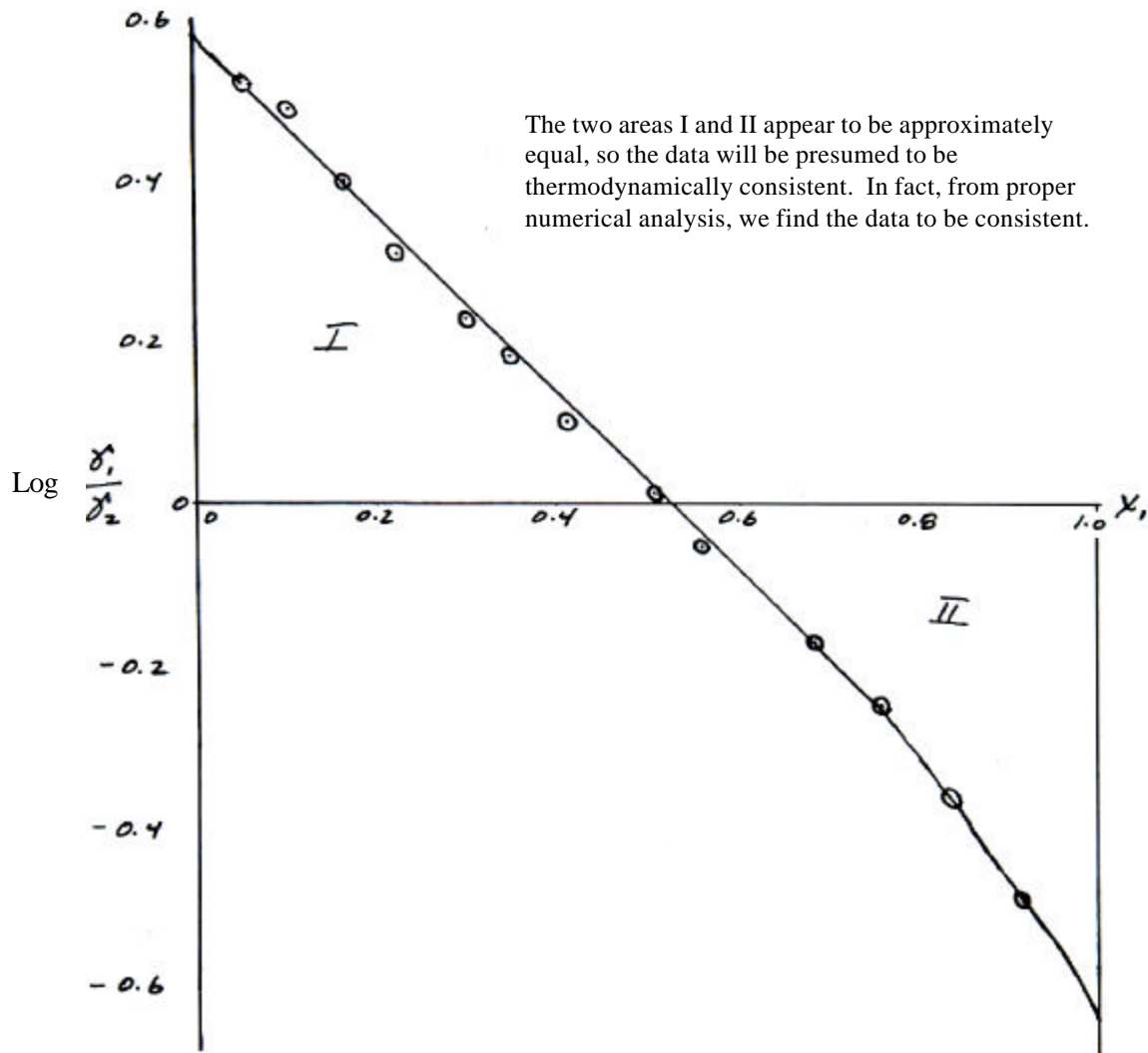Double azeotrope predicted, as indicated.

Therefore, of the models considered only the UNIQUAC model is capable of producing the peculiar behavior of $\underline{G}^{\text{ex}}$ for this system.

8.1-12 From Table 8.1-1 we have (assuming an ideal vapor phase)

x_1	g_1	g_2	$\log_{10}\left(\dfrac{g_1}{g_2}\right)$
0.0503	3.4337	1.0247	0.5251
0.1014	3.1394	1.0192	0.4885
0.1647	2.6218	1.0445	0.3997
0.2212	2.2340	1.0918	0.3109
0.3019	1.9334	1.1332	0.2320
0.3476	1.7879	1.1637	0.1865
0.4082	1.5928	1.2643	0.1003
0.4463	1.5237	1.3068	0.0666
0.5031	1.4284	1.3755	0.0164
0.5610	1.3225	1.4984	−0.0542
0.6812	1.1841	1.7837	−0.1779
0.7597	1.1285	2.0086	−0.2504
0.8333	1.0648	2.4539	−0.3625
0.9180	1.0223	3.1792	−0.4927

See figure below.

Log $\dfrac{\gamma_1}{\gamma_2}$

The two areas I and II appear to be approximately equal, so the data will be presumed to be thermodynamically consistent. In fact, from proper numerical analysis, we find the data to be consistent.

8.1-13

$$P = x_1 \boldsymbol{g}_1 P_1^{\text{vap}} + x_2 \boldsymbol{g}_2 P_2^{\text{vap}}$$

$$\left(\frac{\partial P}{\partial x_2}\right)_T = -\boldsymbol{g}_1 P_1^{\text{vap}} + x_1 P_1^{\text{vap}} \frac{\partial \boldsymbol{g}_1}{\partial x_2} + \boldsymbol{g}_2 P_2^{\text{vap}} + x_2 P_2^{\text{vap}} \frac{\partial \boldsymbol{g}_2}{\partial x_2} ; \text{ where we have used that } \frac{\partial x_1}{\partial x_2} = -1 \text{ as}$$

$$x_2 \to 0 \quad \boldsymbol{g}_1 \to 1 \text{ and } \frac{\partial \boldsymbol{g}_1}{\partial x_2} = 0 . \text{ So}$$

$$\left(\frac{\partial P}{\partial x_2}\right)_{T, x_2 \to 0} = -P_1^{\text{vap}} + \boldsymbol{g}_2 P_2^{\text{vap}} + x_2(\to 0)\frac{\partial \boldsymbol{g}_2}{\partial x_2}$$

so that

$$\boldsymbol{g}_2(x_2 \to 0) = \frac{P_1^{\text{vap}} + \left(\dfrac{\partial P}{\partial x_2}\right)_{T, x_2 \to 0}}{P_2^{\text{vap}}} \qquad \text{constant temperature ebulliometer}$$

Now

$$P = x_1 \boldsymbol{g}_1 P_1^{\text{vap}} + x_2 \boldsymbol{g}_2 P_2^{\text{vap}}$$

and

$$\left(\frac{\partial P}{\partial x_2}\right)_P = 0 = -\boldsymbol{g}_1 P_1^{\text{vap}} + x_1\left(\frac{\partial \boldsymbol{g}_1}{\partial x_2}\right)_P P_1^{\text{vap}} + x_1 \boldsymbol{g}_1 \left(\frac{\partial P_1^{\text{vap}}}{\partial T}\right)\left(\frac{\partial T}{\partial x_2}\right)_P$$

$$+ \boldsymbol{g}_2 P_2^{\text{vap}} + x_2\left(\frac{\partial \boldsymbol{g}_2}{\partial x_2}\right)_P P_2^{\text{vap}} + x_2 \boldsymbol{g}_2 \left(\frac{\partial P_2^{\text{vap}}}{\partial T}\right)_T\left(\frac{\partial T}{\partial x_2}\right)_P$$

as $x_2 \to 0$, $\boldsymbol{g}_1 \to 1$ and $\dfrac{\partial \boldsymbol{g}_1}{\partial x_2} \to 0$

$$0 = -P_1^{\text{vap}} + \frac{dP_1^{\text{vap}}}{dT}\left(\frac{\partial T}{\partial x_2}\right)_P + \boldsymbol{g}_2(x_2 \to 0)P_2^{\text{vap}}$$

or

$$\boldsymbol{g}_2(x_2 \to 0) = \frac{P_1^{\text{vap}} - \left(\dfrac{dP_1^{\text{vap}}}{dT}\right)\left(\dfrac{\partial T}{\partial x_2}\right)_{P, x_2 \to 0}}{P_2^{\text{vap}}} \qquad \text{constant pressure ebulliometer}$$

8.1-14   (also available as a Mathcad worksheet)
Clearly many different thermodynamic models can be used. We will use the van Laar model

$$\ln \boldsymbol{g}_1 = \frac{\boldsymbol{a}}{\left[1 + \frac{\boldsymbol{a} x_1}{\boldsymbol{b} x_2}\right]^2} \quad \text{and} \quad \ln \boldsymbol{g}_2 = \frac{\boldsymbol{b}}{\left[1 + \frac{\boldsymbol{b} x_2}{\boldsymbol{a} x_1}\right]^2}$$

which gives $\ln \boldsymbol{g}_1^{\infty} = \boldsymbol{a}$ and $\ln \boldsymbol{g}_2^{\infty} = \boldsymbol{b}$. Using the data in the problem statement
$\boldsymbol{a} = \ln(1.6931) = 0.5266$ and $\boldsymbol{b} = \ln(1.9523) = 0.6690$. Using these parameter values in the activity

coefficient equations above, together with $P_i = x_i \mathbf{g}_i P_i^{vap}$; $P = P_1 + P_2$ and $y_i = P_i/P$ gives, at $x_1 = 0.2$

$$x_2 = 0.2 \quad y_1 = 0.4483 \quad y_2 = 0.5517 \text{ and } P = 0.6482 \text{ bar}$$

Also

$x_2 = 0.500$	$y_1 = 0.7036$	$y_2 = 0.2946$	$P = 0.8431$
0.700	0.8118	0.1882	0.9262
0.850	0.8943	0.1057	0.9732
0.900	0.9256	0.0744	0.9861
0.950	0.9604	0.0396	0.9972
0.975	0.9795	0.0205	1.0019

8.1-15 (also available as a Mathcad worksheet)
Using Mathcad I obtained the following results

| $T = 300$ K	$K_{EOH-EAC}$	$T = 400$ K	$K_{EOH-EAC}$
$x_{EOH} = 0.1$	5.8340	$x_{EOH} = 0.1$	15.318
0.5	0.4255	0.5	1.1172
0.9	0.03103	0.9	0.0815

Thus the results exhibit strong composition *and* temperature dependence. For an ideal solution

$$x_i P_i^{vap} = y_i P \Rightarrow \frac{y_i}{x_i} = \frac{P_i^{vap}}{P} \Rightarrow K_{ij} = \frac{y_i/x_i}{y_j/x_j} = \frac{P_i^{vap}}{P_j^{vap}}$$

Thus, for an ideal solution, the relative volatility K_{ij} has no composition dependence, but can be dependent on temperature (unless, fortuitously, P_i^{vap} and P_j^{vap} have the same temperature dependence, that is, $\Delta \underline{H}_i^{vap} = \Delta \underline{H}_j^{vap}$). The composition dependence arises from the non-ideal solution behavior. Since the activity coefficients dependent on temperature, nonideal solution behavior also contributes to the temperature dependence of the relative volatility.

8.1-16 This system was used for illustration in the first edition. The figures which appear below are from that source. [I changed to the hexane-triethylamine system since the *x* and *y* were too close in the benzene-ethylene chloride system because the pure component vapor pressures are so close.]
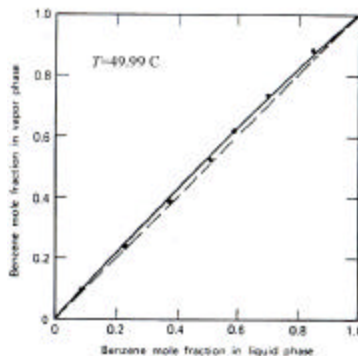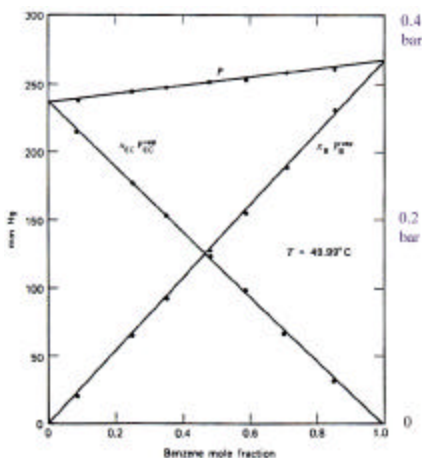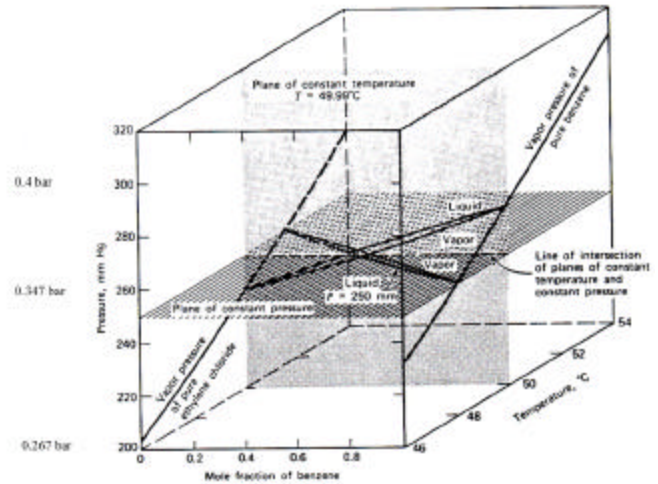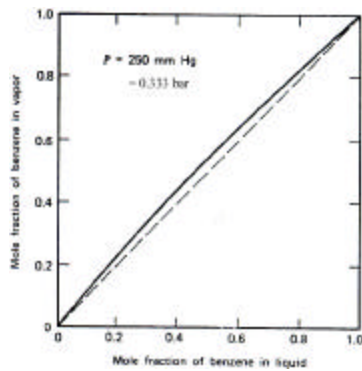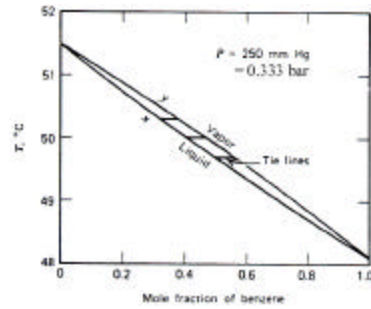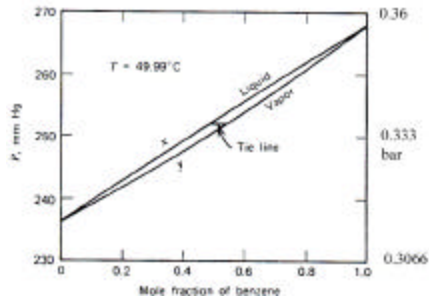
8.1-17

$$x_1 \boldsymbol{g}_1 P_1^{\text{vap}} \left(\frac{f}{P} \right) = y_1 P$$

(a) $\quad \boldsymbol{a}_{21} = \dfrac{y_2/x_2}{y_1/x_1} = \dfrac{\boldsymbol{g}_2 P_2^{\text{vap}}(f/P)_2/P}{\boldsymbol{g}_1 P_1^{\text{vap}}(f/P)_1/P} = \dfrac{\boldsymbol{g}_2 P_2^{\text{vap}}(f/P)_2}{\boldsymbol{g}_1 P_1^{\text{vap}}(f/P)_1} = \dfrac{P_2^{\text{vap}} e^{Ax_1^2/RT}(f/P)_2}{P_1^{\text{vap}} e^{Ax_2^2/RT}(f/P)_1}$

$\qquad = \dfrac{P_2^{\text{vap}}}{P_1^{\text{vap}}} e^{A(x_1^2 - x_2^2)/RT} \dfrac{(f/P)_2}{(f/P)_1} = \dfrac{P_2^{\text{vap}}}{P_1^{\text{vap}}} e^{A(x_1^2 - (1-x_1)^2)/RT} \dfrac{(f/P)_2}{(f/P)_1}$

$\qquad = \underbrace{\dfrac{P_2^{\text{vap}}}{P_1^{\text{vap}}}}_{T\text{ dependence}} \underbrace{e^{-A(1-2x_1)/RT}}_{\substack{\text{Composition} \\ \text{and } T \text{ dependence}}} \underbrace{\dfrac{(f/P)_2}{(f/P)_1}}_{\substack{T \text{ and } P \\ \text{dependence}}}$

(b) Ideal mixture at low pressure

$\qquad A = 0$ above and also all $\left(\dfrac{f}{P} \right) = 1$

$\qquad \boldsymbol{a}_{21} = \underbrace{\dfrac{P_2^{\text{vap}}(T)}{P_1^{\text{vap}}(T)}}_{T \text{ dependence}}$

8.1-18 a) Starting from

$\overline{f}_i^L = \overline{f}_i^L$ we get, for the ideal solution, that $x_i P_i^{\text{vap}} = y_i P$

Now adding such equations for both components, we get

$x_1 P_1^{\text{vap}} + x_2 P_2^{\text{vap}} = P$ so that

$$y_i = \frac{x_i P_i^{\text{vap}}}{x_1 P_1^{\text{vap}} + x_2 P_2^{\text{vap}}};$$

In a equimolar mixture $\qquad y_i(x_1 = 0.5) = \dfrac{P_i^{\text{vap}}}{P_1^{\text{vap}} + P_2^{\text{vap}}}$

b) For the nonideal mixture

$x_i \boldsymbol{g}_i P_i^{\text{vap}} = y_i P$

Now adding these equations for both components, we get

$x_1 \boldsymbol{g}_1 P_1^{\text{vap}} + x_2 \boldsymbol{g}_2 P_2^{\text{vap}} = P$ so that

$$y_i = \frac{x_i \boldsymbol{g}_i P_i^{\text{vap}}}{x_1 \boldsymbol{g}_1 P_1^{\text{vap}} + x_2 \boldsymbol{g}_2 P_2^{\text{vap}}};$$

For the one - constant Margules model

$$y_i = \frac{x_i P_i^{\text{vap}} \exp(a(1-x_i)^2)}{x_1 P_1^{\text{vap}} \exp(a x_2^2) + x_2 P_2^{\text{vap}} \exp(a x_1^2)}$$

In a equimolar mixture with the

$$y_i(x_1 = 0.5) = \frac{0.5 P_i^{\text{vap}} \exp(a(0.5)^2)}{0.5 P_1^{\text{vap}} \exp(a(0.5)^2) + 0.5 P_2^{\text{vap}} \exp(a(0.5)^2)} = \frac{P_i^{\text{vap}}}{P_1^{\text{vap}} + P_2^{\text{vap}}}$$

which is exactly the same result as for the ideal solution. However, these two different models only give the same vapor-phase composition in an equimolar mixture. However, even in this case, the pressures for the ideal and one-constant Margules mixtures are different.

8.1-19

$$\underline{G}^{\text{ex}} = A x_1 x_2 \Rightarrow \boldsymbol{g}_1 = \exp\left(\frac{A x_2^2}{RT}\right); \ \boldsymbol{g}_2 = \exp\left(\frac{A x_1^2}{RT}\right)$$

$x_1 \boldsymbol{g}_1 P_1^{\text{vap}} = y_1 P$

Azeotrope $x_1 = y_1 \Rightarrow \boldsymbol{g}_1 = \dfrac{P}{P_1^{\text{vap}}}$

$$\frac{\boldsymbol{g}_2}{\boldsymbol{g}_1} = \frac{P}{P_2^{\text{vap}}} \cdot \frac{P_1^{\text{vap}}}{P} = \frac{P_1^{\text{vap}}}{P_2^{\text{vap}}} = \frac{e^{A x_1^2/RT}}{e^{A x_2^2/RT}} = e^{A(x_1^2 - x_2^2)/RT}$$

$$\ln\frac{P_1^{\text{vap}}}{P_2^{\text{vap}}} = \frac{A}{RT}(x_1^2 - x_2^2) = \frac{A}{RT}(x_1^2 - (1-x_1)^2) = \frac{A}{RT}(x_1^2 - 1 + 2x_1 - x_1^2)$$

$$\frac{A}{RT}(2x_1 - 1) = \ln\frac{P_1^{\text{vap}}}{P_2^{\text{vap}}} \Rightarrow A = \frac{RT}{2x_1 - 1}\ln\frac{P_1^{\text{vap}}}{P_2^{\text{vap}}} = \frac{RT}{1 - 2x_1}\ln\frac{P_2^{\text{vap}}}{P_1^{\text{vap}}}$$

So for an azeotrope to form

(1) If $P_2^{\text{vap}} > P_1^{\text{vap}}$

Azeotrope will form near $x_1 = 0$ if $A = RT\ln\dfrac{P_2^{\text{vap}}}{P_1^{\text{vap}}}$

Azeotrope will form at $x_1^+ = 0.5$ if $A = \infty$; at $x_1^- = 0.5$ if $A = -\infty$.

Azeotrope will form near $x_1 = 1$ if $A = -RT \ln \dfrac{P_2^{\text{vap}}}{P_1^{\text{vap}}}$

Or in general $x_1 = \dfrac{1}{2}\left(1 - \dfrac{RT}{A}\ln\left(\dfrac{P_2^{\text{vap}}}{P_1^{\text{vap}}}\right)\right)$

So we can draw figures of regions in which azeotropes can be expected to form.

(2) If $P_1^{\text{vap}} > P_2^{\text{vap}}$ then $A = \dfrac{RT}{1 - 2x_1}\ln\dfrac{P_1^{\text{vap}}}{P_2^{\text{vap}}}$

Mirror image of point 1

(b) $T = \dfrac{2Ax_1(1 - x_1)}{R}$; $A = \dfrac{RT}{2x_1(1 - x_1)}$ at $x_1 = 0.5$; $A = 2RT$

8.1-20   (also available as a Mathcad worksheet)

8.1-20

$T := 69$

$p5 := 10.422 - \dfrac{26799}{8.314 \cdot (273.15 + T)}$ $p5 := \exp(p5)$ $p5 = 2.721$

$p6 := 10.456 - \dfrac{29676}{8.314 \cdot (273.15 + T)}$ $p6 := \exp(p6)$ $p6 = 1.024$

$p7 := 11.431 - \dfrac{35200}{8.314 \cdot (273.15 + T)}$ $p7 := \exp(p7)$ $p7 = 0.389$

$x5 := 0.25$ $x6 := 0.45$ $x7 := 0.3$

$P := x5 \cdot p5 + x6 \cdot p6 + x7 \cdot p7$ $P = 1.258$

$y5 := \dfrac{(x5 \cdot p5)}{P}$ $y6 := \dfrac{(x6 \cdot p6)}{P}$ $y7 := \dfrac{(x7 \cdot p7)}{P}$

Bubble point pressure $P = 1.258$

Bubble point compositions $y5 = 0.541$ $y6 = 0.366$ $y7 = 0.093$

Now on to dew point calculation

Initial guesses $P := 1$ $x5 := 0.1$ $x6 := 0.6$ $x7 := 0.3$

$z5 := 0.25$ $z6 := 0.45$ $z7 := 0.3$

GIVEN

$x5 + x6 + x7 = 1$ $x5 \cdot p5 = z5 \cdot P$ $x6 \cdot p6 = z6 \cdot P$ $x7 \cdot p7 = z7 \cdot P$

$\text{soln} := \text{FIND}(x5, x6, x7, P)$

$x5 := \text{soln}_0$ $x6 := \text{soln}_1$ $x7 := \text{soln}_2$ $P := \text{soln}_3$

Dew point pressure $P = 0.768$

Dew point compositions $x5 = 0.071$ $x6 = 0.338$ $x7 = 0.592$

8.1-21 (also available as a Mathcad worksheet)

8.1-21

Solving for the bubble point pressure

$T := 69 \qquad P := 1.013$

$$p5(T) := \exp\left[10.422 - \frac{26799}{8.314 \cdot (273.15 + T)}\right] \qquad p5(T) = 2.721 \qquad K5(T, P) := \frac{p5(T)}{P}$$

$$p6(T) := \exp\left[10.456 - \frac{29676}{8.314 \cdot (273.15 + T)}\right] \qquad p6(T) = 1.024 \qquad K6(T, P) := \frac{p6(T)}{P}$$

$$p7(T) := \exp\left[11.431 - \frac{35200}{8.314 \cdot (273.15 + T)}\right] \qquad p7(T) = 0.389 \qquad K7(T, P) := \frac{p7(T)}{P}$$

$y5 := 0.33 \qquad y6 := 0.33 \qquad y7 := 0.33 \qquad z5 := 0.25 \qquad z6 := 0.45 \qquad z7 := 0.3$

GIVEN

$K5(T, P) \cdot z5 + K6(T, P) \cdot z6 + K7(T, P) \cdot z7 = 1 \qquad y5 = K5(T, P) \cdot z5 \qquad y6 = K6(T, P) \cdot z6 \qquad y7 = K7(T, P) \cdot z7$

$\text{soln} := \text{FIND}(y5, y6, y7, P)$

$y5 := \text{soln}_0 \qquad y6 := \text{soln}_1 \qquad y7 := \text{soln}_2 \qquad P := \text{soln}_3$

$y5 = 0.541 \qquad y6 = 0.366 \qquad y7 = 0.093 \qquad P = 1.258$

This is the bubble-point pressure solution. Now on to the dew-point pressure problem.

$x5 := 0.33 \qquad x6 := 0.33 \qquad x7 := 0.33$ 　　　　Note that xi=yi/Ki

GIVEN

$$\frac{z5}{K5(T, P)} + \frac{z6}{K6(T, P)} + \frac{z7}{K7(T, P)} = 1 \qquad x5 = \frac{z5}{K5(T, P)} \qquad x6 = \frac{z6}{K6(T, P)} \qquad x7 = \frac{z7}{K7(T, P)}$$

$\text{soln} := \text{FIND}(x5, x6, x7, P)$

$x5 := \text{soln}_0 \qquad x6 := \text{soln}_1 \qquad x7 := \text{soln}_2 \qquad P := \text{soln}_3$

$x5 = 0.071 \qquad x6 = 0.338 \qquad x7 = 0.592 \qquad P = 0.768$

This is the dew-point pressure solution.

So for a mixture of the composition z5=0.25, z6=0.45 and z7=0.30, at a temperature of 69 C, the mixture will be all liquid at pressures above 1.258 bar, and all vapor at pressures below 0.768 bar. Vapor-liquid equilibrium will exist at this temperature only between 0.768 and 1.258 bar, so this is the pressure range we will examine.

$T := 69$ $L := 0.99$ $P := 1.2$

GIVEN $K5(T, P) \cdot x5 + K6(T, P) \cdot x6 + K7(T, P) \cdot x7 - (x5 + x6 + x7) = 0$

$x5 \cdot (L \cdot (1 - K5(T, P)) + K5(T, P)) = z5$

$x6 \cdot (L \cdot (1 - K6(T, P)) + K6(T, P)) = z6$

$x7 \cdot (L \cdot (1 - K7(T, P)) + K7(T, P)) = z7$ $soln := FIND(x5, x6, x7, L)$

$x5 := soln_0$ $x6 := soln_1$ $x7 := soln_2$ $L := soln_3$ $V := 1 - L$

$x5 = 0.223$ $x6 = 0.456$ $x7 = 0.32$ $V = 0.094$ $L = 0.906$

$y5 := K5(T, P) \cdot x5$ $y6 := K6(T, P) \cdot x6$ $y7 := K7(T, P) \cdot x7$

$y5 = 0.507$ $y6 = 0.389$ $y7 = 0.104$

$P := 1.1$ $L := 0.80$

GIVEN $K5(T, P) \cdot x5 + K6(T, P) \cdot x6 + K7(T, P) \cdot x7 - (x5 + x6 + x7) = 0$

$x5 \cdot (L \cdot (1 - K5(T, P)) + K5(T, P)) = z5$

$x6 \cdot (L \cdot (1 - K6(T, P)) + K6(T, P)) = z6$

$x7 \cdot (L \cdot (1 - K7(T, P)) + K7(T, P)) = z7$ $soln := FIND(x5, x6, x7, L)$

$x5 := soln_0$ $x6 := soln_1$ $x7 := soln_2$ $L := soln_3$ $V := 1 - L$

$x5 = 0.18$ $x6 = 0.458$ $x7 = 0.362$ $V = 0.264$ $L = 0.736$

$y5 := K5(T, P) \cdot x5$ $y6 := K6(T, P) \cdot x6$ $y7 := K7(T, P) \cdot x7$

$y5 = 0.445$ $y6 = 0.427$ $y7 = 0.128$

$P := 1.0$ $L := 0.60$

GIVEN $K5(T, P) \cdot x5 + K6(T, P) \cdot x6 + K7(T, P) \cdot x7 - (x5 + x6 + x7) = 0$

$x5 \cdot (L \cdot (1 - K5(T, P)) + K5(T, P)) = z5$

$x6 \cdot (L \cdot (1 - K6(T, P)) + K6(T, P)) = z6$

$x7 \cdot (L \cdot (1 - K7(T, P)) + K7(T, P)) = z7$ $soln := FIND(x5, x6, x7, L)$

$x5 := soln_0$ $x6 := soln_1$ $x7 := soln_2$ $L := soln_3$ $V := 1 - L$

$x5 = 0.141$ $x6 = 0.445$ $x7 = 0.414$ $V = 0.451$ $L = 0.549$

$y5 := K5(T, P) \cdot x5$ $y6 := K6(T, P) \cdot x6$ $y7 := K7(T, P) \cdot x7$

$y5 = 0.383$ $y6 = 0.456$ $y7 = 0.161$

$P := 0.9$ $L := 0.40$

GIVEN $K5(T,P) \cdot x5 + K6(T,P) \cdot x6 + K7(T,P) \cdot x7 - (x5 + x6 + x7) = 0$

$x5 \cdot (L \cdot (1 - K5(T,P)) + K5(T,P)) = z5$

$x6 \cdot (L \cdot (1 - K6(T,P)) + K6(T,P)) = z6$

$x7 \cdot (L \cdot (1 - K7(T,P)) + K7(T,P)) = z7$ $soln := FIND(x5, x6, x7, L)$

$x5 := soln_0$ $x6 := soln_1$ $x7 := soln_2$ $L := soln_3$ $V := 1 - L$

$x5 = 0.107$ $x6 = 0.412$ $x7 = 0.481$ $V = 0.663$ $L = 0.337$

$y5 := K5(T,P) \cdot x5$ $y6 := K6(T,P) \cdot x6$ $y7 := K7(T,P) \cdot x7$

$y5 = 0.323$ $y6 = 0.469$ $y7 = 0.208$

$P := 0.8$ $L := 0.20$

GIVEN $K5(T,P) \cdot x5 + K6(T,P) \cdot x6 + K7(T,P) \cdot x7 - (x5 + x6 + x7) = 0$

$x5 \cdot (L \cdot (1 - K5(T,P)) + K5(T,P)) = z5$

$x6 \cdot (L \cdot (1 - K6(T,P)) + K6(T,P)) = z6$

$x7 \cdot (L \cdot (1 - K7(T,P)) + K7(T,P)) = z7$ $soln := FIND(x5, x6, x7, L)$

$x5 := soln_0$ $x6 := soln_1$ $x7 := soln_2$ $L := soln_3$ $V := 1 - L$

$x5 = 0.078$ $x6 = 0.359$ $x7 = 0.563$ $V = 0.91$ $L = 0.09$

$y5 := K5(T,P) \cdot x5$ $y6 := K6(T,P) \cdot x6$ $y7 := K7(T,P) \cdot x7$

$y5 = 0.267$ $y6 = 0.459$ $y7 = 0.274$

$P := 0.77$ $L := 0.10$

GIVEN $K5(T,P) \cdot x5 + K6(T,P) \cdot x6 + K7(T,P) \cdot x7 - (x5 + x6 + x7) = 0$

$x5 \cdot (L \cdot (1 - K5(T,P)) + K5(T,P)) = z5$

$x6 \cdot (L \cdot (1 - K6(T,P)) + K6(T,P)) = z6$

$x7 \cdot (L \cdot (1 - K7(T,P)) + K7(T,P)) = z7$ $soln := FIND(x5, x6, x7, L)$

$x5 := soln_0$ $x6 := soln_1$ $x7 := soln_2$ $L := soln_3$ $V := 1 - L$

$x5 = 0.071$ $x6 = 0.339$ $x7 = 0.59$ $V = 0.995$ $L = 5.309 \cdot 10^{-3}$

$y5 := K5(T,P) \cdot x5$ $y6 := K6(T,P) \cdot x6$ $y7 := K7(T,P) \cdot x7$

$y5 = 0.251$ $y6 = 0.451$ $y7 = 0.298$

$P := 1.25$ $L := 0.95$

GIVEN $K5(T,P) \cdot x5 + K6(T,P) \cdot x6 + K7(T,P) \cdot x7 - (x5 + x6 + x7) = 0$

$x5 \cdot (L \cdot (1 - K5(T,P)) + K5(T,P)) = z5$

$x6 \cdot (L \cdot (1 - K6(T,P)) + K6(T,P)) = z6$

$x7 \cdot (L \cdot (1 - K7(T,P)) + K7(T,P)) = z7$ $soln := FIND(x5, x6, x7, L)$

$x5 := soln_0$ $x6 := soln_1$ $x7 := soln_2$ $L := soln_3$ $V := 1 - L$

$x5 = 0.246$ $x6 = 0.451$ $x7 = 0.303$ $V = 0.013$ $L = 0.987$

$y5 := K5(T,P) \cdot x5$ $y6 := K6(T,P) \cdot x6$ $y7 := K7(T,P) \cdot x7$

$y5 = 0.536$ $y6 = 0.369$ $y7 = 0.094$

$i := 0, 1 .. 9$

$$
PP := \begin{bmatrix} 0.768 \\ .77 \\ .8 \\ .9 \\ 1.0 \\ 1.1 \\ 1.2 \\ 1.25 \\ 1.258 \end{bmatrix}
\quad
xx5 := \begin{bmatrix} 0.071 \\ 0.071 \\ 0.078 \\ 0.107 \\ 0.141 \\ 0.180 \\ 0.223 \\ 0.246 \\ 0.250 \end{bmatrix}
\quad
xx6 := \begin{bmatrix} 0.338 \\ 0.339 \\ 0.359 \\ 0.412 \\ 0.445 \\ 0.458 \\ 0.456 \\ 0.451 \\ 0.450 \end{bmatrix}
\quad
xx7 := \begin{bmatrix} 0.592 \\ 0.590 \\ 0.563 \\ 0.481 \\ 0.414 \\ 0.362 \\ 0.320 \\ 0.303 \\ 0.300 \end{bmatrix}
\quad
LL := \begin{bmatrix} 0 \\ 0.0053 \\ 0.090 \\ 0.337 \\ 0.549 \\ 0.736 \\ 0.906 \\ 0.987 \\ 1.0 \end{bmatrix}
$$

$$
yy5 := \begin{bmatrix} 0.250 \\ 0.251 \\ 0.267 \\ 0.323 \\ 0.383 \\ 0.445 \\ 0.507 \\ 0.536 \\ 0.541 \end{bmatrix}
\quad
yy6 := \begin{bmatrix} 0.450 \\ 0.451 \\ 0.459 \\ 0.469 \\ 0.456 \\ 0.427 \\ 0.389 \\ 0.369 \\ 0.366 \end{bmatrix}
\quad
yy7 := \begin{bmatrix} 0.300 \\ 0.298 \\ 0.274 \\ 0.208 \\ 0.161 \\ 0.128 \\ 0.104 \\ 0.094 \\ 0.093 \end{bmatrix}
$$
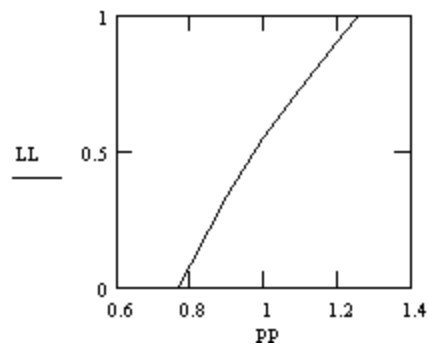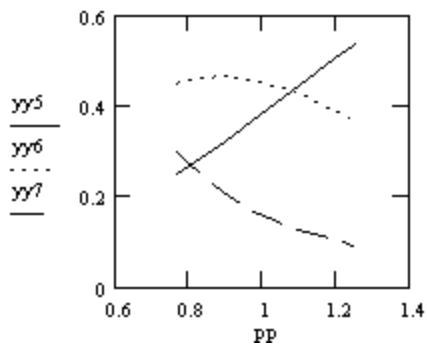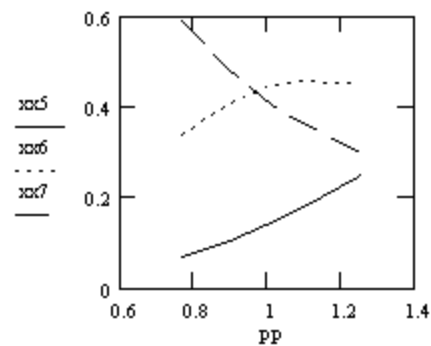
8.1-22   (also available as a Mathcad worksheet)

8.1-22

Solving for the bubble point temperature

$T := 69 \qquad P := 1.013$

$p5(T) := \exp\left[10.422 - \dfrac{26799}{8.314 \cdot (273.15 + T)} \right]$ $\qquad p5(T) = 2.721 \qquad K5(T, P) := \dfrac{p5(T)}{P}$

$p6(T) := \exp\left[10.456 - \dfrac{29676}{8.314 \cdot (273.15 + T)} \right]$ $\qquad p6(T) = 1.024 \qquad K6(T, P) := \dfrac{p6(T)}{P}$

$p7(T) := \exp\left[11.431 - \dfrac{35200}{8.314 \cdot (273.15 + T)} \right]$ $\qquad p7(T) = 0.389 \qquad K7(T, P) := \dfrac{p7(T)}{P}$

$y5 := 0.33$ $y6 := 0.33$ $y7 := 0.33$ $z5 := 0.25$ $z6 := 0.45$ $z7 := 0.3$

GIVEN

$$K5(T,P) \cdot z5 + K6(T,P) \cdot z6 + K7(T,P) \cdot z7 = 1 \quad\quad y5 = K5(T,P) \cdot z5 \quad y6 = K6(T,P) \cdot z6 \quad\quad y7 = K7(T,P) \cdot z7$$

$soln := FIND(y5, y6, y7, T)$

$y5 := soln_0$ $y6 := soln_1$ $y7 := soln_2$ $T := soln_3$

$y5 = 0.548$ $y6 = 0.363$ $y7 = 0.088$ $T = 61.788$

This is the bubble-point temperature solution. Now on to the dew-point temperature problem.

$x5 := 0.33$ $x6 := 0.33$ $x7 := 0.33$ Note that xi=yi/Ki

GIVEN

$$\frac{z5}{K5(T,P)} + \frac{z6}{K6(T,P)} + \frac{z7}{K7(T,P)} = 1 \quad\quad x5 = \frac{z5}{K5(T,P)} \quad\quad x6 = \frac{z6}{K6(T,P)} \quad\quad x7 = \frac{z7}{K7(T,P)}$$

$soln := FIND(x5, x6, x7, T)$

$x5 := soln_0$ $x6 := soln_1$ $x7 := soln_2$ $T := soln_3$

$x5 = 0.074$ $x6 = 0.346$ $x7 = 0.579$ $T = 77.436$

This is the dew-point pressure solution.

So for a mixture of the composition z5=0.25, z6=0.45 and z7=0.30, the mixture will be all liquid at temperatures below 61.79 C, and all vapor at temperatures above 77.44 C. Vapor-liquid equilibrium will exist only between 61.79 and 77.44 C, so this is the temperature range we will examine.

$T := 62$ $L := 0.99$ $P := 1.013$

GIVEN $K5(T,P) \cdot x5 + K6(T,P) \cdot x6 + K7(T,P) \cdot x7 - (x5 + x6 + x7) = 0$

$$x5 \cdot (L \cdot (1 - K5(T,P)) + K5(T,P)) = z5$$

$$x6 \cdot (L \cdot (1 - K6(T,P)) + K6(T,P)) = z6$$

$$x7 \cdot (L \cdot (1 - K7(T,P)) + K7(T,P)) = z7 \quad\quad soln := FIND(x5, x6, x7, L)$$

$x5 := soln_0$ $x6 := soln_1$ $x7 := soln_2$ $L := soln_3$ $V := 1 - L$

$x5 = 0.246$ $x6 = 0.451$ $x7 = 0.303$ $V = 0.012$ $L = 0.988$

$y5 := K5(T,P) \cdot x5$ $y6 := K6(T,P) \cdot x6$ $y7 := K7(T,P) \cdot x7$

$y5 = 0.543$ $y6 = 0.367$ $y7 = 0.09$

$T := 65$ $L := 0.80$

GIVEN $K5(T,P) \cdot x5 + K6(T,P) \cdot x6 + K7(T,P) \cdot x7 - (x5 + x6 + x7) = 0$

$x5 \cdot (L \cdot (1 - K5(T,P)) + K5(T,P)) = z5$

$x6 \cdot (L \cdot (1 - K6(T,P)) + K6(T,P)) = z6$

$x7 \cdot (L \cdot (1 - K7(T,P)) + K7(T,P)) = z7$ soln $:=$ FIND$(x5, x6, x7, L)$

$x5 := \text{soln}_0$ $x6 := \text{soln}_1$ $x7 := \text{soln}_2$ $L := \text{soln}_3$ $V := 1 - L$

$x5 = 0.198$ $x6 = 0.459$ $x7 = 0.343$ $V = 0.187$ $L = 0.813$

$y5 := K5(T,P) \cdot x5$ $y6 := K6(T,P) \cdot x6$ $y7 := K7(T,P) \cdot x7$

$y5 = 0.476$ $y6 = 0.41$ $y7 = 0.114$

$T := 68$ $L := 0.60$

GIVEN $K5(T,P) \cdot x5 + K6(T,P) \cdot x6 + K7(T,P) \cdot x7 - (x5 + x6 + x7) = 0$

$x5 \cdot (L \cdot (1 - K5(T,P)) + K5(T,P)) = z5$

$x6 \cdot (L \cdot (1 - K6(T,P)) + K6(T,P)) = z6$

$x7 \cdot (L \cdot (1 - K7(T,P)) + K7(T,P)) = z7$ soln $:=$ FIND$(x5, x6, x7, L)$

$x5 := \text{soln}_0$ $x6 := \text{soln}_1$ $x7 := \text{soln}_2$ $L := \text{soln}_3$ $V := 1 - L$

$x5 = 0.157$ $x6 = 0.453$ $x7 = 0.389$ $V = 0.365$ $L = 0.635$

$y5 := K5(T,P) \cdot x5$ $y6 := K6(T,P) \cdot x6$ $y7 := K7(T,P) \cdot x7$

$y5 = 0.411$ $y6 = 0.444$ $y7 = 0.144$

$T := 71$ $L := 0.40$

GIVEN $K5(T,P) \cdot x5 + K6(T,P) \cdot x6 + K7(T,P) \cdot x7 - (x5 + x6 + x7) = 0$

$x5 \cdot (L \cdot (1 - K5(T,P)) + K5(T,P)) = z5$

$x6 \cdot (L \cdot (1 - K6(T,P)) + K6(T,P)) = z6$

$x7 \cdot (L \cdot (1 - K7(T,P)) + K7(T,P)) = z7$ soln $:=$ FIND$(x5, x6, x7, L)$

$x5 := \text{soln}_0$ $x6 := \text{soln}_1$ $x7 := \text{soln}_2$ $L := \text{soln}_3$ $V := 1 - L$

$x5 = 0.124$ $x6 = 0.432$ $x7 = 0.443$ $V = 0.551$ $L = 0.449$

$y5 := K5(T,P) \cdot x5$ $y6 := K6(T,P) \cdot x6$ $y7 := K7(T,P) \cdot x7$

$y5 = 0.352$ $y6 = 0.464$ $y7 = 0.183$

$T := 74$ $L := 0.20$

GIVEN $K5(T,P) \cdot x5 + K6(T,P) \cdot x6 + K7(T,P) \cdot x7 - (x5 + x6 + x7) = 0$

$x5 \cdot (L \cdot (1 - K5(T,P)) + K5(T,P)) = z5$

$x6 \cdot (L \cdot (1 - K6(T,P)) + K6(T,P)) = z6$

$x7 \cdot (L \cdot (1 - K7(T,P)) + K7(T,P)) = z7$ soln $:=$ FIND$(x5, x6, x7, L)$

$x5 := \text{soln}_0$ $\qquad$ $x6 := \text{soln}_1$ $\qquad$ $x7 := \text{soln}_2$ $\qquad$ $L := \text{soln}_3$ $\qquad$ $V := 1 - L$

$x5 = 0.098$ $\qquad$ $x6 = 0.398$ $\qquad$ $x7 = 0.504$ $\qquad$ $V = 0.749$ $\qquad$ $L = 0.251$

$y5 := K5(T,P) \cdot x5$ $\qquad$ $y6 := K6(T,P) \cdot x6$ $\quad$ $y7 := K7(T,P) \cdot x7$

$y5 = 0.301$ $\qquad$ $y6 = 0.467$ $\qquad$ $y7 = 0.232$

$T := 76$ $\qquad$ $L := 0.10$

GIVEN $\qquad$ $K5(T,P) \cdot x5 + K6(T,P) \cdot x6 + K7(T,P) \cdot x7 - (x5 + x6 + x7) = 0$

$\qquad$ $x5 \cdot (L \cdot (1 - K5(T,P)) + K5(T,P)) = z5$

$\qquad$ $x6 \cdot (L \cdot (1 - K6(T,P)) + K6(T,P)) = z6$

$\qquad$ $x7 \cdot (L \cdot (1 - K7(T,P)) + K7(T,P)) = z7$ $\qquad$ $\text{soln} := \text{FIND}(x5, x6, x7, L)$

$\qquad$ $x5 := \text{soln}_0$ $\qquad$ $x6 := \text{soln}_1$ $\qquad$ $x7 := \text{soln}_2$ $\qquad$ $L := \text{soln}_3$ $\qquad$ $V := 1 - L$

$x5 = 0.083$ $\qquad$ $x6 = 0.369$ $\qquad$ $x7 = 0.548$ $\qquad$ $V = 0.891$ $\qquad$ $L = 0.109$

$y5 := K5(T,P) \cdot x5$ $\qquad$ $y6 := K6(T,P) \cdot x6$ $\quad$ $y7 := K7(T,P) \cdot x7$

$y5 = 0.27$ $\qquad$ $y6 = 0.46$ $\qquad$ $y7 = 0.27$

$T := 77$ $\qquad$ $L := 0.10$

GIVEN $\qquad$ $K5(T,P) \cdot x5 + K6(T,P) \cdot x6 + K7(T,P) \cdot x7 - (x5 + x6 + x7) = 0$

$\qquad$ $x5 \cdot (L \cdot (1 - K5(T,P)) + K5(T,P)) = z5$

$\qquad$ $x6 \cdot (L \cdot (1 - K6(T,P)) + K6(T,P)) = z6$

$\qquad$ $x7 \cdot (L \cdot (1 - K7(T,P)) + K7(T,P)) = z7$ $\qquad$ $\text{soln} := \text{FIND}(x5, x6, x7, L)$

$\qquad$ $x5 := \text{soln}_0$ $\qquad$ $x6 := \text{soln}_1$ $\qquad$ $x7 := \text{soln}_2$ $\qquad$ $L := \text{soln}_3$ $\qquad$ $V := 1 - L$

$x5 = 0.077$ $\qquad$ $x6 = 0.353$ $\qquad$ $x7 = 0.57$ $\qquad$ $V = 0.966$ $\qquad$ $L = 0.034$

$y5 := K5(T,P) \cdot x5$ $\qquad$ $y6 := K6(T,P) \cdot x6$ $\quad$ $y7 := K7(T,P) \cdot x7$

$y5 = 0.256$ $\qquad$ $y6 = 0.453$ $\qquad$ $y7 = 0.291$

$T := 78$ $\qquad$ $L := 0.05$

GIVEN $\qquad$ $K5(T,P) \cdot x5 + K6(T,P) \cdot x6 + K7(T,P) \cdot x7 - (x5 + x6 + x7) = 0$

$\qquad$ $x5 \cdot (L \cdot (1 - K5(T,P)) + K5(T,P)) = z5$

$\qquad$ $x6 \cdot (L \cdot (1 - K6(T,P)) + K6(T,P)) = z6$

$$x7 \cdot (L \cdot (1 - K7(T, P)) + K7(T, P)) = z7 \qquad soln := FIND(x5, x6, x7, L)$$

$$x5 := soln_0 \qquad x6 := soln_1 \qquad x7 := soln_2 \qquad L := soln_3 \qquad V := 1 - L$$

$$x5 = 0.071 \qquad x6 = 0.337 \qquad x7 = 0.592 \qquad V = 1.045 \qquad L = {}^-0.045$$

$$y5 := K5(T, P) \cdot x5 \qquad y6 := K6(T, P) \cdot x6 \qquad y7 := K7(T, P) \cdot x7$$

$$y5 = 0.242 \qquad y6 = 0.445 \qquad y7 = 0.313$$

$$T := 61 \qquad L := 0.9$$

GIVEN $\qquad K5(T, P) \cdot x5 + K6(T, P) \cdot x6 + K7(T, P) \cdot x7 - (x5 + x6 + x7) = 0$

$$x5 \cdot (L \cdot (1 - K5(T, P)) + K5(T, P)) = z5$$

$$x6 \cdot (L \cdot (1 - K6(T, P)) + K6(T, P)) = z6$$

$$x7 \cdot (L \cdot (1 - K7(T, P)) + K7(T, P)) = z7 \qquad soln := FIND(x5, x6, x7, L)$$

$$x5 := soln_0 \qquad x6 := soln_1 \qquad x7 := soln_2 \qquad L := soln_3 \qquad V := 1 - L$$

$$x5 = 0.264 \qquad x6 = 0.446 \qquad x7 = 0.29 \qquad V = {}^-0.047 \qquad L = 1.047$$

$$y5 := K5(T, P) \cdot x5 \qquad y6 := K6(T, P) \cdot x6 \qquad y7 := K7(T, P) \cdot x7$$

$$y5 = 0.566 \qquad y6 = 0.351 \qquad y7 = 0.083$$

$$i := 0, 1 .. 9$$

$$TT := \begin{bmatrix} 61.788 \\ 62 \\ 65 \\ 68 \\ 71 \\ 74 \\ 76 \\ 77 \\ 77.436 \end{bmatrix} \quad xx5 := \begin{bmatrix} 0.25 \\ 0.246 \\ 0.198 \\ 0.157 \\ 0.124 \\ 0.098 \\ 0.083 \\ 0.077 \\ 0.074 \end{bmatrix} \quad xx6 := \begin{bmatrix} 0.45 \\ 0.451 \\ 0.459 \\ 0.453 \\ 0.432 \\ 0.398 \\ 0.369 \\ 0.353 \\ 0.346 \end{bmatrix} \quad xx7 := \begin{bmatrix} 0.3 \\ 0.303 \\ 0.343 \\ 0.389 \\ 0.443 \\ 0.504 \\ 0.548 \\ 0.570 \\ 0.570 \end{bmatrix} \quad LL := \begin{bmatrix} 1.0 \\ 0.988 \\ 0.813 \\ 0.635 \\ 0.449 \\ 0.251 \\ 0.109 \\ 0.034 \\ 0.0 \end{bmatrix}$$

$$yy5 := \begin{bmatrix} 0.548 \\ 0.543 \\ 0.476 \\ 0.411 \\ 0.352 \\ 0.301 \\ 0.270 \\ 0.256 \\ 0.25 \end{bmatrix} \quad yy6 := \begin{bmatrix} 0.363 \\ 0.367 \\ 0.410 \\ 0.444 \\ 0.464 \\ 0.467 \\ 0.460 \\ 0.453 \\ 0.45 \end{bmatrix} \quad yy7 := \begin{bmatrix} 0.088 \\ 0.090 \\ 0.114 \\ 0.144 \\ 0.183 \\ 0.232 \\ 0.270 \\ 0.291 \\ 0.30 \end{bmatrix}$$
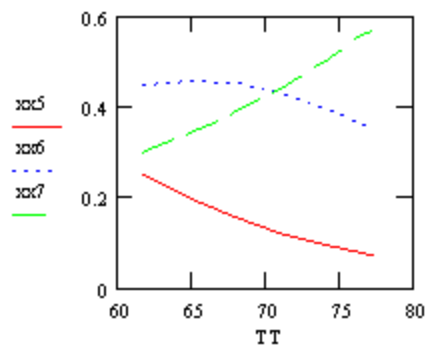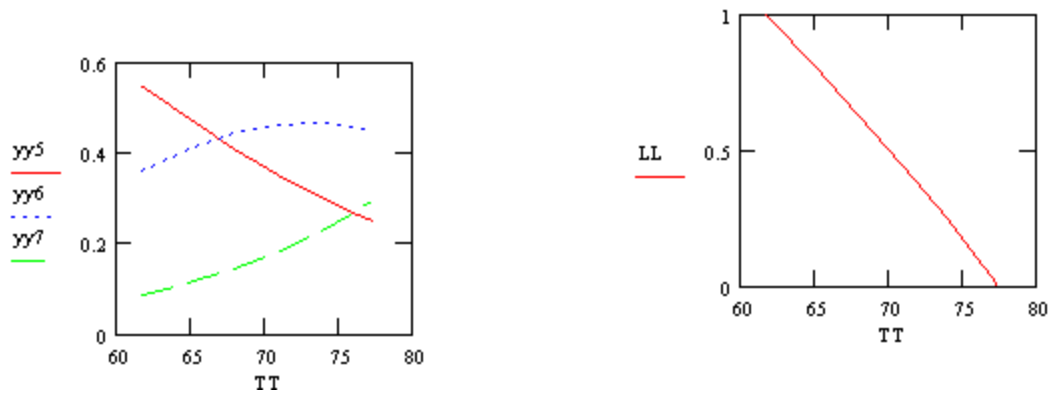
8.1-23   (also available as a Mathcad worksheet)

8.1-23a

$i := 0.. 10$ $x_i := 0.1 \cdot i$

$$P_i := \begin{vmatrix} T \leftarrow 380 \\[2mm] Pvap1 \leftarrow \exp\left(9.3225 - \dfrac{3120.29}{T - 63.63}\right) \\[4mm] Pvap2 \leftarrow \exp\left(9.2508 - \dfrac{3341.62}{T - 57.57}\right) \\[4mm] gam1 \leftarrow \exp\left[\dfrac{\left[630 \cdot \dfrac{T}{323.15} - 335 \cdot \left(1 - \dfrac{T}{323.15}\right)\right] \cdot \left(1 - x_i\right)^2}{8.314 \cdot T}\right] \\[6mm] gam2 \leftarrow \exp\left[\dfrac{\left[630 \cdot \dfrac{T}{323.15} - 335 \cdot \left(1 - \dfrac{T}{323.15}\right)\right] \cdot \left(x_i\right)^2}{8.314 \cdot T}\right] \\[6mm] P_i \leftarrow x_i \cdot gam1 \cdot Pvap1 + \left(1 - x_i\right) \cdot gam2 \cdot Pvap2 \end{vmatrix}$$

$x =$

	0
0	0
1	0.1
2	0.2
3	0.3
4	0.4
5	0.5
6	0.6
7	0.7
8	0.8
9	0.9
10	1

$P =$

	0
0	0.329
1	0.368
2	0.403
3	0.433
4	0.461
5	0.485
6	0.508
7	0.529
8	0.548
9	0.566
10	0.583

P in bar
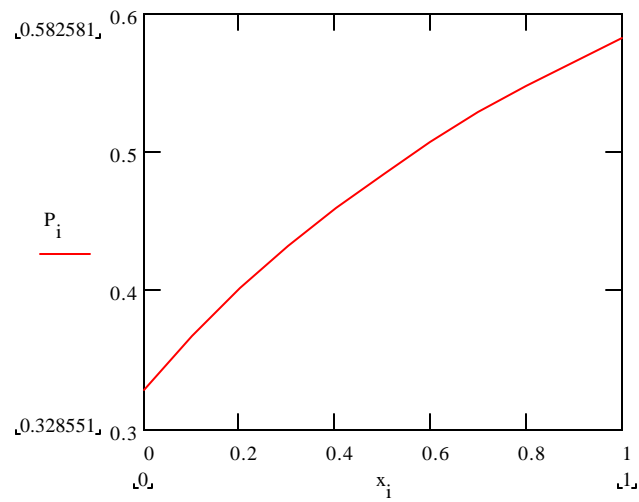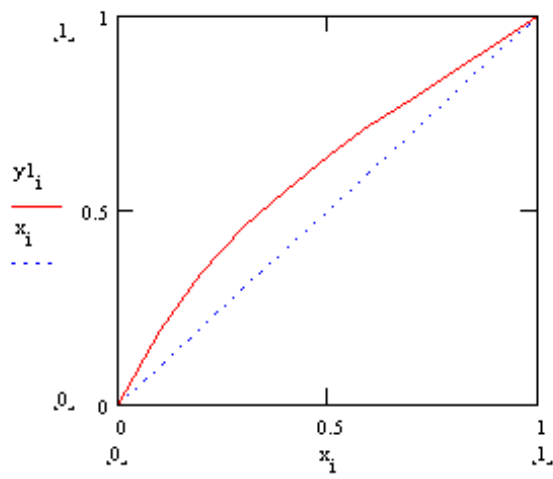
$$T := 380 \qquad Pvap1 := \exp\left(9.3225 - \frac{3120.29}{T - 63.63}\right) \qquad Pvap2 := \exp\left(9.2508 - \frac{3341.62}{T - 57.57}\right)$$

$$gaml_i := \exp\left[\frac{\left[630 \cdot \frac{T}{323.15} - 335 \cdot \left(1 - \frac{T}{323.15}\right)\right] \cdot (1 - x_i)^2}{8.314 \cdot T}\right]$$

$$gam2_i := \exp\left[\frac{\left[630 \cdot \frac{T}{323.15} - 335 \cdot \left(1 - \frac{T}{323.15}\right)\right] \cdot (x_i)^2}{8.314 \cdot T}\right]$$

$$y1_i := \frac{(x_i \cdot gaml_i \cdot Pvap1)}{P_i} \qquad\qquad y2_i := 1 - y1_i$$

8.1-23b generalized at fixed pressure

$$i := 0.. \ 10 \qquad\qquad\qquad x_i := 0.1 \cdot i$$

$$TT_i := \begin{vmatrix} T \leftarrow 373. \\ DT \leftarrow 5 \\ \text{while } \left| DT \right| > 0.00001 \\ \quad \begin{vmatrix} Pvap1 \leftarrow \exp\left(9.3225 - \dfrac{3120.29}{T - 63.63}\right) \\[2ex] Pvap2 \leftarrow \exp\left(9.2508 - \dfrac{3341.62}{T - 57.57}\right) \\[2ex] gam1 \leftarrow \exp\left[\dfrac{\left[630 \cdot \dfrac{T}{323.15} - 335 \cdot \left(1 - \dfrac{T}{323.15}\right)\right] \cdot (1 - x_i)^2}{8.314 \cdot T}\right] \\[3ex] gam2 \leftarrow \exp\left[\dfrac{\left[630 \cdot \dfrac{T}{323.15} - 335 \cdot \left(1 - \dfrac{T}{323.15}\right)\right] \cdot (x_i)^2}{8.314 \cdot T}\right] \\[3ex] P \leftarrow x_i \cdot gam1 \cdot Pvap1 + (1 - x_i) \cdot gam2 \cdot Pvap2 \\[2ex] DT \leftarrow 10 \cdot \ln\left(\dfrac{380}{P \cdot 750}\right) \\[2ex] T \leftarrow T + DT \\ TT_i \leftarrow T \end{vmatrix} \\ TT_i \end{vmatrix}$$

Have to recalculate vapor pressures, activity coefficients and vapor phase mole fractions since these variables are only defined within the subprogram.

$$Pvap1_i := \exp\left(9.3225 - \frac{3120.29}{TT_i - 63.63}\right)$$

$$Pvap2_i := \exp\left(9.2508 - \frac{3341.62}{TT_i - 57.57}\right)$$

$$gam1_i := \exp\left[\frac{\left[630 \cdot \dfrac{TT_i}{323.15} - 335 \cdot \left(1 - \dfrac{TT_i}{323.15}\right)\right] \cdot (1 - x_i)^2}{8.314 \cdot TT_i}\right]$$

$$gam2_i := \exp\left[\frac{\left[630 \cdot \dfrac{TT_i}{323.15} - 335 \cdot \left(1 - \dfrac{TT_i}{323.15}\right)\right] \cdot (x_i)^2}{8.314 \cdot TT_i}\right]$$

$$P_i := x_i \cdot gam1_i \cdot Pvap1_i + (1 - x_i) \cdot gam2_i \cdot Pvap2_i$$

$$y1_i := \frac{x_i \cdot gam1_i \cdot Pvap1_i}{P_i} \qquad\qquad y2_i := \frac{(1 - x_i) \cdot gam2_i \cdot Pvap2_i}{P_i}$$

P =

	0
0	0.507
1	0.507
2	0.507
3	0.507
4	0.507
5	0.507
6	0.507
7	0.507
8	0.507
9	0.507
10	0.507

x =

	0
0	0
1	0.1
2	0.2
3	0.3
4	0.4
5	0.5
6	0.6
7	0.7
8	0.8
9	0.9
10	1

y1 =

	0
0	0
1	0.193
2	0.339
3	0.456
4	0.554
5	0.639
6	0.717
7	0.789
8	0.859
9	0.929
10	1

TT =

	0
0	394.064
1	390.316
2	387.383
3	385.011
4	383.041
5	381.368
6	379.919
7	378.646
8	377.513
9	376.498
10	375.584

gam1 =

	0
0	1.293
1	1.23
2	1.177
3	1.133
4	1.096
5	1.065
6	1.041
7	1.023
8	1.01
9	1.003
10	1

gam2 =

	0
0	1
1	1.003
2	1.01
3	1.023
4	1.041
5	1.065
6	1.095
7	1.132
8	1.175
9	1.227
10	1.286

Pvap1 =

	0
0	0.886
1	0.795
2	0.73
3	0.679
4	0.64
5	0.608
6	0.581
7	0.558
8	0.539
9	0.522
10	0.507

Pvap2 =

	0
0	0.507
1	0.453
2	0.414
3	0.385
4	0.362
5	0.343
6	0.328
7	0.315
8	0.303
9	0.293
10	0.285
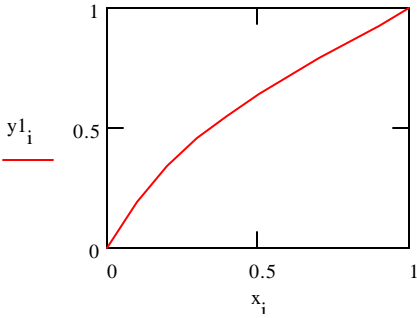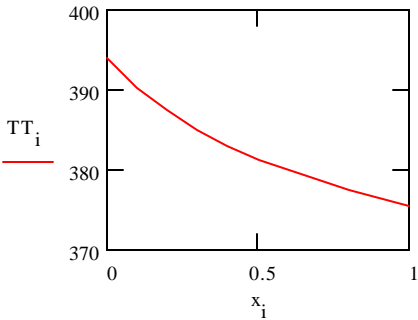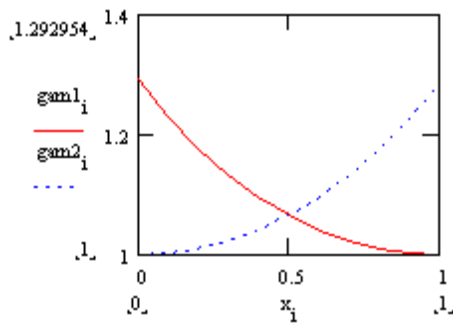
8.1-24   (also available as a Mathcad worksheet)

8.1-24   Benzene activity in benzene - polyisobutylene (40,000) mixtures

$NB := 1$ $NPIB := \dfrac{40000}{104}$ $VB := 88.26$ $VIB := 131.9$ $R := 8.314$ $\chi := 1.0$

$mb := 0.8331$ $mpib := 1$ $WtB := \dfrac{mb}{mb + mpib}$ $WtB = 0.4545$ $WtPIB := 1 - WtB$

$xb := \dfrac{\dfrac{WtB}{78}}{\dfrac{WtB}{78} + \dfrac{WtPIB}{40000}}$ $xpib := 1 - xb$ $PhiB := \dfrac{xb \cdot VB}{xb \cdot VB + xpib \cdot NPIB \cdot VIB}$ $PhiP := 1 - PhiB$

$PhiB = 0.4264$ $xpib = 2.3352 \cdot 10^{-3}$ $PhiP = 0.5736$

$xb = 0.9977$

$m := \dfrac{NPIB \cdot VIB}{NB \cdot VB}$ $m = 574.7878$

$lnGB := \ln\left(\dfrac{PhiB}{xb}\right) + \left(1 - \dfrac{1}{m}\right) \cdot PhiP + \chi \cdot PhiP^2$ $\gamma B := \exp(lnGB)$ $\gamma B = 1.0529$

$lnG2 := \ln\left(\dfrac{PhiP}{xpib}\right) + (1 - m) \cdot PhiB + \chi \cdot PhiB^2$ $\gamma P := \exp(lnG2)$ $\gamma P = 0$

$lnG2 = -238.9603$ $ab := xb \cdot \gamma B$ $ab = 1.0505$

$lnGB = 0.0516$

activity of benzene

    Partial pressure of benzene = $0.0606 \cdot ab = 0.0637$ bar

$mb := 0.5543$ $mpib := 1$ $WtB := \dfrac{mb}{mb + mpib}$ $WtB = 0.3566$ $WtPIB := 1 - WtB$

$xb := \dfrac{\dfrac{WtB}{78}}{\dfrac{WtB}{78} + \dfrac{WtPIB}{40000}}$ $xpib := 1 - xb$ $PhiB := \dfrac{xb \cdot VB}{xb \cdot VB + xpib \cdot NPIB \cdot VIB}$ $PhiP := 1 - PhiB$

$xb = 0.9965$ $PhiB = 0.3309$ $xpib = 3.5056 \cdot 10^{-3}$ $PhiP = 0.6691$

$$\text{lnGB} := \ln\left(\frac{\text{PhiB}}{\text{xb}}\right) + \left(1 - \frac{1}{m}\right)\cdot\text{PhiP} + \chi\cdot\text{PhiP}^2 \qquad \gamma B := \exp(\text{lnGB}) \qquad \gamma B = 1.0133$$

$$\text{lnG2} := \ln\left(\frac{\text{PhiP}}{\text{xpib}}\right) + (1-m)\cdot\text{PhiB} + \chi\cdot\text{PhiB}^2 \qquad \gamma P := \exp(\text{lnG2}) \qquad \gamma P = 0$$

$$\text{lnGB} = 0.0132 \qquad\qquad \text{lnG2} = {}^-184.5044$$

$$ab := xb\cdot\gamma B \qquad ab = 1.0097$$

activity of benzene

Partial pressure of benzene = $0.0606\cdot ab = 0.0612$ bar

$$mb := 0.291 \qquad mpib := 1 \qquad \text{WtB} := \frac{mb}{mb + mpib} \qquad \text{WtB} = 0.2254 \qquad \text{WtPIB} := 1 - \text{WtB}$$

$$xb := \frac{\dfrac{\text{WtB}}{78}}{\dfrac{\text{WtB}}{78} + \dfrac{\text{WtPIB}}{40000}} \qquad xpib := 1 - xb \qquad \text{PhiB} := \frac{xb\cdot\text{VB}}{xb\cdot\text{VB} + xpib\cdot\text{NPIB}\cdot\text{VIB}} \qquad \text{PhiP} := 1 - \text{PhiB}$$

$$xb = 0.9933 \qquad \text{PhiB} = 0.2061 \qquad\qquad xpib = 6.6564\cdot10^{-3} \qquad \text{PhiP} = 0.7939$$

$$\text{lnGB} := \ln\left(\frac{\text{PhiB}}{\text{xb}}\right) + \left(1 - \frac{1}{m}\right)\cdot\text{PhiP} + \chi\cdot\text{PhiP}^2 \qquad \gamma B := \exp(\text{lnGB}) \qquad \gamma B = 0.8608$$

$$\text{lnG2} := \ln\left(\frac{\text{PhiP}}{\text{xpib}}\right) + (1-m)\cdot\text{PhiB} + \chi\cdot\text{PhiB}^2 \qquad \gamma P := \exp(\text{lnG2}) \qquad \gamma P = 0$$

$$\text{lnGB} = {}^-0.1499 \qquad\qquad \text{lnG2} = {}^-113.4422$$

$$ab := xb\cdot\gamma B \qquad ab = 0.8551$$

activity of benzene

Partial pressure of benzene = $0.0606\cdot ab = 0.0518$ bar

Calculation of pure component vapor pressure of benzene
Data from Perry's
Pvap = 40 mm Hg at T = 7.6 C and 60 mm Hg at 15.4 C

$$A := 10 \qquad B := 3000$$

given

$$\ln(40) = A - \frac{B}{273.15 + 7.6} \qquad\qquad \ln(60) = A - \frac{B}{273.15 + 15.4}$$

$$\text{con} := \text{find}(A, B)$$

$$A := \text{con}_0 \qquad\qquad A = 18.6885 \qquad B := \text{con}_1 \qquad B = 4.2111\cdot10^3$$

$$\text{Pvap} := \frac{\exp\left(A - \dfrac{B}{273.15 + 10}\right)}{750} \qquad\qquad \text{Pvap} = 0.0606 \quad \text{bar}$$

8.1-25   (also available as a Mathcad worksheet)

8.1-25   Cyclohexane activity in cyclohexane - polyisobutylene (40,000) mixtures

$$NC := 1 \qquad NPIB := \frac{40000}{104} \qquad VC := \frac{84.16}{.779} \qquad VIB := 131.9 \qquad R := 8.314 \qquad \chi := 0.475$$

$$mc := 1.318 \qquad mpib := 1 \qquad WtC := \frac{mc}{mc + mpib} \qquad WtC = 0.5686 \qquad WtPIB := 1 - WtC$$

$$xc := \frac{\dfrac{WtC}{84.16}}{\dfrac{WtC}{84.16} + \dfrac{WtPIB}{40000}} \qquad xpib := 1 - xc \qquad PhiC := \frac{xc \cdot VC}{xc \cdot VC + xpib \cdot NPIB \cdot VIB} \qquad PhiP := 1 - PhiC$$

$$PhiC = 0.5716 \qquad\qquad xpib = 1.5938 \cdot 10^{-3} \qquad PhiP = 0.4284$$
$$xc = 0.9984$$

$$m := \frac{NPIB \cdot VIB}{NC \cdot VC} \qquad m = 469.5731$$

$$lnGC := \ln\left(\frac{PhiC}{xc}\right) + \left(1 - \frac{1}{m}\right) \cdot PhiP + \chi \cdot PhiP^2 \qquad \gamma C := \exp(lnGC) \qquad \gamma C = 0.9578$$

$$lnG2 := \ln\left(\frac{PhiP}{xpib}\right) + (1 - m) \cdot PhiC + \chi \cdot PhiC^2 \qquad \gamma P := \exp(lnG2) \qquad \gamma P = 0$$

$$lnG2 = -262.067 \qquad\qquad ac := xc \cdot \gamma C \qquad ac = 0.9563$$

$$lnGC = -0.0431$$

activity of cyclohexane

Partial pressure of cyclohexane = $0.1303 \cdot ac = 0.1246$ bar

$$mc := 0.434 \qquad mpib := 1 \qquad WtC := \frac{mc}{mc + mpib} \qquad WtC = 0.3026 \qquad WtPIB := 1 - WtC$$

$$xc := \frac{\dfrac{WtC}{84.16}}{\dfrac{WtC}{84.16} + \dfrac{WtPIB}{40000}} \qquad xpib := 1 - xc \qquad PhiC := \frac{xc \cdot VC}{xc \cdot VC + xpib \cdot NPIB \cdot VIB} \qquad PhiP := 1 - PhiC$$

$$xc = 0.9952 \qquad PhiC = 0.3052 \qquad xpib = 4.8245 \cdot 10^{-3} \qquad PhiP = 0.6948$$

$$lnGC := \ln\left(\frac{PhiC}{xc}\right) + \left(1 - \frac{1}{m}\right) \cdot PhiP + \chi \cdot PhiP^2 \qquad \gamma C := \exp(lnGC) \qquad \gamma C = 0.7716$$

$$lnG2 := \ln\left(\frac{PhiP}{xpib}\right) + (1 - m) \cdot PhiC + \chi \cdot PhiC^2 \qquad \gamma P := \exp(lnG2) \qquad \gamma P = 0$$

$$lnGC = -0.2593 \qquad\qquad lnG2 = -137.998 \qquad ac := xc \cdot \gamma C \qquad ac = 0.7679$$

activity of cyclohexane

Partial pressure of cyclohexane = $0.1303 \cdot ac = 0.1001$ bar

$mc := 0.147$ $mpib := 1$

$WtC := \dfrac{mc}{mc + mpib}$ $WtC = 0.1282$ $WtPIB := 1 - WtC$

$xc := \dfrac{\dfrac{WtC}{84.16}}{\dfrac{PhiC}{84.16} + \dfrac{WtPIB}{40000}}$ $xpib := 1 - xc$ $PhiC := \dfrac{xc \cdot VC}{xc \cdot VC + xpib \cdot NPIB \cdot VIB}$ $PhiP := 1 - PhiC$

$xc = 0.4174$ $PhiC = 0.1556$ $xpib = 0.5826$ $PhiP = 0.8444$

$lnGC := \ln\left(\dfrac{PhiC}{xc}\right) + \left(1 - \dfrac{1}{m}\right) \cdot PhiP + \chi \cdot PhiP^2$ $\gamma C := \exp(lnGC)$ $\gamma C = 1.2146$

$lnG2 := \ln\left(\dfrac{PhiP}{xpib}\right) + (1 - m) \cdot PhiC + \chi \cdot PhiC^2$ $\gamma P := \exp(lnG2)$ $\gamma P = 0$

$lnGC = 0.1944$ $lnG2 = {}^-72.5182$ $ac := xc \cdot \gamma C$ $ac = 0.507$

activity of benzene

Partial pressure of cyclohexane = $0.1303 \cdot ac = 0.0661$ bar

So while not perfect, the value of the Flory parameter chosen, 0.475, gives a reasonably good description of the cyclohexane-polyisobutylene system.

Calculation of pure component vapor pressure of cyclohexane
Data from Perry's
Pvap = 60 mm Hg at T = 14.7 C and 100 mm Hg at 25.5 C

$A := 10$ $B := 3000$

given $\ln(60) \equiv A - \dfrac{B}{273.15 + 14.7}$ $\ln(100) \equiv A - \dfrac{B}{273.15 + 25.5}$

$con := find(A, B)$

$A := con_0$ $A = 18.2201$ $B := con_1$ $B = 4.0661 \cdot 10^3$

$Pvap := \dfrac{\exp\left(A - \dfrac{B}{273.15 + 25}\right)}{750}$ $Pvap = 0.1303$ bar

8.1-26   (also available as a Mathcad worksheet)

8.1-26   Pentane activity in pentane - polyisobutylene (40,000) mixtures

$NP := 1$ $NPIB := \dfrac{40000}{104}$ $VP := \dfrac{72.15}{.630}$ $VIB := 131.9$ $R := 8.314$ $\chi := 0.85$

$mp := 1.405$ $mpib := 1$ $WtP := \dfrac{mp}{mp + mpib}$ $WtP = 0.5842$ $WtPIB := 1 - WtP$

$xp := \dfrac{\dfrac{WtP}{84.16}}{\dfrac{WtP}{84.16} + \dfrac{WtPIB}{40000}}$ $xpib := 1 - xp$ $PhiP := \dfrac{xp \cdot VP}{xp \cdot VP + xpib \cdot NPIB \cdot VIB}$ $PhiPib := 1 - PhiP$

$PhiP = 0.6012$ $xpib = 1.4953 \cdot 10^{-3}$ $PhiPib = 0.3988$ $xp = 0.9985$

$m := \dfrac{NPIB \cdot VIB}{NP \cdot VP}$ $m = 442.9714$

$lnGP := \ln\left(\dfrac{PhiP}{xp}\right) + \left(1 - \dfrac{1}{m}\right) \cdot PhiPib + \chi \cdot PhiPib^2$ $\gamma P := \exp(lnGP)$ $\gamma P = 1.0261$

$lnG2 := \ln\left(\dfrac{PhiPib}{xpib}\right) + (1 - m) \cdot PhiP + \chi \cdot PhiP^2$ $\gamma Pib := \exp(lnG2)$ $\gamma Pib = 0$

$lnGP = 0.0258$ $lnG2 = {}^{-}259.8176$ $aP := xp \cdot \gamma P$ $aP = 1.0246$

activity of n-pentane

Partial pressure of n-pentane = $0.3778 \cdot aP = 0.3871$ bar

$mp := 0.269$ $mpib := 1$ $WtP := \dfrac{mp}{mp + mpib}$ $WtP = 0.212$ $WtPIB := 1 - WtP$

$xp := \dfrac{\dfrac{WtP}{84.16}}{\dfrac{WtP}{84.16} + \dfrac{WtPIB}{40000}}$ $xpib := 1 - xp$ $PhiP := \dfrac{xp \cdot VP}{xp \cdot VP + xpib \cdot NPIB \cdot VIB}$ $PhiPib := 1 - PhiP$

$xp = 0.9922$ $PhiP = 0.224$ $xpib = 7.7609 \cdot 10^{-3}$ $PhiP = 0.224$

$lnGP := \ln\left(\dfrac{PhiP}{xp}\right) + \left(1 - \dfrac{1}{m}\right) \cdot PhiPib + \chi \cdot PhiPib^2$ $\gamma P := \exp(lnGP)$ $\gamma P = 0.8169$

$lnG2 := \ln\left(\dfrac{PhiPib}{xpib}\right) + (1 - m) \cdot PhiP + \chi \cdot PhiP^2$ $\gamma Pib := \exp(lnG2)$ $\gamma Pib = 0$

$lnGP = {}^{-}0.2023$ $lnG2 = {}^{-}94.3441$ $ap := xp \cdot \gamma P$ $ap = 0.8105$

activity of n-pentane

Partial pressure of n-pentane = $0.3778 \cdot ap = 0.3062$ bar

$mp := 0.0294$ $mpib := 1$ $WtP := \dfrac{mp}{mp + mpib}$ $WtP = 0.0286$ $WtPIB := 1 - WtP$

$xp := \dfrac{\dfrac{WtP}{84.16}}{\dfrac{PhiP}{84.16} + \dfrac{WtPIB}{40000}}$ $xpib := 1 - xp$ $PhiP := \dfrac{xp \cdot VP}{xp \cdot VP + xpib \cdot NPIB \cdot VIB}$ $PhiPib := 1 - PhiP$

$xp = 0.1264$ $PhiP = 0.0355$ $xpib = 0.8736$ $PhiPib = 0.9645$

$lnGP := \ln\!\left(\dfrac{PhiP}{xp}\right) + \left(1 - \dfrac{1}{m}\right)\cdot PhiPib + \chi \cdot PhiPib^2$ $\gamma P := \exp(lnGP)$ $\gamma P = 1.6197$

$lnG2 := \ln\!\left(\dfrac{PhiPib}{xpib}\right) + (1 - m)\cdot PhiP + \chi \cdot PhiP^2$ $\gamma Pib := \exp(lnG2)$ $\gamma Pib = 1.7316 \cdot 10^{-7}$

$lnGP = 0.4822$ $lnG2 = {}^{-}15.5691$ $ap := xp \cdot \gamma P$ $ap = 0.2047$

activity of n-pentane

Partial pressure of pentane = $0.3778 \cdot ap = 0.0773$ bar

So while not perfect, the value of the Flory parameter chosen, 0.85, gives a reasonably good description of the pentane-polyisobutylene system.

Calculation of pure component vapor pressure of pentane
Data from Perry's
Pvap = 200 mm Hg at T = 1.9 C and 400 mm Hg at 18.5 C

$A := 10$ $B := 3000$

given $\ln(200) = A - \dfrac{B}{273.15 + 1.9}$ $\ln(400) = A - \dfrac{B}{273.15 + 18.5}$

$con := find(A, B)$

$A := con_0$ $A = 17.4764$ $B := con_1$ $B = 3.3496 \cdot 10^3$

$Pvap := \dfrac{\exp\!\left(A - \dfrac{B}{273.15 + 10}\right)}{750}$ $Pvap = 0.3778$ bar

8.2-1 Using the critical properties in the text, the program VLMU and the following interaction parameters

$$k_{C_2-C_3} = 0.001 \; ; \; k_{C_2-C_4} = 0.010 \; ; \; k_{C_3-C_4} = 0.003$$

I obtain the following

Bubble point, P (bar)	T(K)	y_{C_2}	y_{C_3}	y_{C_4}
1	231.31	0.3444	0.5907	0.0649
5	280.26	0.2222	0.6576	0.1202
10	308.17	0.1738	0.6693	0.1569
15	327.12	0.1460	0.6691	0.1849
20	341.99	0.1261	0.6642	0.2097
25	354.47	0.1102	0.6565	0.2333
30	365.83	0.0932	0.6434	0.2634
35	375.27	0.0835	0.6329	0.2836
40	384.56	0.0699	0.6133	0.3168
42	388.31	0.0632	0.6011	0.3357
43	390.31	0.0588	0.5919	0.3493

8.2-2 Using the same program and information as above, I obtain the following

Dew point, P (bar)	T(K)	x_{C_2}	x_{C_3}	x_{C_4}
1	253.93	0.0038	0.2309	0.7653
5	299.65	0.0081	0.3128	0.6791
10	325.27	0.0117	0.3595	0.6289
15	342.32	0.0148	0.3924	0.5928
20	355.43	0.0180	0.4198	0.5623
25	366.15	0.0213	0.4446	0.5341
30	375.15	0.0257	0.4724	0.5019
32	378.44	0.0271	0.4806	0.4923
35	383.00	0.0296	0.4936	0.4768
38	387.09	0.0331	0.5103	0.4566
40	389.57	0.0361	0.5231	0.4408
42	391.76	0.0402	0.5389	0.4209
43	392.64	0.0434	0.5499	0.4068

See figure on following page.

8.2-3 Again we use the program VLMU and the data from Problem 8.2-1. Also, since, at 20 bar, the bubble point of the mixture is 341.99 K and the dew point is 355.43 K, we only need to consider temperatures between these two extremes. The results follow:

$P = 20$ bar

T(K)	x_1	x_2	x_3	y_1	y_2	y_3	V/L split
342.5	0.0478	0.5670	0.3852	0.0120	0.6648	0.2143	0.0303/0.9697
344.0	0.0418	0.5564	0.4019	0.1069	0.6641	0.2290	0.1265/0.8735
346.0	0.0352	0.5382	0.4263	0.0914	0.6580	0.2506	0.2635/0.7365
348.0	0.0299	0.5170	0.4531	0.0789	0.6464	0.2746	0.4095/0.5905
350.0	0.0258	0.4928	0.4814	0.0690	0.6304	0.3007	0.5612/0.4388
352.0	0.0224	0.4668	0.5107	0.0609	0.6106	0.3285	0.7175/0.2825
354.0	0.0197	0.4397	0.5407	0.0542	0.5878	0.3580	0.8796/0.1204
355.0	0.0185	0.4259	0.5557	0.0512	0.5756	0.3732	0.9628/0.0372

Note to instructor:
Re: Problems 8.2-1, 2 and 3
        You should take time to discuss how the compositions are changing with pressure in each of the cases above. For example, in Problem 8.2-1, at low bubble point pressures the vapor composition is very different than the liquid, with the vapor greatly enriched in the light (C_2) component. However, as the pressure increases, and the critical point is approached, the vapor composition becomes similar to that of the liquid. Analogous comments apply to the dew point case of Problem 8.2-2.

Vapor Liquid Equlibrium
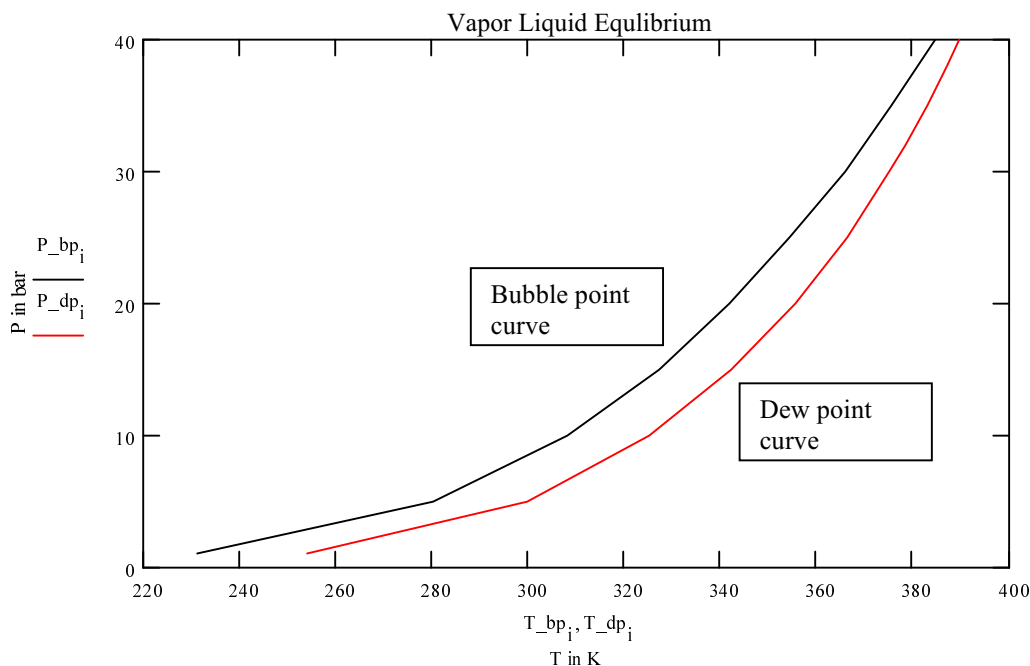
8.2-4   See solution to Problem 4.2. The derivation of Eqs. 8.2-8 is identical to the derivation of eqns. 4.4-29 & 30.

8.2-5 (a and b)   These algorithms are incorporated into the program VLMU Examine that program to see the algorithms used.

8.2-6 (a)   The equations to be used to solve this problem are the mass balances, the equilibrium condition (equality of fugacities) and the energy balance. Writing these equations for an open, steady-flow system, we have (for 1 mole of feed of compositions z_i).

$$\text{Mass balances} \quad z_i = x_i L + y_i V \quad i = 1, 2, \ldots, N \qquad (1)$$

$$1 = L + V \quad \text{(summing equations above over all species)} \qquad (2)$$

phase equilibrium condition $\bar{f}_i^{\,L} = \bar{f}_i^{\,V}$

$$\Rightarrow x_i P \frac{\bar{f}_i^{\,L}}{x_i \cdot P} = y_i P \frac{\bar{f}_i^{\,V}}{y_i \cdot P} \quad i = 1, 2, \ldots, N$$

or

$$x_i \bar{\phi}_i^{\,L}(T, P, \underline{x}) = y_i \bar{\phi}_i^{\,V}(T, P, \underline{y})$$

or

$$K_i = \frac{y_i}{x_i} = \frac{\bar{\phi}_i^{\,L}}{\bar{\phi}_i^{\,V}} = K_i(T, P, \underline{x}) \quad i = 1, 2, \ldots, N \qquad (3)$$

energy balance

$$0 = \sum \left(\dot{N}_i \bar{H}_i \right)_{in} + \sum \left(\dot{N}_i \bar{H}_i \right)_{out}^{V} + \sum \left(\dot{N}_i \bar{H}_i \right)_{out}^{L}$$

or

$$0 = \sum \left(z_i \bar{H}_i \right)_{in} - V \sum \left(x_i \bar{H}_i \right)^{V} - L \sum \left(y_i \bar{H}_i \right)^{L} \qquad (4)$$

Also, we have the summation conditions

$$\sum x_i = 1 \quad \textbf{and} \quad \sum y_i = 1 \qquad (5)$$

(b) With the exception of eq. (4), the other equations are the ones used in the isothermal flash calculation (see eqs. 8.1-14 & 15, and 8.2-4). Therefore the easiest algorithm to implement is to use the one for the isothermal flash with an extra, outer loop which iterates on final temperature. This is done by adding an enthalpy calculation (see eq. 8.2-8a) to the program, and calculating the enthalpy of the feed stream, and the liquid and vapor streams. If eq. (4) is not satisfied, the exit temperature is adjusted, and the calculation repeated.

(c) A Mathcad worksheet (8-02-6.MCD) is available for this calculation. This worksheet is also available as the Adobe PDF file 8-02-6.pdf.

8.2-7 This problem is probably most easily solved using an equation of state, such as the Peng-Robinson equation. Using the program VLMU, the critical properties in Table 4.6-1 and $k_{12} = 0.01$ (from Table 7.4-1) we obtain the following

mole % ethane in liquid	Calculated vapor mol %	P(bar)	Measurement vapor mol %	P(bar)
7.8	6.62	39.68	6.2	39.73
22.8	19.35	37.08	19.7	37.07
30.3	25.81	35.79	25.5	35.60
59.0	52.13	30.94	53.1	32.13
89.0	85.28	25.89	85.4	25.45

Thus we see, using the program VLMU, we obtain very accurate predictions in a simple manner (though, of course, much work went into preparing the program). With the exception of the 59 mol % ethane liquid, the compositions are predicted to about 0.004 mole fraction and 0.4 bar accuracy.

8.2-8 Again the program VLMU will be used with the critical properties in Table 4.6-1 and the value $k_{12} = 0.055$ given in Table 7.4-1. The only question is how to use the program to get K values. I have used the isothermal flash, since that is the only option that allows me to specify T and P. One then has to choose a feed composition that assures that one is in the two-phase region (this can be checked by a collection of bubble point or similar calculations, if desired). This corresponds to methane compositions in the range

$$0.0711 \le x_{C_1} \le 0.9916$$

In this range we find the following

	x	y	K
methane	0.0711	0.9916	13.95
benzene	0.9289	0.0084	0.009083

$$\uparrow$$

asked for in problem statement

8.2-9 We use the program VLMU, critical properties in Table 4.6-1, and a value of $k_{12} = 0.003$ given in Table 7.4-1. The problem must be solved by trial-and-error. The easiest way is to start with the bubble-point P program. This leads to the result that the bubble-point pressure is 8.47 bar. Therefore, a lower pressure than 8.47 bar must be used to produce appreciable vapor. Likewise, using the dew point pressure program gives a dew point pressure of 6.12 bar. Therefore, the pressure must be between 6.12 bar and 8.47 bar to produce appreciable vapor. By trial-and-error we find at $T = 313.15\,\text{K}$, $P = 7.234$ bar $V/L = 0.5/0.5 = 1$ and

	Feed	Liq	Vapor	K
C_3	0.5	0.3699	0.6301	1.703
nC_4	0.5	0.6301	0.3699	0.5871
Phase compressibility, Z		0.0268	0.8594	

8.2-10 Using the program VLMU, critical properties in Table 7.4-1 and the following interaction parameters $k_{C_2-C_3} = 0.001$; $k_{C_2-nC_4} = 0.010$; $k_{C_2-iC_4} = -0.007$; $k_{C_3-nC_4} = 0.003$; $k_{C_3-iC_4} = -0.007$ and $k_{nC_4-iC_4} = 0.0$ we obtain the following

Component	Feed	Liquid	Vapor	K
ethane	0.3100	0.1638	0.4384	2.677
propane	0.3400	0.3372	0.3425	1.016
n - butane	0.2100	0.3084	0.1236	0.4008
i - butane	0.1400	0.1907	0.0955	0.5008
moles	1.0	0.4676	0.5324	
compressibility		0.0548	0.7952	

Therefore, 53.24 mol % of tank contents will be vapor and the remaining 46.76 mol % will be liquid. [If we believe the compressibilities, even though the liquid compressibility has some error, then we have that 5.71% of the volume of the tank is filled with liquid, and the remaining 94.29% is filled with vapor.]

8.2-11 The analysis is similar to that of Problem 8.2-6 except that the energy balance

$$0 = \sum \left(z_i \overline{H}_i\right)_{in} - L \sum \left(x_i \overline{H}_i^{L}\right) - V \sum \left(y_i \overline{H}_i^{V}\right)$$

used there is now replaced with the entropy balance

$$0 = \sum \left(z_i \overline{S}_i\right)_{in} - L \sum \left(x_i \overline{S}_i^{L}\right) - V \sum \left(y_i \overline{S}_i^{V}\right)$$

A Mathcad worksheet (8-02-11.MCD) is available for this calculation. This worksheet can be viewed as the Adobe PDF file 8-02-11.pdf.

8.3-1 (a) $\hat{H}^V$ data are obtained from the Superheated Steam Tables. Also

$\hat{H}^L(T,\ P = 0.1\ \text{MPa}) \approx \hat{H}^L(T,\ \text{any pressure})$ since, at low and moderate pressures, the liquid

enthalpy is independent of pressure to an excellent approximation. Therefore, $\hat{H}^L(T, P)$ is

taken along the saturation line, and then extrapolated to high temperature, as shown below.
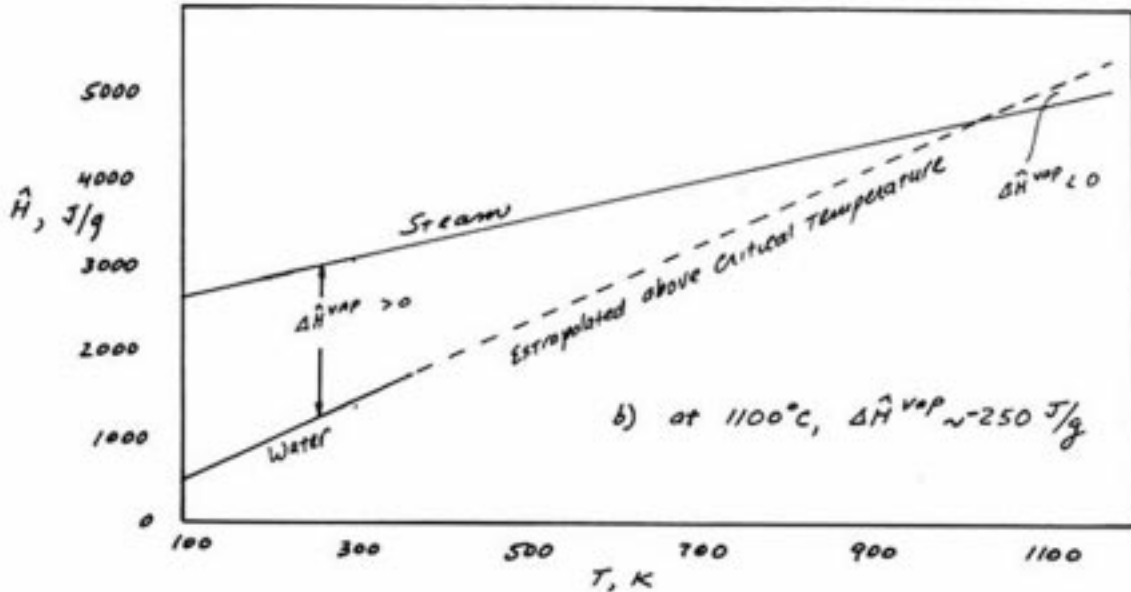
8.3-2 General: The starting point for solving this problem is

$$\bar{f}^L_{N_2} = \bar{f}^V_{N_2} \Rightarrow x_{N_2} \gamma_{N_2} f^L_{N_2} = y_{N_2} P = P_{N_2}$$

where P_{N_2} is the partial pressure of nitrogen in the gas phase. Also, $f^L_{N_2}$ = fugacity of pure

"liquid" nitrogen, is 1000 bar according to the problem statement.

(a) Ideal solution

$$\gamma_{N_2} = 1;\ \textbf{also}\ P_{N_2} = 1\ \textbf{bar (problem statement)}$$

thus

$$x_{N_2} = \frac{P_{N_2}}{f^L_{N_2}} = \frac{1}{1000} = 0.001$$

(b) Non-ideal solution

Here $\ln\gamma_{N_2} = 0.526(1 - x_{N_2})^2$. Since, from the ideal solution case above, x_{N_2} is quite small

(and will be even smaller here), it is reasonable to assume that $1 - x_{N_2} \approx 1$, $\ln\gamma_{N_2} = 0.526$, and

$\gamma_{N_2} = 1.6922$. Thus

$$x_{N_2} = \frac{P_{N_2}}{\gamma_{N_2} f^L_{N_2}} = \frac{1}{1.6922 \times 1000} = 0.591 \times 10^{-3}$$

The Henry's Law Constant is the constant in the expression

$$H_i x_i = \bar{f}^V_i,\ \text{here},\ H_{N_2} x_{N_2} = 1\ \text{bar}$$

thus $H_{N_2} = \dfrac{1 \text{ bar}}{x_{N_2}} = 1692$ bar.

Also, since $H_{N_2} \equiv \gamma_{N_2} f_{N_2}^L$ and $\underline{V}^{ex} = 0$, we have that the activity coefficient γ_{N_2} is independent of pressure. Thus, the only pressure variation of the Henry's law constant will be through the Poynting pressure correction to the "liquid" phase of pure nitrogen.

8.3-3 (a) To compute the ideal solubility, we will use Shair's correlation, Fig. 8.3-1 first we need to compute the reduced temperature

$$T_r = \frac{298.15}{190.6} = 1.564$$

thus,

$$\left. \frac{f^L}{P_C} \right|_{\text{Fig. 8.3-1}} \cong 3.65 \text{ and } f^L = 3.65 \times 46.0 \text{ bar} = 167.9 \text{ bar}$$

Therefore at 1 atm partial pressure of methane

$$x_{CH_4}^{\text{ideal}} = \frac{P_{CH_4}}{f_{CH_4}^L} = \frac{1.013 \text{ bar}}{167.9 \text{ bar}} = 6.03 \times 10^{-3} \text{ (all solvents)}$$

(b) To compute the activity coefficients, we use $x_{CH_4} \gamma_{CH_4} f_{CH_4}^L = 1.013$ bar or

$\gamma_{CH_4} = 1.013 / x_{CH_4} f_{CH_4}^L = 6.03 \times 10^{-3} / x_{CH_4}$ The following results are obtained

$$\begin{array}{llll}
CH_4 \text{ - benzene:} & \gamma_{CH_4} = 2.91 & CH_4 \text{ - } CCl_4 \text{:} & \gamma_{CH_4} = 2.11 \\
CH_4 \text{ - } C_6H_{12} \text{:} & \gamma_{CH_4} = 2.13 & CH_4 \text{ - } C_6H_{14} \text{:} & \gamma_{CH_4} = 1.91 \quad \text{McDaniel} \\
& & & 1.42 \quad\quad \text{Guerry}
\end{array}$$

(c) The regular solution model gives, for the $CH_4 \text{ - } C_6H_{14}$ mixture

$$\gamma_{CH_4} = \exp\left\{ \frac{\underline{V}_{CH_4}^L \left(\delta_{CH_4} - \delta_{C_6H_{14}} \right)^2}{RT} \phi_{C_6H_{14}}^2 \right\} = \exp\left\{ \frac{52 \times (5.68 - 7.3)^2}{1.987 \times 298.2} \right\} = 1.26 \,,$$

Since $\phi_{C_6H_{14}} \approx 1$. Note: CH_4 parameters from Table 8.3-1 C_6H_{14} parameters from Table 7.6-1.

This result is not in agreement with either set of data, but is distinctly closer to Guerry's result!

8.3-4 (a) Start from $\bar{f}_i^L = \bar{f}_i^G \Rightarrow x_i \gamma_i f_i^L = y_i P \left(\dfrac{f}{P} \right)_i$

Determination of nitrogen properties:

$$\left. T_r \right|_{N_2} = \frac{373.15 \text{ K}}{126.2 \text{ K}} = 2.96 \,;\ \left. P_r \right|_{N_2} = \frac{75 \text{ bar}}{33.94 \text{ bar}} = 2.21$$

From   Fig.   5.4-1 $\left(\dfrac{f}{P}\right)_{N_2} \cong 1$.   Now   using   Shair's   correlation   (Fig.   8.3-1)

$$\frac{f_{N_2}^{L}(P = 1.013\ \text{bar})}{P_C} = 6.1\ ;\ \text{however, at 75 bar we have}$$

$$\frac{f_{N_2}^{L}(P = 75\ \text{bar})}{P_C} = \frac{f_{N_2}^{L}(P = 1.013)}{P_C}\exp\left\{\frac{\underline{V}_{N_2}^{L}(P - 1.013)}{RT}\right\}$$

$$= 6.1\exp(0.0784) = 6.6 \Rightarrow f_{N_2}^{L}(P = 75\ \text{bar}) = 224\ \text{bar}$$

Determination of benzene properties:

$$T_r\big|_{C_6H_6} = \frac{373.15\ \text{K}}{562.1\ \text{K}} = 0.664\ \text{and}\ \ P_r\big|_{C_6H_6} = \frac{75\ \text{bar}}{48.96\ \text{bar}} = 1.532$$

From Fig. 7.8-1 $\dfrac{f}{P}\bigg|_{\text{vapor}} \cong 0.23$ and, for the liquid, we need the vapor pressure. From the

Chemical Engineers Handbook we have $P^{\text{vap}} = 1.013$ bar at $T = 80.1°C$, and $P^{\text{vap}} = 2.026$ bar

at $T = 103.8°C$ using $\ln P^{\text{vap}} = \dfrac{A}{T} + B$ as the interpolating formula, we find $P^{\text{vap}} = 1.823$ bar.

From Fig. 5.4-1, we have (with a little extrapolation) that $\left(\dfrac{f}{P}\right)_{sat} \approx 0.96$. [Along the saturation

line]. Thus

$$f_{C_6H_6}^{L} = P_{C_6H_6}^{\text{vap}}\left(\frac{f}{P}\right)_{sat}\exp\left\{\frac{\underline{V}_{C_6H_6}^{L}(P - P^{\text{vap}})}{RT}\right\} = 1.823 \times 0.96 \times \exp\left\{\frac{89 \times 73.173}{83.14 \times 373.15}\right\} = 2.159\ \text{bar}$$

Thus, the equations to be solved are

$$x_{N_2}\gamma_{N_2}\,224\ \text{bar} = y_{N_2}\,75\ \text{bar}$$
$$x_{C_6H_6}\gamma_{C_6H_6}\,2.159\ \text{bar} = y_{C_6H_6}\,75\ \text{bar}$$
$$x_{N_2} + x_{C_6H_6} = 1$$
$$y_{N_2} + y_{C_6H_6} = 1$$

together with

$$\gamma_{N_2} = \exp\left\{\frac{\underline{V}_{N_2}^{L}\left(\delta_{N_2} - \delta_{C_6H_6}\right)^2 \phi_{C_6H_6}^2}{RT}\right\}$$

and

$$\gamma_{C_6H_6} = \exp\left\{\frac{\underline{V}_{C_6H_6}^{L}\left(\delta_{N_2} - \delta_{C_6H_6}\right)^2 \phi_{N_2}^2}{RT}\right\}$$

where the N_2 parameters are gotten from Table 8.3-1 and the benzene parameters from Table 7.6-1. Because of the nonlinear nature of the equations (due to the composition dependence of the activity coefficient), this problem is best solved by trial and error. I chose $x_{N_2} = 0.0$ as the initial guess.

Solution obtained was:

$$x_{N_2} = 0.047 \quad \text{and} \quad y_{N_2} = 0.883$$

Measured values:

$$x_{N_2} = 0.045 \quad \text{and} \quad y_{N_2} = 0.944$$

(b) At 100 bar the calculation is similar, however the numbers are a little different. I find

$$\left.\frac{f}{P}\right|^{V}_{C_6H_6} \approx 0.175 \; ; \; \frac{f^{L}_{N_2}}{P_C} \approx 6.76 \text{ and } f^{L}_{C_6H_6} \approx 2.290$$

Solution obtained was:

$$x_{N_2} = 0.061 \quad \text{and} \quad y_{N_2} = 0.874$$

Measurement yields

$$x_{N_2} = 0.0595 \quad y_{N_2} = 0.968$$

In both cases the liquid compositions are in better agreement with experiment than the vapor compositions!
Note: I have found that some students try to make a large extrapolation of the vapor pressure, rather than using Shair's correlation ... it is a large extrapolation here, since the nitrogen critical temperature is 126.2 K. If we extrapolate the low temperature vapor pressure, and make the (small) fugacity coefficient correction, we obtain $f^{L}_{N_2} = 1195 \text{ bar}$ compared to 224 bar here at 75 bar. This leads to $x_{N_2} = 0.0082$, compared to 0.047 calculated here and 0.045 observed experimentally.
Moral: Use Shair's correlation instead of making large extrapolations of the vapor pressure.

8.3-5 (a) Suppose a small amount of liquid, ΔN is, vaporized, then there are $y\Delta N =$ moles of dissolved gas in the vapor, and $(x - \Delta x)(N - \Delta N) =$ moles of dissolved gas left in the liquid we are interested in a different distillation, i.e., the case where Δx and ΔN will be very small. Thus

$$(x - \Delta x)(N - \Delta N) = xN - x\Delta N - N\Delta x + (\Delta x)(\Delta N)$$
$$\approx xN - x\Delta N - N\Delta x$$

Now writing a mass (mole) balance on the dissolved gas yields

$$xN = y\Delta N + (x - \Delta x)(N - \Delta N) \approx y\Delta N + xN - x\Delta N - N\Delta x$$

Thus

$$\frac{\Delta x}{\Delta N} = \frac{y - x}{N} \text{ and taking the limit as } \Delta N \to 0 \text{ yields } \frac{dx}{dN} = \frac{y - x}{N}$$

(b) Using $y = \dfrac{Hx}{P}$ yields $\dfrac{dx}{dN} = \dfrac{\frac{Hx}{P} - x}{N} = \dfrac{x}{N}\left(\dfrac{H - P}{P}\right)$ or $\dfrac{d \ln x}{d \ln N} = \dfrac{H - P}{P}$. Now integrating between (x_0, N_0) and (x, N) yields

$$\int_{x_0}^{x} d \ln x = \frac{H - P}{P} \int_{N_0}^{N} d \ln N \text{ or } \ln x - \ln x_0 = \frac{H - P}{P}\left[\ln N - \ln N_0\right]$$

which can be rewritten as

$$\frac{x}{x_0} = \left(\frac{N}{N_0}\right)^{(H-P)/P} \quad \text{or} \quad \frac{N}{N_0} = \left(\frac{x}{x_0}\right)^{P/(H-P)}$$

(c) For $\dfrac{x}{x_0} = 0.01$ we have $\dfrac{N}{N_0} = (0.01)^{1/266} = 0.983$. Thus, only 1.7% of initial number of moles of liquid need be vaporized in a differential distillation (i.e., no violent boiling, otherwise equilibrium will not be obtained) to remove 99% of the CO_2.

For $\dfrac{x}{x_0} = 0.0001 \qquad \dfrac{N}{N_0} = (0.0001)^{1/266} = 0.966$

Thus only 3.4% of initial number of moles of liquid need be vaporized to remove 99.99% of the CO_2.

8.3-6 I used the bubble point option of program VLMU treating the liquid mole fraction of CO_2 as an adjustable parameter, until a CO_2 partial pressure of 1.013 bar in the vapor phase was obtained. The results appear below:

x_{CO_2}	P_{tot}	y_{CO_2}	$P_{CO_2} = y_{CO_2} \cdot P_{tot}$
0.006	0.31	0.8680	0.269 bar
0.020	0.96	0.9562	0.918
0.022	1.05	0.960	1.008
0.0221	1.05	0.9601	1.0081
0.0222	1.06	0.9603	1.018

Therefore, the predicted solubility is $x_{CO_2} \approx 0.02215$.

8.3-7 (a) This problem is treated in the same manner as the previous problem. The results are given below:

$$k_{12} = 0$$

x_{CO_2}	P_{tot}	y_{CO_2}	$P_{CO_2} = y_{CO_2} \cdot P_{tot}$
0.015	1.41	0.6729	0.9488
0.016	1.48	0.6869	1.01662
0.0159	1.47	0.6856	1.0078

Therefore, the predicted solubility is $\approx 0.01595 = x_{CO_2}$. This is considerably higher than the experimental value of $x_{CO_2} = 0.00328$

(b) $k_{12} = 0.2$

x_{CO_2}	P_{tot}	y_{CO_2}	$P_{CO_2} = y_{CO_2} \cdot P_{tot}$
0.015	4.94	0.9011	4.4514
0.003	1.36	0.6566	0.89298
0.0033	1.45	0.6775	0.9824
0.0034	1.48	0.6839	1.0121

In this case $x_{CO_2} \approx 0.0034$ which is quite close to the experimental value of 0.00328. This illustrates the importance of the binary interaction parameter k_{12}.

8.3-8 (a) $N = \dfrac{PV}{RT}$ $V = \dfrac{N_G \cdot 8.314 \times 10^{-5} \frac{\text{bar m}^3}{\text{mol K}} \times 273.15 \text{ K}}{1.013 \text{ bar}} = \alpha$

$$N_G = \frac{\alpha \times 1.013}{8.314 \times 10^{-5} \times 273.15} \qquad N_W = \frac{1 \text{ m}^3 \rho_W \text{ g/m}^3}{18.015 \text{ g/mol}}$$

$$x = \frac{N_G}{N_G + N_W} = \frac{1}{1 + \frac{N_W}{N_G}} = \left[1 + \frac{N_W}{N_G}\right]^{-1}$$

$$x = \left[1 + \frac{\rho_W}{18.015} \times \frac{8.314 \times 10^{-5} \times 273.15 \text{ K}}{\alpha \times 1.013}\right]^{-1} = \left[1 + 1.244 \times 10^{-3} \frac{\rho_W}{\alpha}\right]^{-1}$$

(b) $L = \dfrac{\text{volume gas}}{\text{volume liquid}}$; for simplicity, assume 1 m^3 liquid

$$L = \frac{V}{1 \text{ m}^3} = \frac{N_G \cdot 8.314 \times 10^{-5} T}{1.013}; \quad N_G = \frac{V \cdot 1.013}{8.314 \times 10^{-5} T} = \frac{1.013 L}{8.314 \times 10^{-5} T}$$

$$x = \left[1 + \frac{N_W}{N_G}\right]^{-1} = \left[1 + \frac{\rho_W}{18.015} \times \frac{8.314 \times 10^{-5} T}{L \times 1.013}\right]^{-1}$$

$$= \left[1 + 4.555 \times 10^{-6} T \frac{\rho_W}{L}\right]^{-1}$$

(c) $S = V = N_G \cdot 8.314 \times 10^{-5} \text{ bar m}^3/\text{mol K} \times 273.15 \text{ K} \times \dfrac{10^6 \text{ cm}^3/\text{m}^3}{1.013 \text{ bar}}$

$$N_G = S \times \frac{1.013}{8.314 \times 273.15}; \quad N_W = \frac{1}{18.015}$$

$$x = \frac{N_G}{N_G + N_W} = \frac{S \times \frac{1.013}{83.14 \times 273.15}}{\frac{S \times 1.013}{83.14 \times 273.15} + \frac{1}{18.05}} = \frac{S \times 1.013}{S \times 1.013 + 1260.599} = \frac{S}{S + 1244}$$

(d) $xK_H = 1.013 \Rightarrow x = \dfrac{1.013}{K_H}$

(e) $N_G = \dfrac{S_0}{M_S}; \quad N_W = \dfrac{100}{18.015}$

$$x = \frac{N_G}{N_G + N_W} = \frac{\frac{S_0}{M_S}}{\frac{S_0}{M_S} + \frac{100}{18.015}} = \frac{18.015 S_0}{18.015 S_0 + 100 M_S}$$

8.3-9   Condition for equilibrium as the solubility limit is $\bar{f}_i^L = \bar{f}_i^V$ which implies

$$\Delta \underline{G}^{eq} = 0 = RT \ln \frac{\bar{f}_i^L}{\bar{f}_i^V} = RT \ln \frac{x_i^{sol} f_i^L(T,P,x_i=1)}{f_i^V(T,P,y_i=1)} = RT \ln x_i^{sol} + RT \ln \frac{f_i^L(T,P,x_i=1)}{f_i^V(T,P=1.013 \text{ bar})}$$

since the fugacity of the species in the vapor phase as this low pressure is given by the Lewis-Randall rule, and just equal to the fugacity of the pure species at 1.013 bar. Now the last term on the right of this equation is equal to the Gibbs free energy change of transferring the gas from the ideal gas state to a solution of unit mole fraction. Therefore

$$\Delta \underline{G}^{eq} = 0 = RT \ln x_i^{sol} + RT \ln \frac{f_i^L(T,P,x_i=1)}{f_i^V(T,P=1.013 \text{ bar})} = RT \ln x_i^{sol} + \Delta \underline{G}$$

where $\Delta \underline{G}$ is the free energy changed asked for in the problem statement . Therefore $\Delta \underline{G} = -RT \ln x_i^{\text{sol}}$, but

$$\ln x_i^{\text{sol}} = A + \frac{B}{T} + C \ln T + DT + ET^2 \text{, then } \Delta \underline{G} = -RT\left[A + \frac{B}{T} + C \ln T + DT + ET^2\right], \text{ also } \frac{\partial \frac{G}{T}}{\partial \frac{1}{T}} = +H \text{ or}$$

$$\frac{\partial \frac{G}{T}}{\partial T} = -\frac{H}{T^2} \Rightarrow \Delta H = -T^2 \frac{\partial \frac{G}{T}}{\partial T}$$

$$\Delta \underline{H} = \frac{\partial}{\partial T}\left\{-R\left[A + \frac{B}{T} + C \ln T + DT + ET^2\right]\right\}(-T^2) = R\left[-B + CT + DT^2 + 2ET^3\right]$$

$$G = H - TS \Rightarrow S = \frac{H - G}{T} \Delta S = \frac{\Delta H - \Delta G}{T}$$

$$\Delta \underline{S} = \frac{R}{T}\left[-B + CT + DT^2 + 2ET^3 + AT + B + CT \ln T + DT^2 + ET^3\right]$$

$$= \frac{R}{T}\left[AT + CT \ln T + CT + 2DT^2 + 3ET^3\right]$$

$$= R\left[A + C \ln T + C + 2DT + 3ET^2\right]$$

$$C_P = \left(\frac{\partial \underline{H}}{\partial T}\right)_P \Rightarrow \Delta C_P = \left(\frac{\partial \Delta \underline{H}}{\partial T}\right) = R\left[C + 2DT + 6ET^2\right]$$

8.3-10   a) We expect the solubility of bromine in water to be quite low, so that the molar concentration of water will be essentially unchanged. Then the change in free energy for the bromine dissolution process is

$$\Delta G = \frac{M}{M + 55.4} RT \ln \frac{\overline{f}_{Br_2}^{\text{aq}}}{f_{Br_2}} + \frac{55.4}{M + 55.4} RT \ln \frac{\overline{f}_{H_2O}^{\text{aq}}(M)}{\overline{f}_{H_2O}^{\text{aq}}(M = 0)}$$

$$= \frac{M}{M + 55.55} RT \ln \frac{147M}{28.4} + \frac{55.55}{M + 55.55} RT \ln \frac{55.55 + M}{55.55}$$

where 55.55 is the molar concentration of water. Assuming M will be very small, the second term can be neglected and we obtain

$$\Delta G = \frac{M}{M + 55.55} RT \ln \frac{147M}{28.4}$$

The results are plotted below.
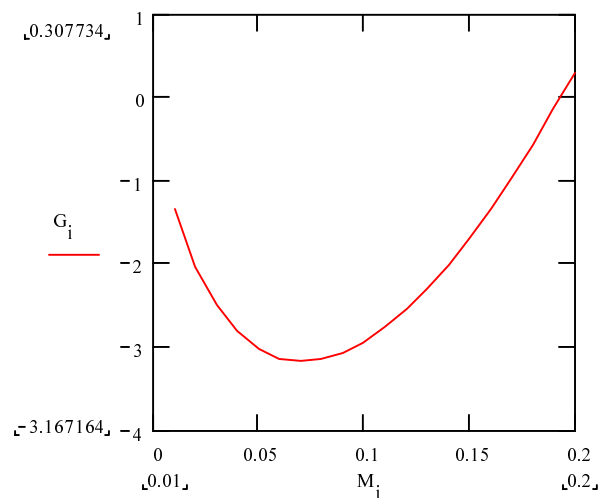
b)   At saturation, the fugacity of liquid bromine equals that of bromine in solution. Therefore

$$\bar{f}^{aq}_{Br_2} = f^L_{Br_2}; \quad \text{or} \quad 147 M = 28.4; \quad \text{so} \quad M = 0.1932$$

Either by using this value in the equation above, or using the graph above, we see that the Free energy change is zero if the liquid is saturated with bromine.

8.3-11 CO_2 $T_C = 304.2$ K $P_C = 73.76$ bar $\omega = 0.225$ $T_B = 194.7$ K

Toluene   591.7   41.13   0.257   383.8

From Prausnitz-Shair Correlation

$T_r = 0.98$; $\dfrac{f^L}{P_C} \cong 0.6$. Assume very little toluene in vapor $y_{CO_2} \sim 1$

$$x_{CO_2} = \frac{y_{CO_2} P(f/P)}{\gamma_{CO_2} f^L_{CO_2}(T, \ P = 1.013 \ \text{bar}) \exp\left\{\left[\underline{V}_{CO_2}(10 - 1.013) \ \text{bar}\right]/RT\right\}}$$

At 10 bar $T_r = 0.98$, $P_r = \dfrac{10}{73.76} = 0.136$

$\dfrac{f}{P}$ (Figure 5.4 - 1) ≈ 0.96

$f^L_{CO_2} = 0.6 \times 73.76 = 44.26$ bar

Now calculate the Poynting correction

$$\exp\left[\frac{55 \ \text{cc/mol} \times 8.987 \ \text{bar}}{298.15 \ \text{K} \times 8.314 \times 10^{-5} \ \text{bar m}^3/\text{mol cc}} \times \frac{1 \ \text{m}^3}{10^6 \ \text{cc}}\right]$$

$$= \exp\left[\frac{5.5 \times 8.987 \times 10^1}{2.9816 \times 10^2 \times 8.314 \times 10^1}\right] = \exp[0.02] = 1.02$$

So ideal "Prausnitz-Shair" solubility

$$x_{CO_2} = \frac{10 \times 0.96}{44.26 \times 1.02} = 0.213$$

Now consider solution nonideality

Table 7.6-1   Table 8.3-1

$\delta_T = 8.9$ $\delta_{CO_2} = 6.0$

$V_T = 107$ $V_{CO_2} = 55$

$$\ln \gamma_{CO_2} = \frac{(55 \text{cc/mol})\phi_T^2 (6.0 - 8.9)^2 \ \text{cal/cc}}{8.314 \ \text{J/mol K} \times 298.15 \ \text{K} \times 0.239 \ \text{cal/J}} = 0.781 \phi_T^2$$

$$\phi_T = \frac{V_T x_T}{V_T x_T + V_{CO_2} x_{CO_2}} = \frac{107(1 - x_{CO_2})}{107(1 - x_{CO_2}) + 55 x_{CO_2}}$$

$$= \frac{107(1 - x_{CO_2})}{107 - (107 - 55) x_{CO_2}} = \frac{107(1 - x_{CO_2})}{107 - 52 x_{CO_2}}$$

So to find the nonideal solubility must solve

$$x_{CO_2} = \frac{0.213}{\exp[0.781 \phi_T^2]} = \frac{0.213}{\exp\left\{0.781\left[107(1 - x_{CO_2})/(107 - 52 x_{CO_2})\right]^2\right\}}$$

which has the solution $x_{CO_2} = 0.102$ (using MATHCAD)

From Program VLMU with $k_{CO_2 - T} = 0.0$

(using flash with equimolar feed)

Pressure $= 10.05$ bar

	x	y
CO_2	0.2062	0.9952
T	0.7938	0.0048

Note $P_{CO_2} = y_{CO_2} \times P = 0.9952 \times 10.05 \sim 10$ bar

$k_{CO_2-T} = 0.10$

	x	y
CO_2	0.1174	0.9949
T	0.8826	0.0051

$P_{CO_2} \sim 10$ bar

Which is reasonably close to the Prausnitz-Shair correlation result, especially given the difference in the methods.

8.3-12 (a) From the Steam Tables $T = 25°C$, $P = 3.169$ kPa

(b) 1 atm $= 1.-10$ kPa

$$y_W = \frac{3.169}{101.3} = 0.0313 \text{ bar} \; ; \; \text{remainder is oxygen and nitrogen.}$$

Initial partial pressure of $N_2 = 0.79 \times (101.3 - 3.2) = 77.5$ kPa

Initial partial pressure of $O_2 = 0.21 \times (101.3 - 3.2) = 20.6$ kPa

Mole fraction N_2 in water $x_{N_2} H_{N_2} = P_{N_2}$

$$x_{N_2} = \frac{77.5 \text{ kPa}/100 \text{ kPa/bar}}{8.48 \times 10^4 \text{ bar/mole fraction}} = \frac{0.775}{8.48 \times 10^4}$$

$$= 0.0914 \times 10^{-4} = 9.14 \times 10^{-6}$$

Mole fraction O_2 in water

$$x_{O_2} = \frac{20.6/100/\text{bar}}{4.35 \times 10^4 \text{ bar/mole fraction}} = \frac{20.6}{100 \times 4.35 \times 10^4} = 4.74 \times 10^{-6}$$

8.4-1 (a) From eqn. (8.4-2) we have, at equilibrium, that

$$x_i^I \boldsymbol{g}_i^I\left(\underline{x}^I\right) = x_i^{II} \boldsymbol{g}_i^{II}\left(\underline{x}^{II}\right) \text{ for all species } i$$

and from regular solution theory we have

$$RT \ln \boldsymbol{g}_i = \underline{V}_i \boldsymbol{f}_j^2 (\boldsymbol{d}_1 - \boldsymbol{d}_2)^2$$

and $\underline{G}^{\mathrm{ex}} = (x_1 \underline{V}_1 + x_2 \underline{V}_2) \boldsymbol{f}_1 \boldsymbol{f}_2 [\boldsymbol{d}_1 - \boldsymbol{d}_2]^2 = \dfrac{x_1 x_2 \underline{V}_1 \underline{V}_2}{x_1 \underline{V}_1 + x_2 \underline{V}_2}(\boldsymbol{d}_1 - \boldsymbol{d}_2)^2 .$ The   critical   solution

temperature is found from

$$\left(\frac{\partial^2 \underline{G}}{\partial x_1^2}\right)_{T,P} = 0 = \left(\frac{\partial^2 \underline{G}^{\mathrm{ex}}}{\partial x_1^2}\right)_{T,P} + \left(\frac{\partial^2 \underline{G}^{\mathrm{IM}}}{\partial x_1^2}\right)_{T,P}$$

where

$$\underline{G}^{\mathrm{IM}} = x_1 \underline{G}_1(T,P) + x_2 \underline{G}_2(T,P) + RT(x_1 \ln x_1 + x_2 \ln x_2)$$

By taking derivatives, we find that

$$\left(\frac{\partial^2 \underline{G}^{\mathrm{IM}}}{\partial x_1^2}\right)_{T,P} = \frac{RT}{x_1 x_2} \text{ and } \left(\frac{\partial^2 \underline{G}^{\mathrm{ex}}}{\partial x_1^2}\right)_{T,P} = -\frac{2\underline{V}_1^2 \underline{V}_2^2 (\boldsymbol{d}_1 - \boldsymbol{d}_2)^2}{(x_1 \underline{V}_1 + x_2 \underline{V}_2)^3}$$

Thus, setting

$$\left(\frac{\partial^2 \underline{G}^{\mathrm{IM}}}{\partial x_1^2}\right)_{T,P} = \left(\frac{\partial^2 \underline{G}^{\mathrm{ex}}}{\partial x_1^2}\right)_{T,P} = 0$$

we obtain

$$RT_C = \frac{2 x_1 x_2 \underline{V}_1^2 \underline{V}_2^2 (\boldsymbol{d}_1 - \boldsymbol{d}_2)^2}{(x_1 \underline{V}_1 + x_2 \underline{V}_2)^3} = 2 \boldsymbol{f}_1 \boldsymbol{f}_2 \frac{\underline{V}_1 \underline{V}_2 (\boldsymbol{d}_1 - \boldsymbol{d}_2)^2}{(x_1 \underline{V}_1 + x_2 \underline{V}_2)} \qquad (*)$$

(b) To find the upper consolute temperature, that is, $T_{C,\mathrm{max}}$, we use $\left(\dfrac{\partial T_C}{\partial x_1}\right)_P = 0$ or

$$R\left(\frac{\partial T_C}{\partial x_1}\right)_P = \frac{2\underline{V}_1^2 \underline{V}_2^2 (\boldsymbol{d}_1 - \boldsymbol{d}_2)^2}{(x_1 \underline{V}_1 + x_2 \underline{V}_2)^3}\left\{x_2 - x_1 - \frac{3 x_1 x_2 (\underline{V}_1 - \underline{V}_2)}{(x_1 \underline{V}_1 + x_2 \underline{V}_2)}\right\} = 0$$

clearly the term $\{\ \ \}$ must be zero at the upper consolute temperature. Thus, we obtain

$$x_1 = \frac{\underline{V}_1}{\underline{V}_1 - \underline{V}_2} \pm \frac{\sqrt{\underline{V}_1^2 + \underline{V}_2^2 - \underline{V}_1 \underline{V}_2}}{(\underline{V}_1 - \underline{V}_2)}$$

Only the negative solution is realistic. Thus, the composition at the upper consolute point is

$$x_1 = 1 - x_2 = \frac{\left(\underline{V}_1^2 + \underline{V}_2^2 - \underline{V}_1\underline{V}_2\right) - \underline{V}_1}{\left(\underline{V}_2 - \underline{V}_1\right)}$$

Note that this composition depends only on the molar volumes of species, and not their solubility parameters! Note also, that as $\underline{V}_2 \to 1$, $x_1 \to 0.5$, as should be expected. Substituting this result into eqn. (*) above yields

$$RT_C = \frac{2\underline{V}_1^2\underline{V}_2^2(\boldsymbol{d}_1 - \boldsymbol{d}_2)^2\left\{\left(\underline{V}_1 + \underline{V}_2\right)\left(\underline{V}_1^2 + \underline{V}_2^2 - \underline{V}_1\underline{V}_2\right)^{1/2} - \underline{V}_1^2 - \underline{V}_2^2\right\}}{\left(\underline{V}_2 - \underline{V}_1\right)^2\left\{\left(\underline{V}_1^2 + \underline{V}_2^2 - \underline{V}_1\underline{V}_2\right)^{1/2} - \left(\underline{V}_1 + \underline{V}_2\right)\right\}^3}$$

8.4-2 For $\underline{G}^{ex} = Ax_1x_2$ we have, from $\overline{G}_i^{ex} = RT\ln\boldsymbol{g}_i = \left(\dfrac{\partial\left(N\underline{G}^{ex}\right)}{\partial N_i}\right)_{T,P,N_{j\neq i}}$. That $RT\ln\boldsymbol{g}_1 = Ax_2^2$ and

$RT\ln\boldsymbol{g}_2 = Ax_1^2$.

(a) The equilibrium curve is one for which $\overline{G}_i^{I} = \overline{G}_i^{II}$ or $x_i^I\boldsymbol{g}_i^I = x_i^{II}\boldsymbol{g}_i^{II}$ for both species (i.e., $i = 1, 2$). Thus, the equilibrium phase envelope is the solution to the equations

$$x_i^I \exp\left\{\frac{A\left(1 - x_i^I\right)^2}{RT}\right\} = x_i^{II}\exp\left\{\frac{A\left(1 - x_i^{II}\right)^2}{RT}\right\}$$

and

$$\left(1 - x_i^I\right)\exp\left\{\frac{Ax_i^{I^2}}{RT}\right\} = \left(1 - x_i^{II}\right)\exp\left\{\frac{Ax_i^{II^2}}{RT}\right\}$$

and we have two equations for the two unknowns: x_i^I, x_i^{II}

(b) Limit of stability criterion is $\left(\dfrac{\partial^2\underline{G}}{\partial x_1^2}\right)_{T,P} = 0$, where

$$\underline{G} = \underbrace{x_1\underline{G}_1 + x_2\underline{G}_2 + RT(x_1\ln x_1 + x_2\ln x_2)}_{\underline{G}^{IM}} + \underbrace{Ax_1x_2}_{\underline{G}^{ex}}$$

setting

$$\left(\frac{\partial^2\underline{G}}{\partial x_1^2}\right)_{T,P} = 0 \text{ yields } x_1x_2 = \frac{RT}{2A} = x_1(1 - x_1) = x_1 - x_1^2$$

solving for x_1 yields $x_1 = \dfrac{1}{2} \pm \dfrac{1}{2}\sqrt{1 - \dfrac{2RT}{A}}$ or $x_i^I = \dfrac{1}{2} - \dfrac{1}{2}\sqrt{1 - \dfrac{2RT}{A}}$ and $x_i^{II} = \dfrac{1}{2} + \dfrac{1}{2}\sqrt{1 - \dfrac{2RT}{A}}$

8.4-3 (a) Regular solution theory suppose that $\underline{S}^{ex} = 0$, or, since $\underline{G}^{ex} = \underline{H}^{ex} - T\underline{S}^{ex}$, that $\underline{G}^{ex} = \underline{H}^{ex}$. This is the case for the C_6H_6-CCl_4 system, but not for the C_6H_6-CS_2 system. Therefore, regular solution theory is not applicable to the C_6H_6-CS_2 system. To test the Hildebrand-Scatchard model we use

$$\underline{G}^{\text{ex}} = \frac{x_1 \underline{V}_1^2 x_2 \underline{V}_2^2}{x_1 \underline{V}_1^2 + x_2 \underline{V}_2^2} (\boldsymbol{d}_1 - \boldsymbol{d}_2)^2$$

at $x_1 = 0.5$ we obtain

$$\underline{G}^{\text{ex}} = \frac{(0.5) \times 89 \times (0.5) \times 61}{0.5(89 + 61)} \times (10 - 9.2)^2 = 11.58 \text{ cal/mol} = 48.45 \text{ J/mol}$$

compared with ≈ 105 J/mol experimentally. Thus, we concluded that while the CCl_4 - C_6H_6 system has $\underline{S}^{\text{ex}} = 0$ and thus may satisfy the regular solution *model*, it is not well represent by Scatchard-Hildebrand regular solution *theory*.

(b) Since $\underline{G}^{\text{ex}}$ is a symmetric function of composition for the CS_2 - C_6H_6 system, we will represent the composition dependence of $\underline{G}^{\text{ex}}$ by the one-constant Margules expression $\underline{G}^{\text{ex}} = Ax_1x_2$ with $A = 1160$ J/mol, so that $\underline{G}^{\text{ex}} = (x_1 = 0.5) = 290$ J/mol, as is observed experimentally. For the one-constant Margules eqn., by eqn. (8.4-14),

$$T_{\text{UC}} = \frac{A}{2R} = \frac{1160}{2 \times 8.314} \approx 70 \text{ K}$$

Thus, if a liquid phase(s) were to exist at very low temperatures, it would exist as two phases below 70 K, and a single stable phase above 70 K. However, since 70 K is well below the melting points of either of the pure components, and, presumably, the eutectic point as well (see section 8.7), no liquid-liquid phase separation will be observed. [Note: we can improve our estimation of the upper consolute temperature by taking into account the temperature dependence of the excess Gibbs free energy. In particular, from $\dfrac{\partial\left(\frac{G}{T}\right)}{\partial T} = -\dfrac{H}{T^2}$ we obtain

$$\left.\frac{\underline{G}^{\text{ex}}}{T}\right|_{T_2} - \left.\frac{\underline{G}^{\text{ex}}}{T}\right|_{T_1} = -\int_{T_1}^{T_2} \frac{\underline{H}^{\text{ex}}}{T^2} dT \approx \underline{H}^{\text{ex}}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where we have *assumed*, for simplicity, that $\underline{H}^{\text{ex}}$ is temperature independent. At $x_1 = 0.5$, $\underline{H}^{\text{ex}} \approx 525$ J/mol. Thus

$$\underline{G}^{\text{ex}}(x_1 = 0.5, T_2) = T_2\left[\frac{290}{298.15} + 525\left\{\frac{1}{T_2} - \frac{1}{298.15}\right\}\right]$$

and, at $T_2 = 80$ K,

$$\underline{G}^{\text{ex}}(x_1 = 0.5, \ 80 \text{ K}) \cong 462 \text{ J/mol}, \text{ and } A(T = 80 \text{ K}) \cong 1848 \text{ J/mol}$$

implying an upper consolute temperature of

$$T_{\text{UC}} = \frac{A}{2R} = 111 \text{ K}$$

Guess again $T_{\text{UC}} = T_2 = 105$ K

$\underline{G}^{\text{ex}}(x_1 = 0.5, \ 105 \text{ K}) = 105.6$ K , $T_{\text{UC}} = 106.4$ K (which is close to guess)

Since this temperature is still well below the melting points of the species, our conclusion does not change, there is no phase separation. We do, however, see the importance of accounting for the temperature dependence of the excess Gibbs free energy (and activity coefficients)!]

(c) For vapor-liquid equilibrium we have $\bar{f}_i^L = \bar{f}_i^V \Rightarrow x_i \boldsymbol{g}_i P_i^{\text{vap}} = y_i P$ at an azeotropic point $x_i = y_i$, so that $\boldsymbol{g}_i P_i^{\text{vap}} = P$ for our system

$$\frac{A}{RT} = \frac{1160}{8.314 \times 319.65} = 0.4365$$

also

$$\boldsymbol{g}_{C_6H_6} P_{C_6H_6}^{vap} = P = \boldsymbol{g}_{CS_2} P_{CS_2}^{vap}$$

or

$$\ln \boldsymbol{g}_{C_6H_6} + \ln P_{C_6H_6}^{vap} = \ln \boldsymbol{g}_{CS_2} + \ln P_{CS_2}^{vap}$$

or

$$0.4365 x_{CS_2}^2 + \ln \frac{P_{C_6H_6}^{vap}}{P_{CS_2}^{vap}} = 0.4365 \left(1 - x_{CS_2}\right)^2$$

This equation has, as its only solution,

$$x_{CS_2} \cong 1.82$$

which is *not* between 0 and 1. Thus, we conclude that no azeotrope is formed. [Note: we could get a better estimate of $\underline{G}^{ex}$ at the temperature of interest by talking into account the temperature dependence of $\underline{G}^{ex}$ as was done in part b. Then we find that

$$\underline{G}^{ex}(T = 46.5^\circ C, \ x_1 = 0.5) = 273 \ \text{J/mol}$$

Thus, the solution becomes even less *non*-ideal, and an azeotrope will not be formed.]

8.4-4 (a) Starting from

$$x_i^{I} \boldsymbol{g}_i^{I} = x_i^{I} \exp\left[\frac{A\left(1 - x_i^{I}\right)^2}{RT}\right] = x_i^{II} \boldsymbol{g}_i^{II} = x_i^{II} \exp\left[\frac{A\left(1 - x_i^{II}\right)^2}{RT}\right]$$

which we can solve for A

$$\frac{A}{RT} = \frac{\ln\left(\frac{x_i^{II}}{x_i^{I}}\right)}{\left(1 - x_i^{I}\right)^2 - \left(1 - x_i^{II}\right)^2}$$

Using the data for benzene $\left(x_B^{I} = 0.48 \text{ and } x_B^{II} = 0.94\right)$ yields $\frac{A}{RT} = 2.52$, while using the data for perfluoro-n-heptane yields $\frac{A}{RT} = 3.31$. Since the two values of A are different, we conclude that the one-constant Margules equation is *not* consistent with the experimental data.

(b) Regular solution theory gives

$$x_i^{I} \boldsymbol{g}_i^{I} = x_i^{I} \exp\left[\frac{\underline{V}_i\left(\boldsymbol{f}_j^{I}\right)^2\left(\boldsymbol{d}_P - \boldsymbol{d}_B\right)^2}{RT}\right] = x_i^{II} \boldsymbol{g}_i^{II} = x_i^{II} \exp\left[\frac{\underline{V}_i\left(\boldsymbol{f}_j^{II}\right)^2\left(\boldsymbol{d}_P - \boldsymbol{d}_B\right)^2}{RT}\right]$$

which, solving for $\left(\boldsymbol{d}_P - \boldsymbol{d}_B\right)^2$ yields

$$\left(\boldsymbol{d}_P - \boldsymbol{d}_B\right)^2 = \frac{RT \ln\left(\frac{x_i^{II}}{x_i^{I}}\right)}{\underline{V}_i\left\{\left(\boldsymbol{f}_j^{I}\right)^2 - \left(\boldsymbol{f}_j^{II}\right)^2\right\}} \ ; \text{ where } \boldsymbol{f}_j = \frac{x_j \underline{V}_j}{x_P \underline{V}_P + x_B \underline{V}_B}$$

From Table 7.6-1 $\underline{V}_B = 89$ cc/mol ; $\underline{V}_P = 0.226$ m^3/mol from the problem statement. Thus

$$\boldsymbol{f}_B^I = 0.2666, \; \boldsymbol{f}_B^{II} = 0.8605, \; \boldsymbol{f}_P^I = 0.7334 \text{ and } \boldsymbol{f}_P^{II} = 0.1395$$

Using the benzene data, we obtain $(\boldsymbol{d}_P - \boldsymbol{d}_B)^2 = 10.8$ cal/mol or $\boldsymbol{d}_P = \boldsymbol{d}_B \pm 3.3 = 12.5$ or 5.9. Note that we can not choose between these two values solely on the basis of the data here. Activity coefficient data on perfluoro-n-heptane in other fluids would be needed to fix $\boldsymbol{d}_P$. The value 5.9 is, however, quite close to the value of 6.0 given in Table 7.6-1.

Doing a similar calculation to the one above, but not using the perfluoro-n-heptane data yields

$$(\boldsymbol{d}_P - \boldsymbol{d}_B)^2 = 7.75 \text{ or } \boldsymbol{d}_P = \boldsymbol{d}_B \pm 2.8 = 12.0 \text{ or } 6.4$$

Thus, regular solution theory is also not completely consistent with the experimental data!

8.4-5   The condition for material stability is that $d^2G > 0$ for all variations at constant T and P. Here this implies

$$\left(\frac{\partial^2 \underline{G}}{\partial x_1^2} \right)_{T,P} > 0 \; \text{ or equivalently } \left(\frac{\partial^2 \Delta \underline{G}_{\text{mix}}}{\partial x_1^2} \right)_{T,P} > 0 .$$

Looking at the curve in the problem statement, we see that at points B and C this derivative is zero, and between points B and C it is negative. This implies phase instability or phase separation, with points B and C being the limits of stability.

The condition of phase equilibrium is

$$\overline{G}_1^I = \overline{G}_1^{II} \text{ and } \overline{G}_2^I = \overline{G}_2^{II} \tag{1}$$

Now from Chapter 6 we have

$$\Delta \underline{V}_{\text{mix}} - x_1 \left(\frac{\partial \Delta \underline{V}_{\text{mix}}}{\partial x_1} \right)_{T,P} = \overline{V}_2 - \underline{V}_2$$

and

$$\Delta \underline{H}_{\text{mix}} - x_1 \left(\frac{\partial \Delta \underline{H}_{\text{mix}}}{\partial x_1} \right)_{T,P} = \overline{H}_2 - \underline{H}_2$$

similarly we have

$$\Delta \underline{G}_{\text{mix}} - x_1 \left(\frac{\partial \Delta \underline{G}_{\text{mix}}}{\partial x_1} \right)_{T,P} = \overline{G}_2 - \underline{G}_2 \tag{2}$$

Therefore, the equilibrium conditions can be written as

$$\Delta \underline{G}_{\text{mix}}\left(T, P, \underline{x}^I\right) - x_2^I \frac{\partial(\Delta \underline{G}_{\text{mix}})}{\partial x_2^I} = \Delta \underline{G}_{\text{mix}}\left(T, P, \underline{x}^{II}\right) - x_2^{II} \frac{\partial(\Delta \underline{G}_{\text{mix}})}{\partial x_2^{II}} \tag{3a}$$

and

$$\Delta \underline{G}_{\text{mix}}\left(T, P, \underline{x}^{II}\right) - x_1^I \frac{\partial(\Delta \underline{G}_{\text{mix}})}{\partial x_1^I} = \Delta \underline{G}_{\text{mix}}\left(T, \; P, \; \underline{x}^{II}\right) - x_1^{II} \frac{\partial(\Delta \underline{G}_{\text{mix}})}{\partial x_1^{II}} \tag{3b}$$

Subtracting the second of these equations from the first yields

$$x_1^{\mathrm{I}}\frac{\partial(\Delta\underline{G}_{\mathrm{mix}})}{\partial x_1^{\mathrm{I}}} - x_2^{\mathrm{I}}\frac{\partial(\Delta\underline{G}_{\mathrm{mix}})}{\partial x_2^{\mathrm{I}}} = x_1^{\mathrm{II}}\frac{\partial(\Delta\underline{G}_{\mathrm{mix}})}{\partial x_1^{\mathrm{I}}} - x_2^{\mathrm{II}}\frac{\partial(\Delta\underline{G}_{\mathrm{mix}})}{\partial x_2^{\mathrm{II}}}$$

and using $dx_2 = -dx_1$ gives

$$\left(x_1^{\mathrm{I}}+x_2^{\mathrm{I}}\right)\frac{\partial(\Delta\underline{G}_{\mathrm{mix}})}{\partial x_1^{\mathrm{I}}} = \left(x_1^{\mathrm{II}}+x_2^{\mathrm{II}}\right)\frac{\partial(\Delta\underline{G}_{\mathrm{mix}})}{\partial x_1^{\mathrm{II}}}$$

or, since $x_1^i + x_2^i = 1$

$$\frac{\partial(\Delta\underline{G}_{\mathrm{mix}})}{\partial x_1^{\mathrm{I}}} = \frac{\partial(\Delta\underline{G}_{\mathrm{mix}})}{\partial x_1^{\mathrm{II}}} \tag{4}$$

Thus, at the equilibrium state not only is $\overline{G}_i^{\mathrm{I}} = \overline{G}_i^{\mathrm{II}}$, but eqn. (4) is satisfied also. Using this last result in eqn. (3a) gives, at equilibrium

$$\Delta\underline{G}_{\mathrm{mix}}\left(T,P,\underline{x}^{\mathrm{I}}\right) - x_i^{\mathrm{I}}\left(\frac{\partial\Delta\underline{G}_{\mathrm{mix}}}{\partial x_1}\right)_{T,P} = \Delta\underline{G}_{\mathrm{mix}}\left(T,P,\underline{x}^{\mathrm{II}}\right) - x_i^{\mathrm{II}}\left(\frac{\partial\Delta\underline{G}_{\mathrm{mix}}}{\partial x_1}\right)_{T,P}$$

Now eqn. (4) implies that the slope of the $\Delta\underline{G}_{\mathrm{mix}}$ curve must be the same at the two points at which the phases are in equilibrium. Further, from eqns. (1 and 2) we have that since $\overline{G}_i^{\mathrm{I}} = \overline{G}_i^{\mathrm{II}}$, the two lines have the same intercept. Since the two tangent lines have the same slope and the same intercept, the lines must be identical, i.e., the equilibrium points are on a common tangent line.

8.4-6 At the bubble point (assuming an ideal vapor phase)

$$\sum x_i \boldsymbol{g}_i P_i^{\mathrm{vap}} = \sum y_i P = P. \text{ So } x_B \boldsymbol{g}_B P_B^{\mathrm{vap}} + x_W \boldsymbol{g}_W P_W^{\mathrm{vap}} = P$$

(a) $(0.04)\boldsymbol{g}_B(0.427) + (0.96)(1)(0.784) = 1.013 \text{ bar} \Rightarrow \boldsymbol{g}_B = 15.244$

so $y_B = \dfrac{15.244 \times 0.04 \times 0.427}{1.013} = 0.257$ and $y_W = 0.96 \times 1 \times \dfrac{0.784}{1.013} = 0.743$

(b) At equilibrium $x_B^{\mathrm{I}}\boldsymbol{g}_B^{\mathrm{I}} = x_B^{\mathrm{II}}\boldsymbol{g}_B^{\mathrm{II}} \Rightarrow \boldsymbol{g}_B^{\mathrm{II}} = \dfrac{x_B^{\mathrm{I}}\boldsymbol{g}_B^{\mathrm{I}}}{x_B^{\mathrm{II}}} = \dfrac{0.04 \times 15.244}{0.4}$ or $\boldsymbol{g}_B^{\mathrm{II}} = 1524$; also

$$\boldsymbol{g}_W^{\mathrm{II}} = \frac{x_W^{\mathrm{I}}\boldsymbol{g}_W^{\mathrm{I}}}{x_W^{\mathrm{II}}} = \frac{0.96 \times 1}{0.6} = 1.60$$

(c) Since $x_i^{\mathrm{I}}\boldsymbol{g}_i^{\mathrm{I}} = x_i^{\mathrm{II}}\boldsymbol{g}_i^{\mathrm{II}}$ and $\sum x_i^{\mathrm{II}}\boldsymbol{g}_i^{\mathrm{II}} P_i^{\mathrm{vap}} = \sum x_i^{\mathrm{I}}\boldsymbol{g}_i^{\mathrm{I}} P_i^{\mathrm{vap}} = P$. The second liquid phase will also have a bubble point pressure of 1.013 bar.

8.4-7 Though the overall composition is 50 mole % isobutane, in fact there are really two phases ... one liquid of composition 11.8 mole % isobutane and the other liquid of composition 92.5 mole % isobutane. Since, at liquid-liquid equilibrium $x_i^{\mathrm{I}}\boldsymbol{g}_i^{\mathrm{I}} = x_i^{\mathrm{II}}\boldsymbol{g}_i^{\mathrm{II}}$ and

$$P_{\mathrm{bubble}} = \sum x_i^{\mathrm{I}}\boldsymbol{g}_i^{\mathrm{I}} P_i^{\mathrm{vap}} = \sum x_i^{\mathrm{II}}\boldsymbol{g}_i^{\mathrm{II}} P_i^{\mathrm{vap}}.$$

we need to calculate the bubble point pressure for one phase since the other phase will have the same bubble point pressure. Also, since the pressures are not expected to be very high, we will assume an ideal vapor phase. So the equations we will use are

$$x_i \boldsymbol{g}_i P_i^{\mathrm{vap}} = y_i P \text{ and } \sum x_i \boldsymbol{g}_i P_i^{\mathrm{vap}} = \sum y_i P = P$$

We will use the 92.5 mole % liquid for the calculations.

$$g_{isob}(x_{isob} = 0.925) = 1.019 \text{ from the problem statement}$$
$$g_{furf}(x_{isob} = 0.925) = ?$$

However, from the liquid-liquid equilibrium condition we have

$$x_{furf}^I g_{furf}^I = x_{furf}^{II} g_{furf}^{II} \Rightarrow g_{furf}^I(x_{isob} = 0.925) = \frac{x_{furf}^{II} g_{furf}^{II}}{x_{furf}^I} = \frac{0.882 \times 1.033}{0.075} = 12.148$$

Therefore

$$P = \sum x_i g_i P = 0.925 \times 1.019 \times 4.909 + 12.148 \times 0.075 \times 4.93 \times 10^{-3} = 4.632 \text{ bar}$$

$$y_{isob} = 0.925 \times 1.019 \times \frac{4.909}{4.632} = 0.999 ; \ y_{furf} = 0.001$$

8.4-8 (a) At LLE $x_i^I g_i^I = x_i^{II} g_i^{II}$. Here this implies

$$x_1^I \exp\left\{\frac{A}{RT}\left(1 - x_1^I\right)^2\right\} = x_1^{II} \exp\left\{\frac{A}{RT}\left(1 - x_1^{II}\right)^2\right\}$$

and

$$\left(1 - x_1^I\right)\exp\left\{\frac{A}{RT}\left(x_1^I\right)^2\right\} = \left(1 - x_1^{II}\right)\exp\left\{\frac{A}{RT}\left(x_1^{II}\right)^2\right\}$$

These equations are symmetric with respect to the interchange on the subscripts 1 and 2 (that is replacing x_1 by $x_2 = 1 - x_1$ and $x_2 = (1 - x_1)$ by x_1 yields exactly the same set of equations). This suggests that the equilibrium is symmetric. Of course, that is exactly what we would expect with the one-constant Margules expression. Therefore, we have

$$x_H^I = 0.0902 \qquad\qquad x_H^{II} = 0.9098$$
$$\text{and}$$
$$x_{EtOH}^I = 0.9098 \qquad\qquad x_{EtOH}^{II} = 0.0902$$

(b) Here, as in the previous two problems, the bubble point pressure can be computed from either liquid phase since $x_i^I g_i^I = x_i^{II} g_i^{II}$. Assuming an ideal vapor phase, we have

$$x_i g_i P_i^{vap} = y_i P \ \text{ and } \ P = \sum x_i g_i P_i^{vap}$$

where the activity coefficients and vapor pressure are given in the problem statement. The solution (putting all the equations into Mathcad) is

$$P = 1.9657 \text{ bar}, \ y_H = 0.5795, \ y_{EtOH} = 0.4205$$

8.4-9   The condition for liquid-liquid equilibrium is $x_i^I g_i^I = x_i^{II} g_i^{II}$ using the one-constant Margules eqn.

we have $RT \ln g_i^I = A\left(1 - x_i^I\right)^2$. Now

$$0.097 g_1(x_1 = 0.097) = 0.903 g_1(x_1 = 0.903) \Rightarrow \ln\frac{g_1(x_1 = 0.097)}{g_1(x_1 = 0.903)} = \ln\frac{0.903}{0.097}$$

$$= \frac{A}{RT}\left[(1 - 0.097)^2 - (1 - 0.903)^2\right] \Rightarrow \frac{A}{RT} = 2.768$$

so that
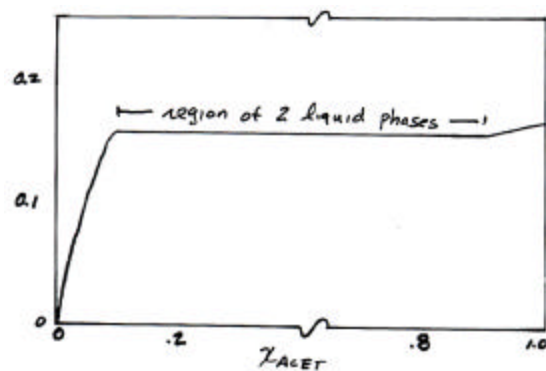
$$g_1 = \exp\left(2.768(1-x_1)^2\right)$$

$$g_2 = \exp\left(2.768(1-x_2)^2\right)$$

Now to compute the pressure in the one phase liquid region we use

$$P = x_1 g_1 P_1^{\text{vap}} + x_2 g_2 P_2^{\text{vap}}$$

$$= x_1\left[\exp\left(2.768(1-x_1)^2\right)\right]0.167 + (1-x_1)\left[\exp\left(2.768x_1^2\right)3.13\times10^{-3}\right]$$

x_{acet}	$P(\text{bar})$
0	0.00313
0.02	0.0507
0.04	0.0887
0.06	0.1186
0.08	0.1420
0.09	0.1517
0.097	0.1577
Two	phase
region	
0.903	0.1577
0.92	0.1590
0.94	0.1607
0.96	0.1626
0.98	0.1647
1.0	0.167

8.4-10 Since we have the concentrations of the coexisting equilibrium liquid phase we can determine two binary parameters. Also, since we are interested in two different temperatures (LLE at $20°C$ and VLE at $73.4°C$) we want an activity coefficient model with some built in temperature dependence (otherwise, we will get LLE with the same compositions at all temperatures.) Consequently, I will use the two constant Margules equation

$$\Rightarrow RT\ln\mathbf{g}_1 = x_2^2\left(\mathbf{a}_1 + B_1 x_2\right)$$
$$RT\ln\mathbf{g}_2 = x_1^2\left(\mathbf{a}_2 + B_2 x_1\right)$$

where $\mathbf{a}_i = A + 3(-1)^{i+1}B$; $B_i = 4(-1)^i B$. These equations are to be used with $x_1^I \mathbf{g}_1^I = x_1^{II}\mathbf{g}_1^{II}$; $x_2^I \mathbf{g}_2^I = x_2^{II}\mathbf{g}_2^{II}$; $x_1^I = 0.0850$; $x_2^I = 1 - x_1^I$; $x_1^{II} = 0.6363$; $x_2^{II} = 1 - x_2^I$. Putting all this into Mathcad, I find

$$A = 4833.4 \text{ J/mol} \quad B = -1980.2 \text{ J/mol}$$

Now using $T = 73.4°\text{C}$, the same constants as above, I find

x_{MEK}	P(bar)	y_{MEK}
0	0.3603	0
.1	0.7241	0.540
.2	0.8313	0.617
.3	0.8601	0.637
.4	0.8696	0.646
.5	0.8776	0.656
.6	0.8867	0.677
.7	0.8931	0.714
.8	0.8903	0.775
.9	0.8718	0.867
1.0	0.8337	1.000

Azeotrope is predicted to occur at $x_{\text{MEK}} \approx 0.7287$ and $P = 0.8935$ bar
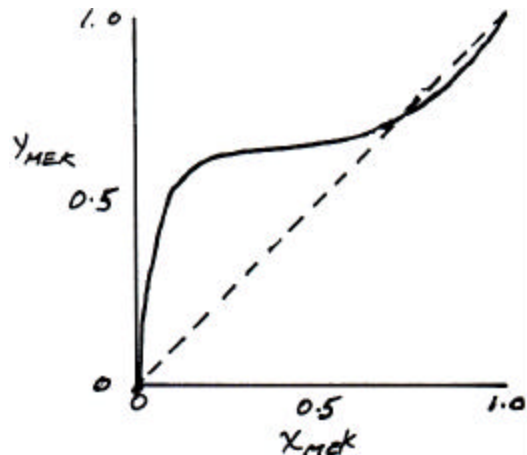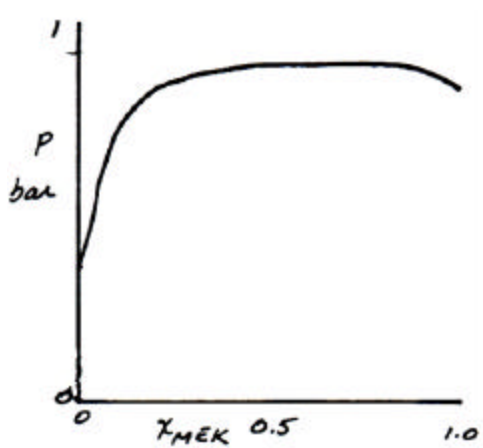
Note: LLE does not occur at this higher temperature. If it did the calculated $P - x$ diagram would have both an interior maximum and minimum as a function of temperature, and the predicted x-y diagram would be like a sideways S, with the x-y line crossing the $x = y$ line twice.

8.4-11   The Wilson model is

$$\underline{G}^{\text{ex}} = -RT \sum x_i \ln\left[\sum_j x_j \Lambda_{ij}\right]$$

with

$$\Lambda_{ij} = \frac{V_j^L}{V_i^L} \exp\left[-\frac{(\boldsymbol{l}_{ij} - \boldsymbol{l}_{ji})}{RT}\right]$$

which, for a binary mixture, reduces to

$$\underline{G}^{\text{ex}} = -RT\{x_1 \ln(x_1 + x_2\Lambda_{12}) + x_2 \ln(x_1\Lambda_{21} + x_2)\}$$

and

$$\underline{G}^{\text{IM}} = x_1\underline{G}_1 + x_2\underline{G}_2 + RT(x_1 \ln x_1 + x_2 \ln x_2)$$

so

$$\underline{G} = x_1\underline{G}_1 + x_2\underline{G}_2 + RT\left(x_1 \ln\frac{x_1}{x_1 + x_2\Lambda_{12}} + x_2 \ln\frac{x_2}{x_1\Lambda_{21} + x_2}\right)$$

Now we look at the derivative of $\underline{G}$

$$\left(\frac{\partial \underline{G}}{\partial x_1}\right)_{T,P} = \underline{G}_1 - \underline{G}_2 + RT \ln\frac{x_1}{x_1 + x_2\Lambda_{12}}$$

$$+ RTx_1 \frac{x_1 + x_2\Lambda_{12}}{x_1} \frac{\partial}{\partial x_1}\left(\frac{x_1}{x_1 + x_2\Lambda_{12}}\right)$$

$$- RT \ln\frac{x_2}{x_1\Lambda_{21} + x_2} + RTx_2 \frac{x_1\Lambda_{21} + x_2}{x_2} \frac{\partial}{\partial x_1}\left(\frac{x_2}{x_1\Lambda_{21} + x_2}\right)$$

$$= \underline{G}_1 - \underline{G}_2 + RT \ln\frac{x_1}{x_1 + x_2\Lambda_{12}}$$

$$+ RT(x_1 + x_2\Lambda_{12})\left\{\frac{1}{x_1 + x_2\Lambda_{12}} - \frac{x_1(1 - \Lambda_{12})}{(x_1 + x_2\Lambda_{12})^2}\right\}$$

$$- RT \ln\frac{x_2}{x_1\Lambda_{21} + x_2}$$

$$+ RT(x_1\Lambda_{21} + x_2)\left\{\frac{-1}{x_1\Lambda_{21} + x_2} - \frac{x_2(\Lambda_{21} - 1)}{(x_1\Lambda_{21} + x_2)^2}\right\}$$

$$= \underline{G}_1 - \underline{G}_2 + RT \ln\frac{x_1}{x_1 + x_2\Lambda_{12}}$$

$$+ \frac{RT}{(x_1 + x_2\Lambda_{12})}\{x_1 + x_2\Lambda_{12} - x_1 + x_1\Lambda_{12}\} - RT \ln\frac{x_2}{x_1\Lambda_{21} + x_2}$$

$$+ \frac{RT}{(x_1\Lambda_{21} + x_2)}\{-x_1\Lambda_{21} - x_2 - x_2\Lambda_{21} + x_2\}$$

$$= \underline{G}_1 - \underline{G}_2 + RT \ln\frac{x_1}{x_1 + x_2\Lambda_{12}} + \frac{RT\Lambda_{12}}{x_1 + x_2\Lambda_{12}}$$

$$- RT \ln\frac{x_2}{x_1\Lambda_{21} + x_2} - \frac{RT\Lambda_{21}}{x_1\Lambda_{21} + x_2}$$

Then

$$\left(\frac{\partial^2 \underline{G}}{\partial x_1^2}\right)_{T,P} = RT\frac{x_1 + x_2\Lambda_{12}}{x_1}\frac{\partial}{\partial x_1}\left(\frac{x_1}{x_1 + x_2\Lambda_{12}}\right) - \frac{RT\Lambda_{12}}{(x_1 + x_2\Lambda_{12})^2} = (1 - \Lambda_{12})$$

$$- RT\frac{x_1\Lambda_{21} + x_2}{x_2}\frac{\partial}{\partial x_1}\left(\frac{x_2}{x_1\Lambda_{21} + x_2}\right) + \frac{RT\Lambda_{21}}{(x_1\Lambda_{21} + x_2)^2}(\Lambda_{21} - 1)$$

$$= \frac{RT}{x_1(x_1 + x_2\Lambda_{12})}\{(x_1 + x_2\Lambda_{12}) - x_1(1 - \Lambda_{12})\}$$

$$+ \frac{RT}{x_2(x_1\Lambda_{21} + x_2)^2}\{(x_1\Lambda_{21} + x_2) + x_2(\Lambda_{21} - 1)\}$$

So

$$\left(\frac{\partial^2 \underline{G}}{\partial x_1^2}\right)_{T,P} = RT\left[\frac{\Lambda_{12}^2}{x_1(x_1 + x_2\Lambda_{12})^2} + \frac{\Lambda_{21}^2}{x_2(x_1\Lambda_{21} + x_2)^2}\right] = 0$$

at upper critical solution temperature

Now $0 \le x_1 \le 1$ and $0 \le x_2 \le 1$; in particular, neither x_1 nor x_2 is negative. Also, clearly

$$\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}}\right)^2 > 0 \text{ and } \left(\frac{\Lambda_{21}}{x_1\Lambda_{21} + x_2}\right)^2 > 0$$

So, for the Wilson model, the only way for $\left(\frac{\partial^2 \underline{G}}{\partial x_1^2}\right)_{T,P} = 0$ is if $T = 0\,\text{K}$. Thus, the upper

consolute temperature for the Wilson model is $T = 0\,\text{K}$, and there is no liquid-liquid equilibrium.

8.4-12 (a) Clearly from

$$RT\ln\boldsymbol{g}_i = 8.163x_j^2 \quad \text{we have}$$

$$\underline{G}^{\text{ex}} = x_1 RT\ln\boldsymbol{g}_1 + x_2 RT\ln\boldsymbol{g}_2 = x_1 8.163x_2^2 + x_2 8.163x_1^2$$

$$= x_1 x_2 8.163(x_1 + x_2) = x_1 x_2 8.163 \quad \frac{\text{kJ}}{\text{mol}}$$

Therefore, the upper consolute temperature for this model is

$$T_{\text{uc}} = \frac{A}{2R} = \frac{8163}{2 \times 8.314} = 490.9\,\text{K}$$

First do the LLE calculation. At LLE $x_i^{\text{I}}\boldsymbol{g}_i^{\text{I}} = x_i^{\text{II}}\boldsymbol{g}_i^{\text{II}}$. Here this implies

$$x_1^{\text{I}}\exp\left\{\frac{A}{RT}\left(1 - x_1^{\text{I}}\right)^2\right\} = x_1^{\text{II}}\exp\left\{\frac{A}{RT}\left(1 - x_1^{\text{II}}\right)^2\right\}$$

and

$$\left(1 - x_1^{\text{I}}\right)\exp\left\{\frac{A}{RT}\left(x_1^{\text{I}}\right)^2\right\} = \left(1 - x_1^{\text{II}}\right)\exp\left\{\frac{A}{RT}\left(x_1^{\text{II}}\right)^2\right\}$$

where A=8163. The results using the MATHCAD worksheet with this problem number are

T (K)	$x_{\mathrm{H}}^{\mathrm{I}}$	$x_{\mathrm{H}}^{\mathrm{II}}$
250	0.023	0.977
275	0.035	0.965
300	0.050	0.950
325	0.0688	0.9312
350	0.0921	0.9079
375	0.1206	0.8794
400	0.1558	0.8442
425	0.2001	0.7999
450	0.2584	0.7416
475	0.3461	0.6539
485	0.4053	0.5949

Now do VLE calculation. Basis is $x_i \exp\left(-\dfrac{Ax_j^2}{RT}\right)P_i^{\mathrm{vap}} = y_i P$ and that $\sum_i x_i \exp\left(-\dfrac{Ax_j^2}{RT}\right)P_i^{\mathrm{vap}} = P$

The results using the MATHCAD worksheet with this problem number are

	P=0.1013 bar		P=1.013 bar		P=10.13 bar	
x_{H}	y_{H}	T K	y_{H}	T K	y_{H}	T K
0	0	300.18	0	351.56	0	424.17
0.01	0.4276	290.08				
0.02	0.6305	282.65	0.3185	342.29		
0.025					0.1578	418.62
0.03	0.7359	277.28				
0.04	0.7959	273.22	0.4892	335.70		
0.05					0.2642	414.45
0.06			0.5867	331.07		
0.07			0.6197	329.31		
0.075					0.3376	411.36
0.08			0.6457	327.84		
0.09						
0.10			0.6827	325.60	0.3888	409.09
0.125					0.4250	407.45
0.15					0.4505	406.29
0.175					0.4683	405.49
0.825					0.4568	405.41
0.85					0.4718	406.44
0.875					0.4934	407.95
0.9			0.5818	327.24	0.5249	410.17
0.91						
0.92			0.6110	328.39		
0.925					0.5717	413.43
0.93						
0.94			0.6540	330.06		
0.95					0.6444	418.30
0.96	0.7503	274.67	0.7188	332.50		
0.97	0.7898	275.60				
0.975					0.7661	425.85
0.98	0.8409	276.75	0.8216	336.15		
0.99	0.9083	278.22	0.8973	338.66	0.885	432.58
1.00	1.0	280.10	1.0	341.86	1.0	438.59

Mole fraction of *n*-hexane
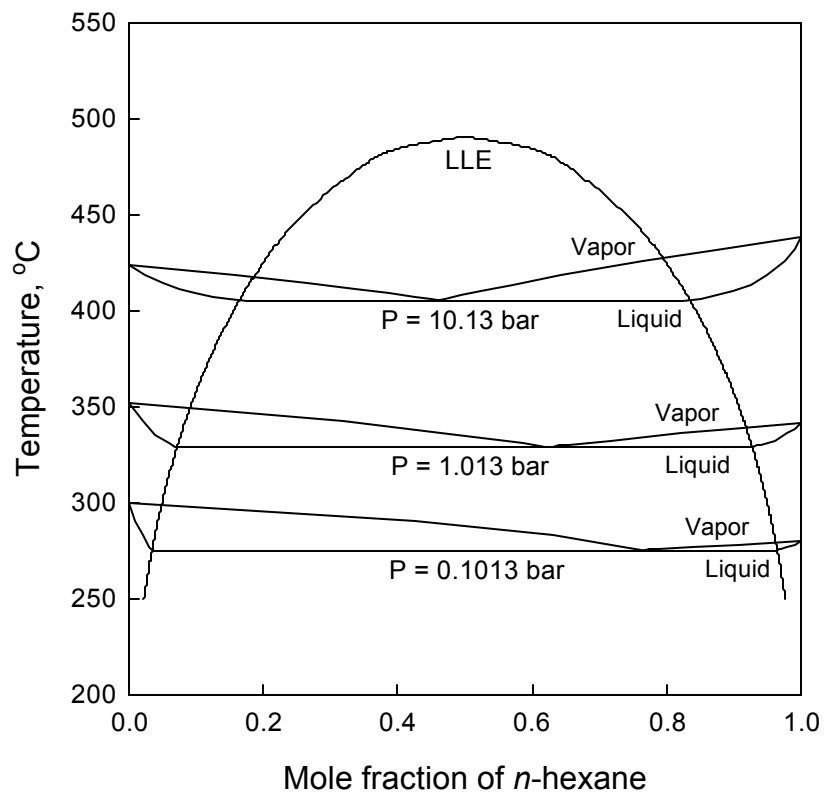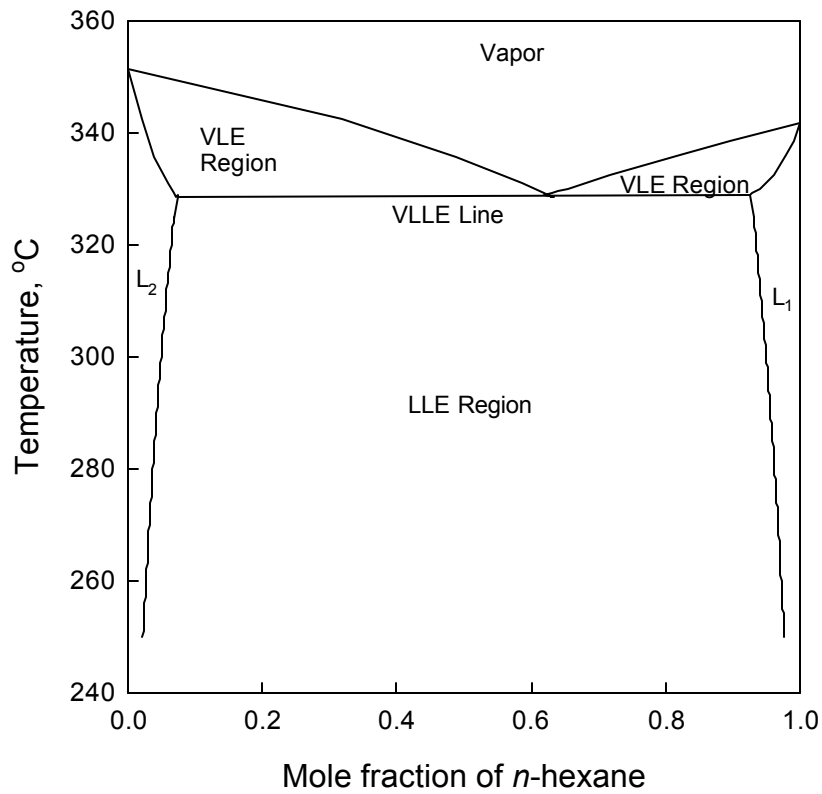
8.4-13(a)   Bubble point pressure.   Assume vapor phase is ideal. Then
$$x_i \boldsymbol{g}_i P_i^{\text{vap}} = y_i P$$

Solvent

$$x_1 \exp\left[\ln\frac{\boldsymbol{f}_1}{x_1} + \left(1 - \frac{1}{m}\right)\boldsymbol{f}_2 + x\boldsymbol{f}_2^2\right]P_1^{\text{vap}} = y_1 P \quad \Rightarrow \boldsymbol{f}_1 \exp\left[\left(1 - \frac{1}{m}\right)\boldsymbol{f}_2 + x\boldsymbol{f}_2^2\right]P_1^{\text{vap}} = y_1 P$$

(1)

Polymer

$$x_2 \exp\left[\ln\frac{\boldsymbol{f}_2}{x_2} - (m-1)\boldsymbol{f}_1 + x\boldsymbol{f}_1^2\right]P_2^{\text{vap}} = y_2 P \quad \Rightarrow \boldsymbol{f}_2 \exp\left[\left(1 - \frac{1}{m}\right)\boldsymbol{f}_2 + x\boldsymbol{f}_2^2\right]P_2^{\text{vap}} = y_2 P$$

but for the polymer
$$P_2^{\text{vap}} \sim 0 \Rightarrow y_2 \sim 0, \ y_1 \sim 1$$

Therefore, from eqn. (1)

$$P = P_{\substack{\text{bubble} \\ \text{point}}} = \boldsymbol{f}_1 \exp\left[\left(1 - \frac{1}{m}\right)\boldsymbol{f}_2 + x\boldsymbol{f}_2^2\right]P_1^{\text{vap}}$$

(b)   Liquid-liquid equilibrium

$$x_1^{\mathrm{I}} \exp\left[\ln\frac{f_1^{\mathrm{I}}}{x_1^{\mathrm{I}}} + \left(1-\frac{1}{m}\right)f_2^{\mathrm{I}} + x\left(f_2^{\mathrm{I}}\right)^2\right]P_1^{\mathrm{vap}}$$

$$= x_1^{\mathrm{II}} \exp\left[\ln\frac{f_1^{\mathrm{II}}}{x_1^{\mathrm{II}}} + \left(1-\frac{1}{m}\right)f_2^{\mathrm{II}} + x\left(f_2^{\mathrm{II}}\right)^2\right]P_1^{\mathrm{vap}}$$

$$\Rightarrow f_1^{\mathrm{I}}\exp\left[\left(1-\frac{1}{m}\right)f_2^{\mathrm{I}} + x\left(f_2^{\mathrm{I}}\right)^2\right] = f_1^{\mathrm{II}}\exp\left[\left(1-\frac{1}{m}\right)f_2^{\mathrm{II}} + x\left(f_2^{\mathrm{II}}\right)^2\right]$$

Similarly

$$f_2^{\mathrm{I}}\exp\left[(1-m)f_1^{\mathrm{I}} + x\left(f_1^{\mathrm{I}}\right)^2\right] = f_2^{\mathrm{II}}\exp\left[(1-m)f_1^{\mathrm{II}} + x\left(f_1^{\mathrm{II}}\right)^2\right]$$

Data needed
(a) bubble point   volume of solvent
                      volume of polymer
                      solvent-polymer c parameter
                      vapor pressure of solvent
(b) liquid-liquid equilibrium
                      volume of solvent
                      volume of polymer
                      solvent-polymer c parameter

8.4-14   Consider the condition for liquid-liquid phase equilibrium of a solute assuming that undissolved solute is also present

$$\overline{f}_i^{\mathrm{I}}\left(T, P, \underline{x}^{\mathrm{I}}\right) = \overline{f}_i^{\mathrm{II}}\left(T, P, \underline{x}^{\mathrm{II}}\right) = f_i^{\mathrm{L}}(T, P)$$

or

$$x_i^{\mathrm{I}}g\left(T, P, \underline{x}^{\mathrm{I}}\right)f_i^{\mathrm{L}}(T, P) = x_i^{\mathrm{II}}g\left(T, P, \underline{x}^{\mathrm{II}}\right)f_i^{\mathrm{L}}(T, P) = f_i^{\mathrm{L}}(T, P)$$

and then

$$x_i^{\mathrm{I}}g\left(T, P, \underline{x}^{\mathrm{I}}\right) = x_i^{\mathrm{II}}g\left(T, P, \underline{x}^{\mathrm{II}}\right) = 1$$

Therefore, if the activity of a species in solution is ever greater than unity, a separate phase pure (or very concentrated) in that species will form and reduce the activity of the species in the other phases to unity.

8.4-15 (also available as a MATHCAD worksheet)

8.4-15

$V1 := 1.6\cdot10^5$ $V2 := 1.5\cdot10^5$ $m := \dfrac{V2}{V1}$ $\mathrm{chi}(T) := \dfrac{1895}{T}$

$\mathrm{phi11(x11)} := \dfrac{x11\cdot V1}{x11\cdot V1 + (1-x11)\cdot V2}$ $\mathrm{phi21(x11)} := 1 - \mathrm{phi11(x11)}$

$\mathrm{phi12(x12)} := \dfrac{x12\cdot V1}{x12\cdot V1 + (1-x12)\cdot V2}$ $\mathrm{phi22(x12)} := 1 - \mathrm{phi12(x12)}$

$x11 := 0.01$ $x12 := 0.99$ $x21 := 1 - x11$ $x22 := 1 - x12$

$T := 600$

Given

$$\ln\left(\frac{phi11(x11)}{phi12(x12)}\right) + (phi12(x12) - phi11(x11)) \cdot \left(1 - \frac{1}{m}\right) + chi(T) \cdot \left(phi21(x11)^2 - phi22(x12)^2\right) = 0$$

$$\ln\left(\frac{phi21(x11)}{phi22(x12)}\right) + (phi11(x11) - phi12(x12)) \cdot (1 - m) + chi(T) \cdot \left(phi11(x11)^2 - phi12(x12)^2\right) = 0$$

$v := find(x11, x12)$
$$v = \begin{bmatrix} 0.05979 \\ 0.94392 \end{bmatrix}$$

$T := 700$ Given

$$\ln\left(\frac{phi11(x11)}{phi12(x12)}\right) + (phi12(x12) - phi11(x11)) \cdot \left(1 - \frac{1}{m}\right) + chi(T) \cdot \left(phi21(x11)^2 - phi22(x12)^2\right) = 0$$

$$\ln\left(\frac{phi21(x11)}{phi22(x12)}\right) + (phi11(x11) - phi12(x12)) \cdot (1 - m) + chi(T) \cdot \left(phi11(x11)^2 - phi12(x12)^2\right) = 0$$

$v := find(x11, x12)$
$$v = \begin{bmatrix} 0.11360 \\ 0.89956 \end{bmatrix}$$

$T := 800$ Given

$$\ln\left(\frac{phi11(x11)}{phi12(x12)}\right) + (phi12(x12) - phi11(x11)) \cdot \left(1 - \frac{1}{m}\right) + chi(T) \cdot \left(phi21(x11)^2 - phi22(x12)^2\right) = 0$$

$$\ln\left(\frac{phi21(x11)}{phi22(x12)}\right) + (phi11(x11) - phi12(x12)) \cdot (1 - m) + chi(T) \cdot \left(phi11(x11)^2 - phi12(x12)^2\right) = 0$$

$v := find(x11, x12)$
$$v = \begin{bmatrix} 0.21265 \\ 0.83659 \end{bmatrix}$$

$T := 825$ Given

$$\ln\left(\frac{phi11(x11)}{phi12(x12)}\right) + (phi12(x12) - phi11(x11)) \cdot \left(1 - \frac{1}{m}\right) + chi(T) \cdot \left(phi21(x11)^2 - phi22(x12)^2\right) = 0$$

$$\ln\left(\frac{phi21(x11)}{phi22(x12)}\right) + (phi11(x11) - phi12(x12)) \cdot (1 - m) + chi(T) \cdot \left(phi11(x11)^2 - phi12(x12)^2\right) = 0$$

$v := find(x11, x12)$
$$v = \begin{bmatrix} 0.25958 \\ 0.81687 \end{bmatrix}$$

T := 835   Given

$$\ln\left(\frac{phi11(x11)}{phi12(x12)}\right) + (phi12(x12) - phi11(x11)) \cdot \left(1 - \frac{1}{m}\right) + chi(T) \cdot \left(phi21(x11)^2 - phi22(x12)^2\right) = 0$$

$$\ln\left(\frac{phi21(x11)}{phi22(x12)}\right) + (phi11(x11) - phi12(x12)) \cdot (1 - m) + chi(T) \cdot \left(phi11(x11)^2 - phi12(x12)^2\right) = 0$$

v := find(x11, x12)

$$v = \begin{bmatrix} 0.28957 \\ 0.80795 \end{bmatrix}$$

T := 843   Given

$$\ln\left(\frac{phi11(x11)}{phi12(x12)}\right) + (phi12(x12) - phi11(x11)) \cdot \left(1 - \frac{1}{m}\right) + chi(T) \cdot \left(phi21(x11)^2 - phi22(x12)^2\right) = 0$$

$$\ln\left(\frac{phi21(x11)}{phi22(x12)}\right) + (phi11(x11) - phi12(x12)) \cdot (1 - m) + chi(T) \cdot \left(phi11(x11)^2 - phi12(x12)^2\right) = 0$$

v := find(x11, x12)

$$v = \begin{bmatrix} 0.34590 \\ 0.79783 \end{bmatrix}$$

The temperature 843 K is the highest at which a nontrivial solution is obtained. At higher temperature on the trivial solution of both phases being equal is obtained. Thus, the FH model predicts that LLE will occur up to this temperature. That is, 916.2 is the UCST for SAN and PMMA. Of course, at this high temperature the polymers are likely to decompose.

8.4-16   There are many different algorithms that could be used. One is a sequential one of first testing for LLE, if LLE does not occur then test for VLE. If LLE occurs, one must also test for VLLE, etc. In all the possibilities that must be tested for are only a liquid phase as stable phase, only a vapor as the stable phase, VLE with a liquid rich in component 1 as the equilibrium phases, VLE with a liquid rich in component 2 as the equilibrium phases, or VLLE.

8.5-1 Following Illustration 8.5-1 we have

$$\ln x_1 = -\frac{123(9.9 - \delta_2)\phi_2^2}{1.987 \times 293.2} - 1.3158$$

where $\phi_2 = x_2 \dfrac{\underline{V}_2}{x_1 \underline{V}_1 + x_2 \underline{V}_2}$

Benzene: $\underline{V}_2 = 89$ cc/mol, $\delta_2 = 9.2$(cal cc)$^{1/2}$ by iteration we find that $x_1 = 0.256$ (exp't $= 0.241$)

Toluene: $\underline{V}_2 = 107$, $\delta_2 = 8.9$ by iteration we find that $x_1 = 0.239$ (exp't $= 0.224$)

Carbon tetrachloride: $\underline{V}_2 = 97$, $\delta_2 = 8.6$ by iteration we find that $x_1 = 0.221$ (exp't $= 0.205$)

Chlorobenzene is a somewhat more complicated calculation in that the regular solution parameters are not available. From Perry's "Chemical Engineer's Handbook", the following data is obtained:

$$\text{molecular weight } = 112.56 \quad \text{specific gravity } = 1.107$$

P^{vap}(Pa)	133.3	666.7	1333.3	2666.7	5333.3
T(°C)	-13.0	10.6	22.2	35.3	49.7

Using this data we find $\underline{V}_2 = 101.68$ cc/mol ; $\dfrac{\Delta \underline{H}^{\text{vap}}}{RT^2} = 0.05613$ K^{-1} ; $\Delta \underline{U}^{\text{vap}} = 39011$ J/mol and

$$\delta_2 = \left(\frac{\Delta \underline{U}^{\text{vap}}}{\underline{V}_2}\right)^{1/2} = 9.58 \text{ (cal/cc)}^{1/2} \text{ with these parameters, by iteration, we find } x_1 = 0.2655$$

(exp't $= 0.256$). Thus, the order of our predictions is correct, but our predictions are between 4 and 8% too high!

8.5-2 We will, again, use regular solution theory. Following illustration 8.5-1, we have

$$\ln x_1 = -0.21113(9.9 - \delta_2)\phi_2^2 - 1.316 \text{ for a single solvent} \qquad (1)$$

and

$$\ln x_1 = -0.21113(9.9 - \overline{\delta})^2 - 1.316 \text{ for mixed solvents} \qquad \textbf{(2)}$$

where

$$\overline{\delta} = \sum_j \phi_j \delta_j \text{ and } \phi_j = \frac{x_j \underline{V}_j}{\sum_l x_l \underline{V}_l}$$

and the sums extend over all solvent and solute species. The parameters used in the calculation are listed below

	$\underline{V}$(cc/mol)	δ(cal/cc)$^{1/2}$
n-hexane	132	7.3
CCl$_4$	97	8.6

Since the mole fraction of naphthalene appears on the right-hand side of eqns. (1) and (2), through the volume fraction and solubility parameter terms, these equations must be solved by trial and error. The results are given below

Composition of initial mixture		Equilibrium solubility of naphthalene	Equilibrium composition of mixture	
x_H	x_{CCL_4}	x_{NA}	x_H	x_{CCL_4}
1.0	0	0.079	0.921	0
0.75	0.25	0.107	0.670	0.223
0.50	0.50	0.143	0.429	0.429
0.25	0.75	0.183	0.204	0.613
0	1.0	0.222	0	0.778

8.5-3 In the book "The Properties of Gases and Liquids", 4th edition, by Reid, Prausnitz & Poling (McGraw-Hill, 1987), we find the following properties for biphenyl $T_C = 789$ K , $P_C = 385$ bar , $\omega = 0.372$, $T_B = 529.3$ K . The vapor pressure is given by

$$\ln \frac{P^{\text{vap}}}{P_C} = (1-x)^{-1}\left[-7.6400x + 1.23008x^{1.5} - 3.67908x^3 - 2.29172x^6\right]$$

$$\text{where } x = 1 - \frac{T}{T_C} \text{ (liquid range)}$$

Also, the liquid density is 0.990 g/cc and $MW = 154.212$ The "Handbook of Chemistry and Physics" gives the following for the sublimation pressure of biphenyl

$$\log_{10} P(\text{mm Hg}) = 11.168 - \frac{3959}{T} \text{ for } 6°C \le T \le 26°C$$

Neither of these expression is good for the temperature range of interest to us here, but we will use the expression above. In this way the following results are obtained

$T = 49°C$

P_B^{vap}	$P(\text{bar})$	P_{Poynting}	$f_B(\text{bar})$	$y_B(\exp)$	$y_B(calc)$
1.008×10^{-4}	155.6	2.4717	2.4916×10^{-4}	0.01782	0.0082
	204.5	3.2847	3.3112×10^{-4}	0.02689	0.015
	296.5	5.6087	5.6540×10^{-4}	0.03605	0.0295
	379.4	9.0833	9.1566×10^{-4}	0.03795	0.050

$T = 55.2°C$

1.7200	110.6	1.8796	3.2330×10^{-4}	0.00447	0.0112
	132.6	2.1310	3.6654×10^{-4}	0.01031	0.0038
	167.2	2.5961	4.4654×10^{-4}	0.01829	0.0095
	252.5	4.2237	7.2649×10^{-4}	0.03516	0.0265
	334.6	6.7474	1.1606×10^{-3}	0.05615	0.057
	412.8	10.5418	1.8132×10^{-3}	0.07918	0.290
	469.9	14.6018	2.5116×10^{-3}	0.11054	0.325
	482.7	15.7081	2.7019×10^{-3}	0.12669	0.335

$T = 57.5°C$

	361.4	7.7502	1.6171×10^{-3}	0.06365	0.30
	430.4	11.4580	2.3907×10^{-3}	0.09208	0.34

Here the Poynting factor was calculated from $\exp\left[\dfrac{\left(P-P_B^V\right)\cdot\frac{154.212}{0.990}}{83.14\cdot T}\right]$. To proceed, we now must

choose a k_{CO_2-B} value. I have not done an extensive study, but based on the $T=49°C$ isotherm,

$k_{CO_2-B}=0.08$ seems like a reasonable compromise value. This value was used to obtain the
predicted vapor mole fractions by using VLMU (species fugacity option) and, by trial and error
choices of the compositions, matching the biphenyl fugacity. [Note, if you or your students obtain
a better correlation, please let me know.] Clearly, the overall agreement is not very good. It is
qualitatively, but not quantitatively, correct.

8.5-4   (a)   From the data in the problem statement, the fugacity of solid naphthalene at $50°C$ and 60 bar is

$$f_N = 1.11\times10^{-3}\,\text{bar}\times$$
$$\exp\left\{\frac{\left(60-1.11\times10^{-3}\right)\times0.112\ \text{bar}\cdot\text{m}^3/\text{kmol}}{(273.15+50)\text{K}\times83.14\ \text{bar}\cdot\text{cm}^3/\text{kmol}\times10^{-6}\ \text{m}^3/\text{cm}\times10^3\ \text{mol}/\text{kmol}}\right\}$$
$$=1.425\times10^{-3}\ \text{bar}$$

The fugacity coefficient for the virial equation of state is
$$\ln\phi_i = \left(2\sum y_j B_{ij}-B\right)\frac{P}{RT}\ ;\ \text{with}\ B=\sum\sum y_i y_j B_{ij}$$

Now we will assume that y_N is small so that $y_N\approx0$. In this case $B\cong B_{CO_2}$ and

$$\left(2\sum_j y_j B_{ij}-B\right)=\left(2\times B_{N-CO_2}-B_{CO_2-CO_2}\right)\ \text{so}$$

$$\ln\phi = \left\{\left(2\times(-0.405)-(-0.103)\right)\frac{\text{m}^3}{\text{kmol}}\times\frac{60\ \text{bar}}{323.15\ \text{K}\times10^3\ \frac{\text{mol}}{\text{kmol}}\times8.314\times10^{-5}\ \frac{\text{bar m}^3}{\text{mol K}}}\right\}$$
$$=-1.579\Rightarrow\phi_N=0.206$$

so

$$y_N = \frac{f_N^{sat}\exp\left[\frac{V\left(P-P^{sat}\right)}{RT}\right]}{\phi_N} = \frac{1.425\times10^{-3}}{0.206}=0.692\times10^{-2}=0.00692$$

(b)   Now using the Peng-Robinson Equation of state. We use the program VLMU (species fugacity option), at the specified T and P, with $k_{CO_2-N}=0.103$ (as in illustration 8.5-4) and adjust the

composition of naphthalene until a vapor phase fugacity of naphthalene of 1.425×10^{-3} bar is obtained. By trial and error, I find $y_N=0.000225$, which is much lower than the virial equation result. Since, at somewhat different temperatures and pressures, the Peng-Robinson model was in reasonably good agreement with experimental data, I have more confidence in this result.

8.6-1   Notation:

N_i = total number of moles of species i

N_i^J = number of moles of species i in phase J

$N^J = \sum_i N_i^J$ = total number of moles in phase J

x_i^J = mole fraction of species i in phase $J = \dfrac{N_i^J}{\sum_j N_j^J}$

(a) Two liquid phases

Equilibrium conditions: $\bar{f}_i^{\,I}\left(T,P,\underline{x}^{I}\right) = \bar{f}_i^{\,II}\left(T,P,\underline{x}^{II}\right)$ $i = 1, 2, 3$

Mass balance constraints: $N_i = N_i^I + N_i^{II}$ $i = 1, 2, 3$

Thus we have six equations for the six unknowns N_i^J; $J = I, II$ $i = 1, 2, 3$

Alternatively, we can treat x_1^I, x_2^I, x_1^{II}, x_2^{II}, N^I and N^{II} as the six unknowns.

(b) Two liquid phases, but species 2 and 3 completely immiscible.

$$\text{Equilibrium condition } \bar{f}_1^{\,I}\left(T,P,\underline{x}^{I}\right) = \bar{f}_1^{\,II}\left(T,P,\underline{x}^{II}\right) \tag{1}$$

$$\text{Mass balance constraint } N_1 = N_1^I + N_1^{II} \tag{2}$$

Also

$$N_2 = N_2^I \quad N^I = N_1^I + N_2^I \quad x_1^I = \frac{N_1^I}{N_1^I + N_2^I}$$

$$N_3 = N_3^{II} \quad N^{II} = N_1^{II} + N_3^{II} \quad x_1^{II} = \frac{N_1^{II}}{N_1^{II} + N_3^{II}}$$

Basically, we have two equations [(1) and (2)] for the two unknowns N_1^I and N_1^{II}. The other equations merely relate the unknown N_1^I and N_1^{II} to the mole fractions that appear in eqn. (1).

(c) Three liquid phases:

equilibrium conditions $\begin{cases} \bar{f}_i^{\,I}\left(T,P,\underline{x}^{I}\right) = \bar{f}_i^{\,II}\left(T,P,\underline{x}^{II}\right) & i = 1, 2, 3 \\ \bar{f}_i^{\,I}\left(T,P,\underline{x}^{I}\right) = \bar{f}_i^{\,III}\left(T,P,\underline{x}^{III}\right) & i = 1, 2, 3 \end{cases}$

mass balance constraints $N_i = N_i^I + N_i^{II} + N_i^{III}$ $i = 1, 2, 3$

Thus we have 9 equations for the 9 unknown N_i^J, $i = 1, 2, 3$; $J = 1, 2, 3$ or x_1^I, x_2^I, x_1^{II}, x_2^{II}, x_1^{III}, x_2^{III}, N^I, N^{II}, N^{III}.

8.6-2   Preliminary calculations

$\text{MW}_{C_7H_6O_5} = 170$ g/mol ; $C_{C_7H_6O_5} = 0.01176$ mol/liter

p-hydroxybenzoic acid

$\text{MW}_{C_7H_8O_3} = 138$ g/mol ; $C_{C_7H_8O_3} = 0.0145$ mol/liter

Notation

II = aqueous phase, I = diethyl ether phase

$$\frac{C_i^I}{C_i^{II}} \equiv K_i \text{ or } C_i^{II} = \frac{C_i^I}{K_i} \tag{1}$$

Also

$$C_i^I V^I + C_i^{II} V^{II} = N_i = \text{ initial number of moles of species } i$$

or, using eqn. (1)

$$C_i^{\mathrm{I}} V^{\mathrm{I}} + \frac{C_i^{\mathrm{I}} V^{\mathrm{II}}}{K_i} = N_i$$

Thus,

$$C_i^{\mathrm{I}} = \frac{N_i}{\left(V^{\mathrm{I}} + K_i^{-1} V^{\mathrm{II}}\right)} \text{ and } C_i^{\mathrm{II}} = K_i^{-1} C_i^{\mathrm{I}} = \frac{K_i^{-1} N_i}{\left(V^{\mathrm{I}} + K_i^{-1} V^{\mathrm{II}}\right)}$$

Since diethyl ether and water are so insoluble, and since relatively small amounts of gallic acid and p-hydroxybenzoic acid will be transferred, I will assume that V^{I} and V^{II} are unchanged during the partitioning process.

Finally $N_i = V^{\mathrm{II}} \times C_i^0$, where $C_i^0 =$ concentration of species in the water-phase before it is contacted with the diethyl ether.

(a) Here $\qquad V^{\mathrm{I}} = 5$, $\qquad V^{\mathrm{II}} = 1$; $\qquad C_{\mathrm{C_7H_6O_5}}^{\mathrm{I}} = \dfrac{0.01176}{5 + \frac{1}{0.25}} = 0.001307$ mol/liter ;

$$C_{\mathrm{C_7H_6O_5}}^{\mathrm{II}} = \frac{C_{\mathrm{C_7H_6O_5}}^{\mathrm{I}}}{0.25} = 0.005227 \text{ mol/liter ;} \qquad C_{\mathrm{C_7H_8O_3}}^{\mathrm{I}} = \frac{0.0145}{5 + \frac{1}{8}} = 0.002829 \text{ mol/liter ;}$$

$$C_{\mathrm{C_7H_8O_3}}^{\mathrm{II}} = \frac{C_{\mathrm{C_7H_8O_3}}^{\mathrm{I}}}{8} = 0.000354 \text{ mol/liter}$$

(b and c)

Using 2 batches of diethyl ether, each of 2.5 liters
1st batch

$$\left[C_{\mathrm{C_7H_6O_5}}^{\mathrm{I}}\right]_1 = \frac{0.01176}{2.5 + \frac{1}{0.25}} = \left[C_{\mathrm{C_7H_6O_5}}^{\mathrm{II}}\right]_1 = \frac{\left[C_{\mathrm{C_7H_6O_5}}^{\mathrm{I}}\right]_1}{0.25}$$

$$\left[C_{\mathrm{C_7H_8O_3}}^{\mathrm{I}}\right]_1 = \frac{0.0145}{5 + \frac{1}{8}} = \left[C_{\mathrm{C_7H_8O_3}}^{\mathrm{II}}\right]_1 = \frac{\left[C_{\mathrm{C_7H_8O_3}}^{\mathrm{I}}\right]_1}{8}$$

After second batch

$$\left[C_{\mathrm{C_7H_6O_5}}^{\mathrm{I}}\right]_2 = \frac{\left[C_{\mathrm{C_7H_6O_5}}^{\mathrm{II}}\right]_1}{2.5 + \frac{1}{0.25}} = \frac{\frac{\left[C_{\mathrm{C_7H_6O_5}}^{\mathrm{I}}\right]_1}{K_{\mathrm{C_7H_6O_5}}}}{2.5 + \frac{1}{0.25}} = \frac{\frac{\left[C_{\mathrm{C_7H_6O_5}}^{0}\right]}{K_{\mathrm{C_7H_6O_5}}}}{\left(2.5 + \frac{1}{0.25}\right)^2}$$

or, in general

$$\left[C_{\mathrm{C_7H_6O_5}}^{\mathrm{I}}\right]_n = \frac{C_{\mathrm{C_7H_6O_5}}^{0}}{K_{\mathrm{C_7H_6O_5}}^{n-1}\left[\frac{V^{\mathrm{I}}}{V^{\mathrm{II}}} + \frac{1}{K_{\mathrm{C_7H_6O_5}}}\right]^n} = \frac{C_{\mathrm{C_7H_6O_5}}^{0} K_{\mathrm{C_7H_6O_5}}}{\left[1 + K_{\mathrm{C_7H_6O_5}} \frac{V^{\mathrm{I}}}{V^{\mathrm{II}}}\right]^n}$$

$$\left[C_{\mathrm{C_7H_6O_5}}^{\mathrm{II}}\right]_n = \frac{C_{\mathrm{C_7H_6O_5}}^{0}}{K_{\mathrm{C_7H_6O_5}}^{n}\left[\frac{V^{\mathrm{I}}}{V^{\mathrm{II}}} + \frac{1}{K_{\mathrm{C_7H_6O_5}}}\right]^n} = \frac{C_{\mathrm{C_7H_6O_5}}^{0}}{\left[1 + K_{\mathrm{C_7H_6O_5}} \frac{V^{\mathrm{I}}}{V^{\mathrm{II}}}\right]^n}$$

with a similar expression for p-hydroxybenzoic acid. Using these equations we obtain the following results

		% initial $C_7H_6O_5$ in aq. phase	% initial $C_7H_8O_3$ in aq. phase
1.	5 liter batch		
	$n = 1$, $V^I = 5$	44.45	2.44
2.	$2\frac{1}{2}$ liter batches		
	$n = 2$, $V^I = 2.5$	37.87	0.227
5.	1 liter batches		
	$n = 5$, $V^I = 1$	32.77	0.001693

↑

Note the huge purification in five stages

8.6-3 Regular solution theory

$$\ln \gamma_1 = \underline{V}_1 \phi_2^2 \frac{(\delta_1 - \delta_2)^2}{RT} \; ; \; \ln \gamma_2 = \underline{V}_2 \phi_1^2 \frac{(\delta_1 - \delta_2)^2}{RT}$$

Here

$$\underline{V}_{Br}^L = 51 \text{ cc/mol} \qquad \delta_{Br} = 11.5 \text{ (cal/cc)}^{1/2}$$
$$\underline{V}_{CCl_4}^L = 97 \text{ cc/mol} \quad \delta_{CCl_4} = 8.6 \text{ (cal/cc)}^{1/2}$$

$$\ln \gamma_{Br} = 51 \left[\frac{97 x_{CCl_4}}{51 \times x_{Br} + 97 x_{CCl_4}} \right]^2 \frac{(11.5 - 8.6)^2}{1.987 \times 2.98.2}$$

$$= 0.7239 \left(\frac{97(1 - x_{Br})}{51 x_{Br} + 97(1 - x_{Br})} \right)^2$$

Thus

x_{Br}	3.85×10^{-3}	9.6×10^{-3}	0.047	0.0923	0.135	0.177	0.217
$\gamma_{Br}^{CCl_4}$	2.06	2.047	1.990	1.920	1.856	1.794	1.736
$\gamma_{Br}^{H_2O} = \dfrac{x_{Br}^{CCl_4} \gamma_{Br}^{CCl_4}}{x_{Br}^{H_2O}}$	293.8	298.0	301.7	298.8	290.6	294.0	292.0

8.6-4 Regular solution parameters

$$Br_2 \quad \underline{V}^L = 51 \text{ cc/mol} \quad \delta = 11.5 \text{ (cal/cc)}^{1/2}$$
$$CS_2 \quad \underline{V}^L = 61 \text{ cc/mol} \quad \delta = 10.0 \text{ (cal/cc)}^{1/2}$$

$$RT \ln \gamma_{Br_2} = \underline{V}_{Br_2}^L \phi_{CS_2}^2 \left(\delta_{Br_2} - \delta_{CS_2} \right)^2$$

In CS_2 phase, let

$x = $ mol CS_2/liter of solution; $y = $ mol Br_2/liter of solution

Assuming no volume change on mixing, we then have

$$0.051y + 0.061x = 1 \; \text{ or } \; x = \frac{(1 - 0.051y)}{0.061}$$

Now at

extremes of Br_2 conc. in CS_2 $\left(\begin{array}{l} y = 0.005 \Rightarrow x = 16.39 \quad x_{Br_2} = 3.05 \times 10^{-4} \quad \phi_{CS_2} \approx 1 \\ y = 0.095 \Rightarrow x = 16.31 \quad x_{Br_2} = 5.79 \times 10^{-4} \quad \phi_{CS_2} \approx 1 \end{array} \right.$

Thus we can take $\phi_{CS_2} \approx 1$ over the whole composition range, and

$$\ln\gamma_{Br_2}^{CS_2} = 51 \times 1^2 \times \frac{(11.5-10.0)^2}{1.987 \times 298.15} = 0.1937$$

or $\gamma_{Br_2}^{CS_2} \approx 1.214$ over whole composition range. Now

$$K = \frac{x_1^{I}}{x_1^{II}} = \frac{\gamma_1^{II}}{\gamma_1^{I}} \quad \text{where} \quad \begin{array}{l} \text{I = aqueous phase} \\ \text{II = organic phase} \end{array}$$

$$\Rightarrow \gamma_1^{I} = \frac{\gamma_1^{II}}{K}$$

where

$$K = \frac{x_{Br_2} \text{ in aqueous phase}}{x_{Br_2} \text{ in organic phase}} = \frac{\frac{\text{moles Br}_2}{\text{moles Br}_2 + \text{moles H}_2\text{O}}}{\frac{\text{moles Br}_2}{\text{moles Br}_2 + \text{moles CS}_2}}$$

Now we expect

$$\begin{array}{l} \text{moles H}_2\text{O} >> \text{moles Br}_2 \\ \text{moles CS}_2 >> \text{moles Br}_2 \end{array} \Rightarrow K \approx \frac{\frac{\text{moles Br}_2}{\text{moles H}_2\text{O}}}{\frac{\text{moles Br}_2}{\text{moles CS}_2}}$$

Data given in problem statement is for

$$K' = \frac{\frac{\text{moles Br}_2}{\text{liter aqueous solution}}}{\frac{\text{moles Br}_2}{\text{liter CS}_2 \text{ solution}}}$$

Thus

$$K = K' = \frac{\frac{18}{1000} \frac{\text{liters}}{\text{mol water}}}{\frac{76.18}{1000 \times 1.263} \frac{\text{liters}}{\text{mol CS}_2}} = 0.2984 K'$$

Also

$$\gamma_{Br_2}^{H_2O} = \frac{\gamma_{Br_2}^{CS_2}}{0.2984 K'}$$

From which we obtain the following

y	x_{Br_2}	$\gamma_{Br_2}^{H_2O}$		
		$1/16\,m$	$1/4\,m$	$1/2\,m$
0.005	3.1×10^{-4}	58.45	23.45	
0.02	1.2×10^{-3}	62.48	24.36	13.43
0.03	1.8×10^{-3}	65.51	24.96	13.65
0.04	2.5×10^{-3}		25.59	13.88
0.05	3.1×10^{-3}		26.25	14.13
0.06	3.7×10^{-3}		26.94	14.37
0.095	5.8×10^{-3}			15.01

To infer a relationship between $\gamma_{Br_2}^{H_2O}$ and the salt molarity m I plotted $\ln\gamma_{Br_2}^{H_2O}$ versus $\ln m$ and various powers of m using the data at $y = 0.02$. I found that the expression $\ln_{Br_2}^{H_2O} = Cm^{-1/4}$ gave a very good fit of the data. The parameter C is a weakly increasing function of the bromine mole fraction; I did not attempt to determine this dependence.

8.6-5 Consistency relation between P^{vap}, H and solubility

$$x_i H_i = P_i = x_i \gamma_i P_i^{vap} = x_i \gamma_i^{\infty} P_i^{vap}$$

$$H_i = \gamma_i^{\infty} P_i^{vap}$$

For a substance above it's melting point (liquid as a pure component) but only of limited solubility

$$x_i^{\text{sat}} \gamma_i^{\infty} = 1 , \ \gamma_i^{\infty} = \frac{1}{x_i^{\text{sat}}} \quad \Rightarrow H_i = \frac{P_i^{\text{vap}}}{x_i^{\text{sat}}}$$

Now in Table 8.6-1 data are for H in $C_i H_i' = P_i = C_{\text{W}} x_i H_i' = x_i H_i$ so

$$H_i' = \frac{H_i}{C_{\text{W}}} = \frac{P_i^{\text{vap}}}{C_{\text{W}} x_i^{\text{sat}}} = \frac{P_i^{\text{vap}}}{C_i^{\text{sat}}}$$

Example 1: 1, 3 butadiene $MW_{C_4 H_8} = 48 + 8 = 56$

$$H_i' = \frac{281 \text{ kPa}}{735 \text{ mg/L} \times (1 \text{ g}/1000 \text{ mg}) \times (1000 \text{ L}/\text{m}^3) \times (1 \text{ mol}/56 \text{ g})}$$

$$= 21.4 \text{ kPa}/\text{m}^3\text{mol} = 0.214 \text{ bar}/\text{m}^3\text{mol (compared to 0.2016)}$$

Example 2: 1, 2, 4 Trichlorobenzene $MW_{C_6 H_3 Cl_3} = 72 + 3 + 3 \times 35.5 = 181.5$

$$H_i' = \frac{0.039}{48.8/181.5} = \frac{0.039 \times 181.5}{48.8} = 0.145 \text{ kPa m}^3/\text{mol}$$

$$= 1.45 \times 10^{-1} \text{ kPa m}^3/\text{mol}$$

$$= 1.45 \times 10^{-3} \text{ bar m}^3/\text{mol (compared to } 1.44 \times 10^{-3})$$

Example 3: Aniline

$P_i^{\text{vap}} = 0.065 \text{ kPa} = 6.5 \times 10^{-4} \text{ bar}$

Solubility $= 3.607 \times 10^4 \text{ ppm} = 36070 \text{ mg/L}$

$$H_i' = \frac{6.5 \times 10^{-4} \text{ bar}}{3.6070 \times 10^4 \text{ mg/L} \times (1 \text{ g}/1000 \text{ mg}) \times (1000 \text{ L}/\text{m}^3) \times (1 \text{ mol}/93.12)}$$

$$= \frac{6.5 \times 10^{-8}}{3.6070} \times 93.12 \text{ bar}/\text{m}^3 \text{ mol}$$

$$= 167.8 \times 10^{-8} = 1.678 \times 10^{-6} \text{ bar}/\text{m}^3\text{mol (something wrong in this case, compare with 0.138)}$$

Example 4: 1, 2-Dichlorobenzene $P^{\text{vap}} = 0.196 \text{ kPa} = 1.96 \times 10^{-3} \text{ bar}$
Solubility $= 156 \text{ mg/L} ;\ MW = 147.01$

$$H_i' = \frac{1.96 \times 10^{-3} \text{ bar}}{156 \text{ mg/L} \times (1 \text{ g}/1000 \text{ mg}) \times (1000 \text{ L}/\text{m}^3) \times (1 \text{ mol}/147.01)}$$

$$= 1.85 \times 10^{-3} \text{ bar}/\text{m}^3\text{mol (compared to } 1.2 \times 10^{-3})$$

Example 5: Ethyl benzene $P^{\text{vap}} = 1.27 \text{ kPa} = 1.27 \times 10^{-2} \text{ bar} ;\ MW = 106.16$

$$H_i' = \frac{1.27 \times 10^{-2}}{161/106.16} = \frac{1.27 \times 10^{-2} \times 106.16}{161} = 8.374 \times 10^{-3} \text{ bar}/\text{m}^3 \text{ mol}$$

$$\left(\text{compared to } 8.96 \times 10^{-3} \right)$$

Example 6: Napthalene $P^{\text{vap}} = 1.1 \times 10^{-2} \text{ kPa} = 1.1 \times 10^{-4} \text{ bar} ;\ MW = 128.16$

$$H_i' = \frac{1.1 \times 10^{-4} \times 128.16}{31.7} = 4.45 \times 10^{-4} \text{ bar}/\text{m}^3 \text{ mol} (\text{compared to } 5.0 \times 10^{-4} \text{ bar}/\text{m}^3 \text{ mol})$$

Example 7: Styrene $P^{\text{vap}} = 0.88 \text{ kPa} = 8.8 \times 10^{-3} \text{ bar} ;\ MW = 104.14$

$$H_i' = \frac{8.8 \times 10^{-3} \times 104.14}{310} = 2.96 \times 10^{-3} \text{ bar}/\text{m}^3 \text{ mol (compared to } 2.85 \times 10^{-3} \text{ bar}/\text{m}^3 \text{ mol})$$

8.7-1   Let T_{NB} = normal boiling temperature of the solvent; T_B = actual (elevated) boiling temperature of solvent. At the actual boiling temperature

$$\bar{f}_1^{\,L}(T_B, P, \underline{x}) = \bar{f}_1^{\,V}(T, P, \underline{y}) = f_1^{\,V}(T_B, P)$$

Since the vapor at the vapor-liquid interface of either a pure boiling species or, as here, a liquid with a nonvolatile solution is the pure solvent species. Now,
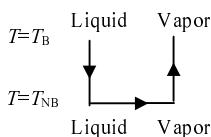
$$\bar{f}_1^{\,L}(T_B, P, \underline{x}) = x_1\,{}_1(\underline{x}) f_1^{\,L}(T_B, P)$$

So that

$$x_1\,{}_1(\underline{x}) = \frac{f_1^{\,V}(T_B, P)}{f_1^{\,L}(T_B, P)}$$

and

$$\ln[x_1\,{}_1(\underline{x})] = \ln\frac{f_1^{\,V}(T_B, P)}{f_1^{\,L}(T_B, P)} = \frac{\underline{G}_1^{\,V}(T_B, P) - \underline{G}_1^{\,L}(T_B, P)}{RT_B}$$

Now following the constant pressure path below

$$T=T_B \quad \text{Liquid} \quad \text{Vapor}$$
$$T=T_{NB} \quad \text{Liquid} \quad \text{Vapor}$$

we obtain

$$\Delta\underline{H}^{\mathrm{vap}}(T_B, P) = \Delta\underline{H}^{\mathrm{vap}}(T_{NB}) + \int_{T_{NB}}^{T_B} \Delta C_{\mathrm{P}} dT$$

$$\Delta\underline{S}^{\mathrm{vap}}(T_B, P) = \Delta\underline{S}^{\mathrm{vap}}(T_{NB}) + \int_{T_{NB}}^{T_B} \frac{\Delta C_{\mathrm{P}}}{T} dT$$

where

$$\Delta C_{\mathrm{P}} = C_{\mathrm{P}}^{V} - C_{\mathrm{P}}^{L}$$

Since $\Delta\underline{G}^{\mathrm{vap}}(T_{NB}, P) = \Delta\underline{H}^{\mathrm{vap}}(T_{NB}) - T_{NB}\Delta\underline{S}^{\mathrm{vap}}(T_{NB}) = 0$. By equilibrium requirement for pure fluid at the normal boiling point,

$$\Delta\underline{S}^{\mathrm{vap}}(T_{NB}) = \frac{\Delta\underline{H}^{\mathrm{vap}}(T_{NB})}{T_{NB}}$$

and

$$\Delta\underline{G}^{\mathrm{vap}}(T_B, P) = \Delta\underline{H}^{\mathrm{vap}}(T_{NB})\left[1 - \frac{T_B}{T_{NB}}\right] + \int_{T_{NB}}^{T_B} \Delta C_{\mathrm{P}} dT - T_B \int_{T_{NB}}^{T_B} \frac{\Delta C_{\mathrm{P}}}{T} dT$$

so that we obtain

$$\ln x_1\,{}_1(x_1) = \frac{\Delta\underline{H}^{\mathrm{vap}}(T_{NB})}{RT_B}\left[1 - \frac{T_B}{T_{NB}}\right] + \frac{1}{RT_B}\int_{T_{NB}}^{T_B} \Delta C_{\mathrm{P}} dT - \frac{1}{R}\int_{T_{NB}}^{T_B} \frac{\Delta C_{\mathrm{P}}}{T} dT$$

compare with eqn. (8.7-2).

   If ΔC_{P} is independent of temperature we obtain

$$\ln x_1 \,_1(x_1) = \frac{\Delta \underline{H}^{vap}(T_{NB})}{RT_B}\left[1 - \frac{T_B}{T_{NB}}\right] + \frac{\Delta C_P}{R}\left[1 - \frac{T_{NB}}{T_B} - \ln \frac{T_B}{T_{NB}}\right]$$

Furthermore, for small solute concentrations
$$_1(x_1) \approx 1 \text{ and } \ln x_1 = \ln(1 - x_2) \approx -x_2$$

so that

$$-x_2 = \frac{\Delta \underline{H}^{vap}(T_{NB})}{RT_B}\left[1 - \frac{T_B}{T_{NB}}\right] + \frac{\Delta C_P}{R}\left[1 - \frac{T_{NB}}{T_B} - \ln \frac{T_B}{T_{NB}}\right]$$

and, when the ΔC_P terms may be neglected

$$-x_2 = \frac{\Delta \underline{H}^{vap}(T_{NB})}{RT_{NB}}\left(\frac{T_{NB} - T_B}{T_B}\right)$$

or

$$(T_B - T_{NB}) = \underset{\substack{\uparrow \\ \text{boiling point elevation}}}{\Delta T_B} \cong \frac{RT_B T_{NB} x_2}{\Delta \underline{H}^{vap}(T_{NB})} \approx \frac{RT_{NB}^2 x_2}{\Delta \underline{H}^{vap}(T_{NB})}$$

compare with freezing point depression equation

$$T_m - T_f = \underset{\substack{\uparrow \\ \text{freezing point depression}}}{\Delta T} \cong \frac{RT_m^2 x_2}{\Delta \underline{H}^{fus}(T_m)}$$

Since $\Delta \underline{H}^{vap} > \Delta \underline{H}^{fus}$, it follows that the addition of a solute depresses the freezing point to a greater extent than it raises the boiling point!

8.7-2 Since methanol, ethanol, glycerol and water all have -OH groups they are, in some sense, similar. Also, since no activity coefficient data are given, we will assume that the mixtures involved are ideal. [One really should go to the library and try to find activity coefficient data for these systems, or data from which activity coefficients can be computed or use the van Laar constants in Table 7.5-1]. Assuming ideal solution behavior we obtain, from eqn. (8.7-2).

$$\ln x_1 = -\frac{\Delta \underline{H}^{fus}(T_m)}{R}\left[\frac{T_m - T_f}{T_m T_f}\right] - \frac{\Delta C_P}{R}\left[1 - \frac{T_m}{T_f} + \ln \frac{T_m}{T_f}\right]$$

Now $\Delta \underline{H}^{fus} = 6003$ J/mol and from Problem 5.26

$$\Delta C_P = C_P^L - C_P^S = (4.22 - 2.1) \text{ J/g}^\circ\text{C} \times 18 \text{ g/mol} = 38.16 \text{ J/mol}^\circ\text{C}$$

Thus, for $T_m = 0^\circ\text{C} = 273.15$ K and $T_f = -12^\circ\text{C} = 261.15$

$$\ln x_1 = -\frac{6003}{8.314}\left[\frac{273.15 - 261.15}{273.15 \times 261.15}\right] - \frac{38.16}{8.314}\left[1 - \frac{273.15}{261.15} + \ln \frac{273.15}{261.15}\right] = -0.1169$$

Thus $x_{H_2O} = 0.8831$ to cause a freezing point depression to -12°C, that is, we must add 0.1169 mole fraction of solute.

   Let $y =$ grams of solute that need be added to 1000 grams H_2O; $m =$ molecular weight of solvent.

   Thus we need

$$x_2 = 0.1169 = \frac{\frac{y}{m}}{\frac{y}{m} + \frac{1000}{18}} \quad \text{or} \quad y = 7.354m$$

Now for   methanol $m = 32.04$ $y = 235.6g$

ethanol $m = 46.07$ $y = 338.8g$

glycerol $m = 92.09$ $y = 677.2g$

are needed per 1000 grams H_2O to lower freezing point to $-12°C$

Note: suppose we took into account solution non-idealities ... since the van Laar coefficients for these systems (see Table 7.5-1) are positive, the activity coefficients with be greater than unity, and $\ln \gamma_{H_2O} > 0$. Thus instead of $\ln x_{H_2O} = -0.1169$ we will have

$\ln x_{H_2O} \gamma_{H_2O} = -0.1169$ or $\ln x_{H_2O} = -0.1169 - \ln \gamma_{H_2O}$ so that x_{H_2O} will be less than here, and more solute must be added!

For these solutions the effects of nonidealities are not too large. Using van Laar parameters in Table 7.5-1 for methanol-H_2O at $25°C$, we find $x \approx 0.881$ (instead of 0.8831 here), so that $y_{meth} \cong 240.4$ grams/1000 g H_2O (instead of 235.6 grams here). Below are freezing point depression data for various aqueous solutions (methanol and ethanol data from the Handbook of Chemistry and Physics, glycerol data from "Glycerol'" edited by C. S. Miner and N.N. Dalton, Reinhold Publishing, New, York, 1953, p. 270-271). From these data we find that to lower solution freezing temperature to $-12°C$ we need 16.5 wt% methanol (vs 19.1 wt % in our calculations), 21 wt % ethanol (vs 25.3 wt % calculated), and 35.5 wt % glycerol (40.4wt % calculated).
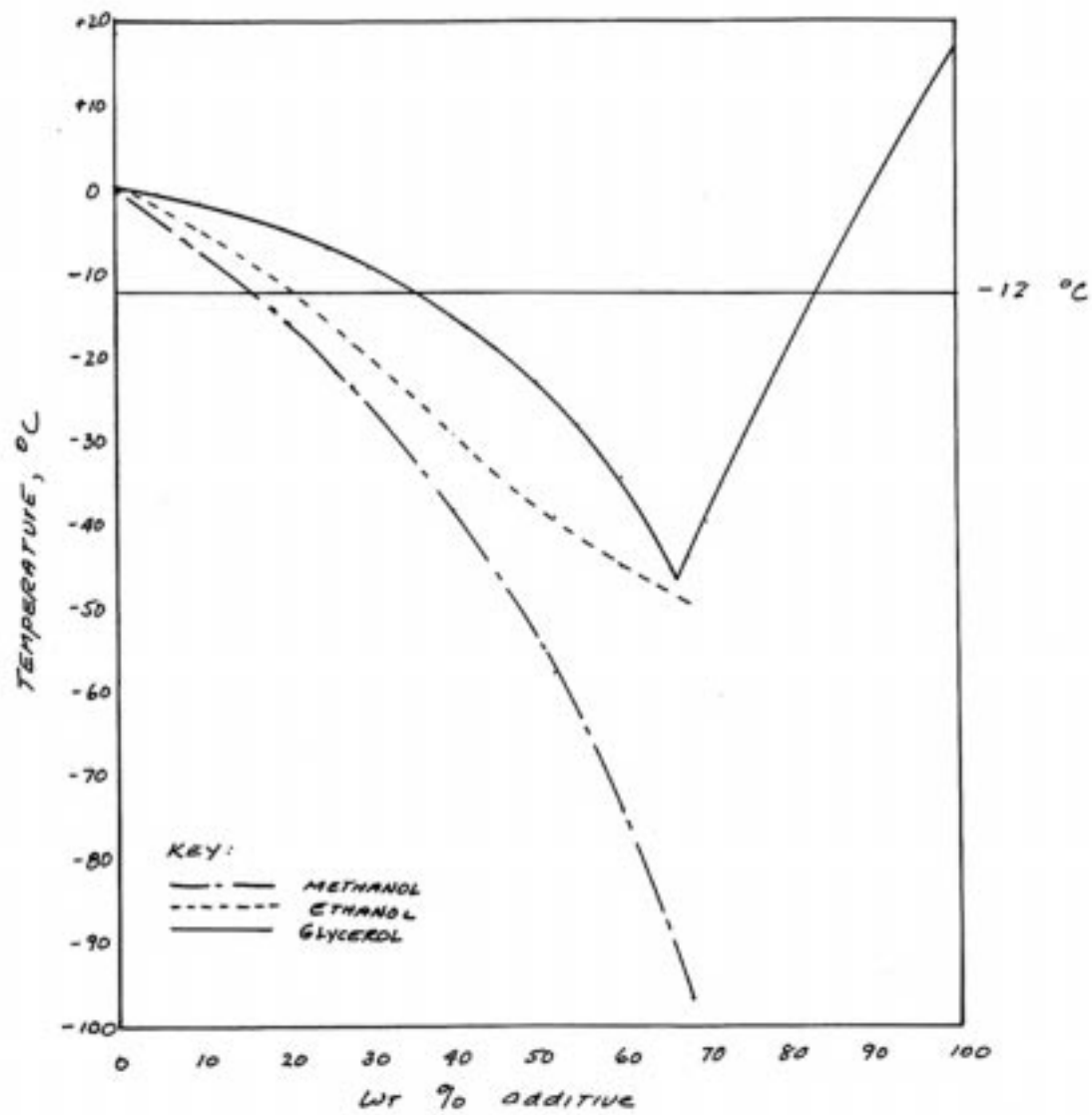
8.7-3　　Assume ideal solutions to begin, also neglect ΔC_{P} term

$$\ln x_{\mathrm{H_2O}} = -\frac{\Delta \underline{H}^{fus}(T_m)}{R}\left(\frac{T_m - T_f}{T_m T_f}\right) = -\frac{6003}{4.184}\left(\frac{273.15 - T_f}{273.15 \times T_f}\right)$$

H_2O freezing out			EG Freezing		Calc at -10^oC	
$x_{H_2O}^{ID}$	$x_{H_2O}^{REAL}$	T_f	T_f	x_{H_2O}	H_2O	EG
1.0	1.0	273.15			1.00	2.265
0.99	0.986	272.63	179.41	0.0048	1.004	2.090
.95	0.942	270.51	201.55	0.0307	1.008	1.628
.9	0.879	267.78	212.86	0.0750	1.024	1.334
.8	0.756	262.02	225.52	0.182	1.058	1.096
.7	0.647	255.78	233.65	0.294	1.082	1.021
.6	0.549	248.94	239.78	0.400	1.093	1.001
.5	0.457	241.31	244.76	0.500	1.094	1.000
.4	0.368	232.58	248.99	0.598	1.088	1.004
.3		222.22	252.68		1.083	1.007
.2		209.09	255.97		1.086	1.006
.1		189.90	258.93		1.110	1.003
.05		173.94	260.32		1.134	1.001
.01		145.55	261.39		1.163	1.000

$$\ln x_{EG} = -\frac{10998.3}{4.184}\left(\frac{261.65 - T_f}{261.65 \times T_f}\right)$$

For nonideal solutions

$$x = \frac{x^{ideal}}{\gamma}$$
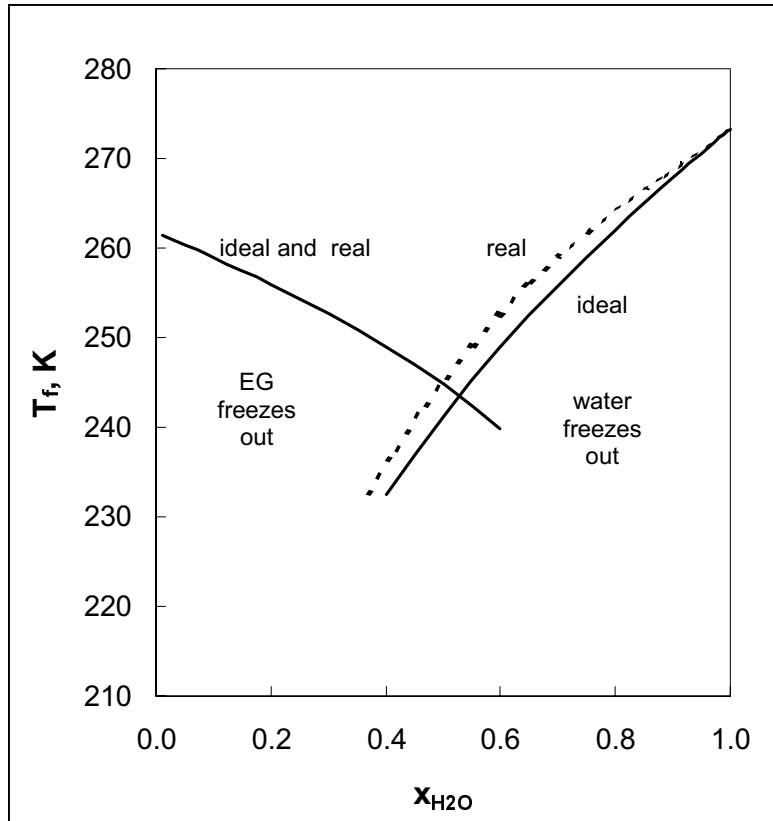
8.7-4 $\Delta \underline{H}_f = 10,000$ J/mol

x	T_f component 1	T_f component 2
0		200
.05	172.34	199.23
.1	177.82	198.58
.2	181.73	197.62
.3	182.79	197.06
.4	182.92	196.82
.5	182.76	196.76
.6	182.62	196.69
.7	182.68	196.26
.8	183.05	194.71
.9	183.80	189.91
.95	184.34	183.52
1.0	185	131.48
.99		167.5
.98		174.3
.97		178.42
.96		181.31

LLE

		x_1^I	x_1^{II}
$T =$	195 K	0.458	0.542
	190	0.357	0.643
	185	0.304	0.696
	183	0.287	0.713
	180	0.264	0.736

LLE $T_C = \dfrac{A}{2R} = \dfrac{3250}{2 \times 8.314} = 195.45$

$x = 0.5$ $T = 273.15$

given $x = \exp\left[-\dfrac{6003}{4.184} \cdot \left(\dfrac{273.15 - T}{273.15 \cdot T}\right)\right]$ $T = \text{find}(T)$ $T = 241.307$

$y = 1 - x$

given $y = \exp\left[-\dfrac{10998.3}{4.184} \cdot \left(\dfrac{261.65 - T}{261.65 \cdot T}\right)\right]$ $T = \text{find}(T)$ $T = 244.763$

For comparison, we also show the results for $\Delta \underline{H}_f = 5000 \dfrac{\text{J}}{\text{mol}}$

8.8-1 System:

System:

P_1 P_2
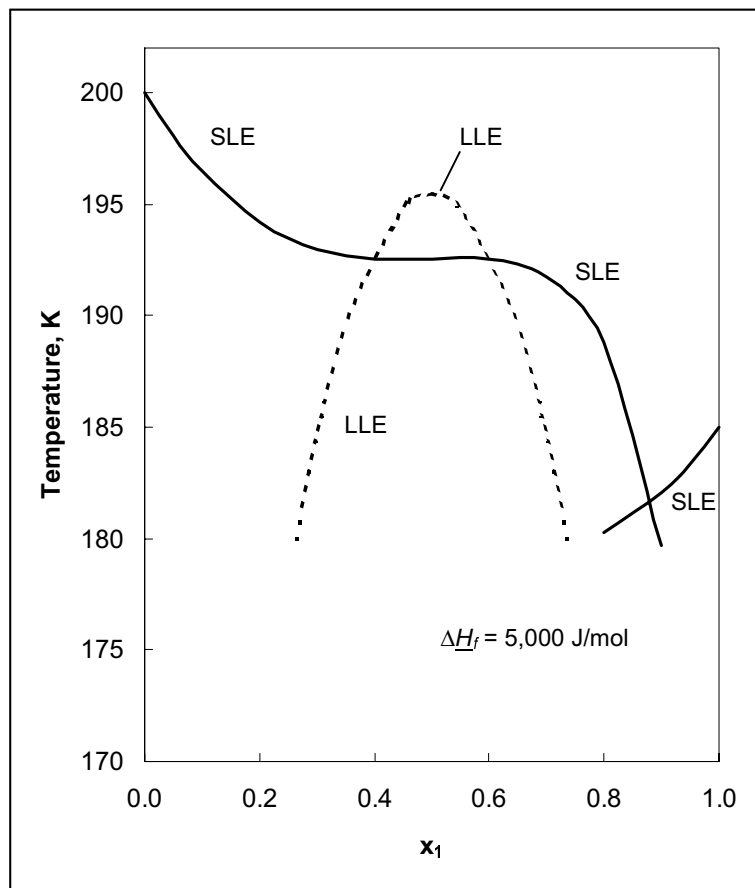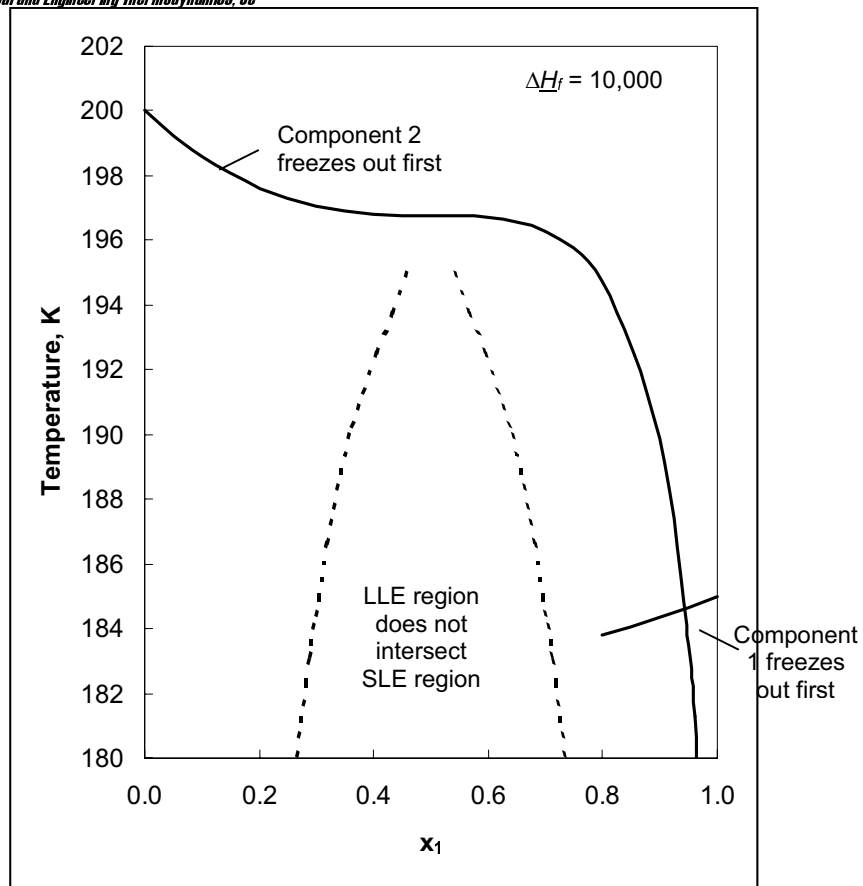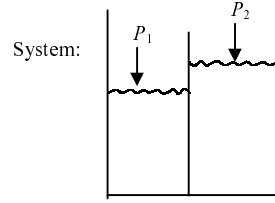
energy balance:

$$\frac{dU}{dt} = \dot{Q} + \dot{W}_S - P^I \frac{dV^I}{dt} - P^{II} \frac{dV^{II}}{dt}$$

entropy balance:

$$\frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{S}_{gen}$$

Constraints: $\dot{W}_S = 0$, system is isothermal, P^I and P^{II} are constant thus

$$\dot{Q} = T\frac{dS}{dt} - T\dot{S}_{gen} = \frac{d}{dt}(TS) - T\dot{S}_{gen}$$

and

$$\frac{dU}{dt} = \frac{d}{dt}(TS) - T\dot{S}_{gen} - P^I \frac{dV^I}{dt} - P^{II} \frac{dV^{II}}{dt}$$

$$= \frac{d}{dt}(TS) - T\dot{S}_{gen} - \frac{d}{dt}(P^I V^I) - \frac{d}{dt}(P^{II} V^{II})$$

$$\Rightarrow \frac{d}{dt}(U - TS + P^I V^I + P^{II} V^{II}) = \frac{dG^*}{dt} = -T\dot{S}_{gen}$$

where we have defined G^* to be $G^* = U - TS + P^I V^I + P^{II} V^{II}$.

Consequently

$$\frac{dG^*}{dt} = -T\dot{S}_{gen} \leq 0 \Rightarrow G^* = \text{ minimum at equilibrium}$$

and

$$G^* = U - TS + P^I V^I + P^{II} V^{II} = (U^I + U^{II}) - T(S^I + S^{II}) - P^I V^I - P^{II} V^{II}$$

$$= G^I(T, P^I, N^I) + G^{II}(T, P^{II}, N^{II})$$

only system variation possible is in N_i^I and N_i^{II} for all species i which can pass through the membrane. However, since $N_i^I + N_i^{II} = $ constant, $dN_i^{II} = -dN_i^I$. Thus

$$G^* = \sum N_j^I \overline{G}_j^I(T, P^I, \underline{x}^I) + \sum N_j^{II} \overline{G}_j^{II}(T, P^{II}, \underline{x}^{II})$$

and

$$\left(\frac{\partial G^*}{\partial N_i^I}\right)_{T,P,N_{j\neq i}} = \overline{G}_i^I(T, P^I, \underline{x}^I) + \sum N_j^I \left(\frac{\partial \overline{G}_j^I(T, P^I, \underline{x}^I)}{\partial N_i^I}\right)_{T,P,N_{j\neq i}}$$

$$\underset{\uparrow}{-} \left[\overline{G}_i^{II}(T, P^{II}, \underline{x}^{II}) + \sum N_j^{II} \left(\frac{\partial \overline{G}_j^{II}(T, P^{II}, \underline{x}^I)}{\partial N_i}\right)_{T,P,N_{j\neq i}}\right]$$

minus sign arises from $dN_i^{II} = -dN_i^I$

Now both summation terms vanish upon application of the Gibbs-Duhem equation to each phase. Thus we have, at equilibrium, that

$$\left(\frac{\partial G^*}{\partial N_i^{\mathrm{I}}}\right)_{T,P,N_{j\neq i}} = 0 = \overline{G}_i^{\mathrm{I}}\left(T,P^{\mathrm{I}},\underline{x}^{\mathrm{I}}\right) - \overline{G}_i^{\mathrm{II}}\left(T,P^{\mathrm{II}},\underline{x}^{\mathrm{II}}\right)$$

$$\Rightarrow \overline{G}_i^{\mathrm{I}}\left(T,P^{\mathrm{I}},\underline{x}^{\mathrm{I}}\right) = \overline{G}_i^{\mathrm{II}}\left(T,P^{\mathrm{II}},\underline{x}^{\mathrm{II}}\right)$$

for each permeable i species, or equivalently

$$\bar{f}_i^{\mathrm{I}}\left(T,P^{\mathrm{I}},\underline{x}^{\mathrm{I}}\right) = \bar{f}_i^{\mathrm{II}}\left(T,P^{\mathrm{I}},\underline{x}^{\mathrm{II}}\right)$$

8.8-2   Let $C = $ number of components

$C_p = $ number of components that can pass through membrane (clearly, $C \geq C_p$)

The system consists of two homogeneous regions (that can be thought of as two phases), and there are no chemical reactions occurring.

Since $C+1$ variables are needed to fix the thermodynamic state of a single phase, there are $2(C+1)$ apparent unknowns here. However, we have the following equilibrium conditions:

$$T^{\mathrm{I}} = T^{\mathrm{II}} \qquad \text{(1 relation)}$$
$$\overline{G}_i^{\mathrm{I}} = \overline{G}_i^{\mathrm{II}} \quad \text{for } i = 1,\ 2,\ \ldots,\ C_p \quad \left(C_p \text{ relations}\right)$$

We also know the number of moles of the impermeable species in each cell (they are the same as in the initial state). However, since this is not information about an intensive property, it is not of help here. Thus, the actual number of degrees of freedom are

$$F = 2(C+1) - \left(1 + C_p\right) = 2C - C_p + 1$$

For a binary system, with a membrane permeable to only one of the species, we have

$$F = 2 \cdot 2 - 1 + 1 = 4 \ \textbf{degrees of freedom}$$

Thus if we specify temperature, the two pressures, and one phase composition, we can, in principal, compute the composition of the other phase. Alternatively, as in the illustration in this section, we can specify T, x_1^{I}, x_1^{II}, and P^{I}, and then compute the value of P^{II}, needed to maintain equilibrium.

8.8-3 (a) $\overline{G}_i(T,P,\underline{x}) = \underline{G}_i(T,P) + \phi_{i,s} RT \ln x_i = \underline{G}_i + RT \ln \gamma_i x_i$

$$\Rightarrow \phi_{i,s} \ln x_i = \ln x_i + \ln \gamma_i$$

    or $\left(\phi_{i,s} - 1\right) \ln x_i = \ln \gamma_i$ **(1)**

(b)   molarities of the salts in seawater are in the following ratios:

$$m_{\mathrm{NaCl}} : m_{\mathrm{KCl}} : m_{\mathrm{mgCl}_2} : m_{\mathrm{MgSO}_4} = 1 : 0.0210 : 0.0761 : 0.0598$$

since the major salt composition is NaCl we will, for simplicity assume only NaCl is present. When converting to mole fraction from ionic strength; that is, we will assume all $z_i = 1$. Also, we will assume that the addition of sea salt increases the density of the water solution, but leaves the water molar concentration unchanged at 55.56 moles/liter . In this case,

$$x_s = \frac{55.56}{55.56 + 2I} \qquad\qquad\qquad (2)$$

where $I = $ ionic strength.

Using the data in the problem statement, and eqns. (1) and (2), we obtain the results in the table below.

To get the osmotic pressure, we use eqn. (8.8-3), or the equivalent relation

$$\overline{G}_{\text{solvent}}\left(T, P^{\text{II}}, x_s^{\text{II}}\right) = \overline{G}_{\text{solvent}}\left(T, P^{\text{I}}, x_s^{\text{I}}\right)$$

Now

$$\overline{G}_{\text{solvent}}(T, P, x_s) = \underline{G}_{\text{solvent}}(T, P) + \phi_s RT \ln x_s$$

$$\underline{G}_{\text{solvent}}\left(T, P^{\text{II}}\right) - \underline{G}_{\text{solvent}}\left(T, P^{\text{I}}\right) = +\underline{V}_{\text{solvent}}\left(P^{\text{II}} - P^{\text{I}}\right)$$

(where we have assumed the liquid solvent, here water, is incompressible), and we will take $x_s^{\text{I}} = 1$. Thus we obtain

$$\underline{G}_{\text{solvent}}\left(T, P^{\text{II}}\right) + \phi_s RT \ln x_s^{\text{II}} = \underline{G}_{\text{solvent}}\left(T, P^{\text{I}}\right) \Rightarrow \phi_s RT \ln x_s^{\text{II}}$$

$$= -\left(\underline{G}_{\text{solvent}}\left(T, P^{\text{II}}\right) - \underline{G}_{\text{solvent}}\left(T, P^{\text{I}}\right)\right) = -\underline{V}_{\text{solvent}}\left(P^{\text{II}} - P^{\text{I}}\right)$$

or

$$\Delta P = P^{\text{II}} - P^{\text{I}} = -\phi_s RT \ln \frac{x_s^{\text{II}}}{\underline{V}_{\text{solvent}}} = -1378\phi_s \ln x_s^{\text{II}} \text{ bar}$$

The osmotic pressure ΔP is given in the table below.

I	x_s^{II}	$\ln x_s$	$\ln \gamma_s$	γ_s	ϕ_i	ΔP(bar)
0.5	0.982	−0.01784	0.00175	1.00175	0.9018	22.17
1.0	0.965	−0.03537	0.00299	1.00299	0.9155	44.63
2.0	0.933	−0.06953	0.00265	1.00265	0.9619	92.16
4.0	0.874	−0.13453	−0.01262	0.9875	1.0938	202.8
6.0	0.822	−0.19557	−0.04960	0.9516	1.2536	337.9

8.8-4   The program VLMU is used for the calculations in this solution. No value of the binary interaction parameter k_{ij} for hydrogen containing mixtures are given in Table 7.4-1. Therefore, a number of different values will be tried. The results are given below

Hydrogen-propane system at $80°C$ and 34.5 bar

x_{H_2}	0.2801	0.4452	0.5935	0.7298	0.8215
ϕ^{exp}	1.283	1.106	1.058	1.028	1.033

	ϕ^{calc}				
$k_{\text{H}_2-\text{C}_3} = 0.00$	1.231				1.020
$k_{\text{H}_2-\text{C}_3} = 0.20$	1.246				1.020
$k_{\text{H}_2-\text{C}_3} = 0.67$	1.282	1.145	1.076	1.038	1.022

Hydrogen-propane system at $130°C$ and 34.5 bar

x_{H_2}	0.2649	0.4715	0.5449	0.7827	0.8354
ϕ^{exp}	1.22	1.116	1.096	1.047	1.038

	ϕ^{calc}				
$k_{\text{H}_2-\text{C}_3} = 0.67$	1.186				1.017
$k_{\text{H}_2-\text{C}_3} = 0.80$	1.194				
$k_{\text{H}_2-\text{C}_3} = 1.00$	1.205				
$k_{\text{H}_2-\text{C}_3} = 1.30$	1.223	1.107	1.080	1.025	1.019

Hydrogen-methane system at $130°C$ and 34.5 bar

x_{H_2}	0.2155	0.4594	0.5355	0.7901	0.8494
ϕ^{exp}	1.223	1.134	1.125	1.115	1.121

ϕ^{calc}					
$k_{H_2-C_1} = 0.0$	1.029				1.011
$k_{H_2-C_1} = 0.1$	1.032				1.011
$k_{H_2-C_1} = 0.5$	1.046				1.011
$k_{H_2-C_1} = 1.0$	1.063		1.028		1.012

The most obvious conclusion from these results is that the Peng-Robinson equation of state does not fit the data very well unless very large values of the k_{ij} parameter, or binary interaction parameters, are used. Indeed, unrealistically large values must be used (i.e., of the order of 1, rather than the 0.1 or less for many other of the systems we have considered). The most probable reason for this is that the temperature function in the $a(T)$ term of the Peng-Robinson equation of state does not represent very supercritical components such as hydrogen at the conditions here very well. In particular, the temperature function

$$a(T) = 0.45724 \frac{R^2 T_c^2}{P_c} \alpha(T); \ \sqrt{\alpha(T)} = 1 + \kappa \left(1 - \sqrt{\frac{T}{T_c}}\right)$$

with $\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$ was obtained by (1) fitting data a long the vapor-liquid saturation curve (i.e., $T_r \leq 1.0$) while, for hydrogen we have $T_r = \frac{80 + 273.15}{33.2} = 10.64$. This is an enormous extrapolation, and undoubtedly greatly in error. Second, the acentric factor dependence of κ was found by using vapor pressure data for argon and methane $(\omega \approx 0.0)$ and the normal paraffins $(\omega > 0)$. Therefore, the use of this function with hydrogen $(\omega = -0.22)$ also represents an extrapolation. Since hydrogen is, probably, so poorly represented by the Peng-Robinson equation, it is not surprising that hydrogen-containing mixtures are poorly described. If this suggestion is true, then the hydrogen-methane system should be more poorly represented than the hydrogen-propane system since, in the former system, methane is also supercritical $\left(T_r = \frac{80 + 273.15}{190.6} = 1.853\right)$.

      Finally, we note that the sensitivity of the fugacity coefficient (or the species fugacity) to the binary interaction parameters is relatively low for the mixtures considered here in that large variations in k produce rather small variations in ϕ_{H_2}.

8.8-5   The solvent is unspecified, but we will consider it to be water, since water in the most common solvent for molecular weight determinations. Assume we put 0.01 g solute in 0.99 g of water. Then

$$x_{solute} = \frac{\frac{0.01}{MW_{solute}}}{\frac{0.01}{MW_{solute}} + \frac{0.99}{18}}$$

where MW_{solute} = molecular weight of solute. Therefore

MW_{solute}	100	1000	1,000,000
x_{solute}	1.815×10^{-3}	1.818×10^{-4}	1.818×10^{-7}

i)   Freezing point depression using eqn. (8.7-5)

$$\Delta T = \frac{RT_m^2}{\Delta H_f} x_{\text{solute}} = \frac{8.314 \times (273.15)^2}{6025} x_{\text{solute}}$$

Thus

MW_{solute}	100	1000	1,000,000
ΔT, K	0.1868	0.1871×10^{-1}	0.1871×10^{-4}

ii) Boiling point elevation

$$\bar{f}_i^{\text{W}} = 1.013 \text{ bar} = x_{\text{W}} P_{\text{W}}^{\text{vap}}(T) = P_{\text{W}}^{\text{vap}}(T = 100°\text{C})$$

Assume $\ln P_{\text{W}}^{\text{vap}} = A - \dfrac{B}{T+C}$ so

$$\ln x_{\text{W}} = \ln P_{\text{W}}^{\text{vap}}(T = 100°\text{C}) - \ln P^{\text{vap}}(T)$$

$$\ln x_{\text{W}} = \ln(1 - x_{\text{S}}) \approx -x_{\text{S}} = -\frac{B}{(T_{100}+C)} + \frac{B}{(T+C)} = B\left[\frac{1}{T+C} - \frac{1}{T_{100}+C}\right]$$

$$\Rightarrow -x_S = B\left[\frac{T_{100}+C-(T+C)}{(T+C)(T_{100}+C)}\right] \approx \frac{B(T_{100}-T)}{(T_{100}+C)^2}$$

Assuming ΔT is small, so T and T_{100} are not very different and

$$\Delta T = T - T_{100} = \frac{x_{\text{S}}(T_{100}+C)^2}{B}$$

For water, from Reid, Prausnitz and Sherwood,

$$\ln P_{\text{W}}^{\text{vap}}(\text{mmHg}) = 18.3036 - \frac{3816.44}{T(\text{K})-46.13}; \text{ so } \Delta T = x_{\text{S}} \frac{(373.15-46.13)^2}{3816.44}$$

MW_S	100	1000	1,000,000
ΔT, K	0.05086	5.094×10^{-3}	5.095×10^{-6}

iii) Osmotic pressure: $\Delta P = \dfrac{RTx_{\text{solute}}}{V_{\text{solute}}}$ eqn. (8.8-6)

$$\Rightarrow \Delta P = \frac{8.314 \times 10^{-5} \text{ bar m}^3/\text{mol K} \cdot 293.15 \text{ K} \cdot x_S \cdot 750 \text{ mm Hg/bar}}{18 \text{ cm}^3/\text{mol} \times 10^{-6} \text{ m}^3/\text{cm}^3}$$

MW_S	100	1000	1,000,000
ΔP(mm Hg)	1843	184.6	0.1846

Summary
Freezing point depression: can easily be used for $MW = 100$, may be possible for depression $MW = 1000$; not likely to be usable for $MW = 1,000,000$.
Boiling point: may be possible for $MW = 100$, difficult or impossible elevation for $MW = 1000$; not possible for $MW = 1,000,000$
Osmotic pressure: Measurable ΔP for all cases. Possibility of finding a suitable membrane very doubtful for a substance of $MW = 100$ or 1000, very easy for a protein or polymer or other substance of $MW = 1,000,000$ (i.e., filter paper).

8.9-1 (also available as a Mathcad worksheet)

8.9-1

$$kow := 10^{5.5} \qquad ksedw := 0.4 \cdot 0.05 \cdot 1.3 \cdot kow \qquad\qquad ksw := 0.4 \cdot 0.02 \cdot 1.5 \cdot kow$$

$$ksedw = 8.221922 \cdot 10^3 \qquad\qquad ksw = 3.794733 \cdot 10^3$$

$$xs := \frac{\left(\dfrac{0.0001}{250}\right)}{\dfrac{1000}{18}} \qquad xs = 7.2 \cdot 10^{-9} \quad \begin{array}{l}\text{equilibrium}\\ \text{solubility}\end{array} \qquad gam := \frac{1}{xs} \qquad gam = 1.388889 \cdot 10^8$$

$$H := 2 \cdot 10^{-7} \cdot 1.013 \cdot gam \qquad H = 28.138889 \qquad \text{bar/mol frac}$$

$$kaw := 0.2164 \cdot \frac{H}{298.15} \qquad kaw = 0.020423$$

$$cw := 0.3 \cdot 10^{-9} \quad \text{g/g water or} \qquad cw := 0.3 \cdot 10^{-3} \quad \text{g/m^3 of water}$$

$$cb := 0.05 \cdot kow \cdot cw \qquad cb = 4.743416 \qquad\qquad \text{g/m^3 water or 4743 ppb by weight}$$

$$ca := kaw \cdot cw \qquad ca = 6.127039 \cdot 10^{-6} \quad \begin{array}{l}\text{g/m^3 of air}\end{array}$$

$$cs := ksw \cdot cw \qquad\qquad cs = 1.13842 \quad \text{g/m^3 of soil}$$

$$cs := \frac{cs}{1.5 \cdot 10^6} \qquad cs = 7.589466 \cdot 10^{-7} \quad \text{g/g soil or 0.7589 ppm by wt.}$$

$$csed := ksedw \cdot cw \qquad csed = 2.466577 \qquad \text{g/m^3 of sediment}$$

$$csed := \frac{csed}{1.3 \cdot 10^6} \qquad csed = 1.897367 \cdot 10^{-6} \quad \text{g/g sediment or 1.897 ppm by wt.}$$

8.9-2   (also available as a Mathcad worksheet)

8.9-2

$$i := 0 .. 3 \qquad LKow_0 := 5.52 \qquad LKow_1 := 5.16 \qquad LKow_2 := 3.66 \qquad LKow_3 := 3.31$$

$$S_0 := 27 \qquad\qquad S_1 := 140 \qquad\qquad S_2 := 7000 \qquad\qquad S_3 := 40000$$

$$S_i := S_i \cdot 10^{-9} \quad \text{solubility in g/liter}$$

$$C_i := 0.05 \cdot S_i \cdot 10^{LKow_i}$$

$$C = \begin{bmatrix} 4.47 \cdot 10^{-4} \\ 1.012 \cdot 10^{-3} \\ 1.6 \cdot 10^{-3} \\ 4.083 \cdot 10^{-3} \end{bmatrix} \qquad \text{Fish concentration in g/liter}$$

$$CP_i := C_i \cdot 1000 \qquad\qquad CP = \begin{bmatrix} 0.447 \\ 1.012 \\ 1.6 \\ 4.083 \end{bmatrix} \qquad \text{Fish concentration in ppm}$$

8.9-3 (also available as a Mathcad worksheet)

Water $= 4\ \text{m}^3$;

fish $= 200\ \text{cm}^3 = 2 \times 10^2\ \text{cm}^3 \times 10^{-6}\ \text{m}^3/\text{cm}^3 = 2 \times 10^{-4}\ \text{m}^3$

Soil $= 3\ \text{m}^3$

air $= 10 - 4 - 3 - 0.0002 = 2.9998\ \text{m}^3$

(a) Benzene

vapor pressure $(25\,°C) = 0.127\ \text{bar}$

solubility in water $(25\,°C) = 0.0405\ \text{mol \%}$

$$x_B^{\text{sat}} \boldsymbol{g}_B^\infty \sim 1 \Rightarrow \boldsymbol{g}^\infty = \frac{1}{0.000405} = 2.469 \times 10^3$$

$$H_B = \boldsymbol{g}^\infty P_i^{\text{vap}} = 0.127 \times 2.469 \times 10^3 = 313.6\ \text{bar/mol fraction}$$

$$K_{\text{AW}} = 313.6 \times \frac{0.2164}{298.15} = 0.2276$$

$$\log_{10} K_{\text{OW}} = 2.13;\ K_{\text{OW}} = 135;\ K_{\text{BW}} = 0.05 \times 135 = 6.75;$$

$$K_{\text{SW}} = 0.4 \times 0.02 \times 135 = 1.08$$

By a mass balance

$$10 \times 10^{-3}\ \text{g} = 4\ \text{m}^3_{\text{H}_2\text{O}} C_{\text{B,H}_2\text{O}} + 3\ \text{m}^3_{\text{soil}} C_{\text{B,soil}} + 2.9998\ \text{m}^3\ \text{air} \times C_{\text{B,air}}$$

$$+ 2 \times 10^{-4}\ \text{m}^3_{\text{fish}} \times C_{\text{B,fish}}$$

$$= 4 C_{\text{B,H}_2\text{O}} \left(\text{g}/\text{m}^3\right) + 3 K_{\text{SW}} C_{\text{B,H}_2\text{O}} \left(\text{g}/10^6\ \text{g soil}\right) 1.5$$

$$+ 2.9998\ \text{m}^3\ \text{air} \times K_{\text{AW}} C_{\text{B,H}_2\text{O}}$$

$$+ 2 \times 10^{-4}\ \text{m}^3_{\text{f}} K_{\text{BW}} C_{\text{B,H}_2\text{O}} \left(\text{g}/\text{m}^3\ \text{B}\right)$$

$$10 \times 10^{-3}\ \text{g}$$

$$= C_{\text{B,H}_2\text{O}} \left(4 + 3 \times 1.08 \times 1.5 + 2.9998 \times 0.2276 + 2.4 \times 10^{-4} \times 6.75\right)$$

$$C_{\text{B,H}_2\text{O}} = 1.048 \times 10^{-3}\ \text{g}/\text{m}^3 = 1.048\ \text{ppb};\ \text{in water } 1\ \text{g}/\text{m}^3 = 1\ \text{ppm}$$

$$C_{\text{B,soil}} = 1.08 \times 1.048 \times 10^{-3} = \frac{1.132 \times 10^{-3}\ \text{g}}{10^6\ \text{g soil}} = 1.698 \times 10^{-3}\ \text{g}/\text{m}^3$$

$$C_{\text{B,air}} = 0.2276 \times 1.048 \times 10^{-3} = 0.239 \times 10^{-3}\ \text{g}/\text{m}^3$$

$$C_{\text{B,fish}} = 6.75 \times 1.048 \times 10^{-3} = 7.074 \times 10^{-3}\ \text{g}/\text{m}^3$$

(b) DDT $K_{AW,DDT} = 9.5 \times 10^{-4}$

$K_{0W,DDT} = 1.549 \times 10^{6}$

Proceeding the same way

$C_{DDT,H_2O} = 1.793 \times 10^{-7}$ g/m^3 = 17.93 ppt

$C_{DDT,air} = 3.332 \times 10^{-3}$ g/m^3

$C_{DDT,fish} = 13.883 \times 10^{-3}$ g/m^3 = 13.88 ppb

8.9-4 (also available as a Mathcad worksheet).

8.9-4

$Kow := 224$ $Pvap := 3 \cdot \dfrac{10^{-2}}{750}$ bar $S := 440$ mg/liter $MW := 157.5$

$x := \dfrac{\left(\dfrac{0.440}{157.5}\right)}{\dfrac{1000}{18}}$ $x = 5.029 \cdot 10^{-5}$ mole fraction of ClNO2benzene

$Gam := \dfrac{1}{x}$ $Gam = 1.989 \cdot 10^{4}$ $H := Pvap \cdot Gam$ $H = 0.795$ bar/mole fr

Mass balance: 100 kg = CW*7*10^6 + CA*6*10^9 + CS*4.5*10^4 + Csed*2.1*10^4

Equilibrium relations: CA=Kaw*CW   Kaw=0.2164*H/298.15

                CS=Ksw*CW   Ksw=0.02*0.4*Kow*1.5 (g/m^3)/(g/m^3)

                Csed=Ksedw*Cw   Ksedw=0.05*0.4*Kow*1.3

$Ksw := 0.02 \cdot 0.4 \cdot Kow \cdot 1.5$ $Ksedw := 0.05 \cdot 0.4 \cdot Kow \cdot 1.3$ $Kaw := 0.2164 \cdot \dfrac{H}{298.15}$

$Ksw = 2.688$ $Ksedw = 5.824$ $Kaw = 5.773 \cdot 10^{-4}$

$Cw := \dfrac{(100 \cdot 1000)}{\left(7 \cdot 10^6 + 6 \cdot 10^9 \cdot Kaw + 4.5 \cdot 10^4 \cdot Ksw + 2.1 \cdot 10^4 \cdot Ksedw\right)}$

$Cw = 9.339 \cdot 10^{-3}$ g/m^3 or 9.339 ppb by wt

$Ca := Kaw \cdot Cw$ $Ca = 5.392 \cdot 10^{-6}$ g/m^3

$Cs := Ksw \cdot Cw$ $Cs = 0.025$ g/m^3 or $Cs := Cs \cdot \dfrac{1000}{1.5}$ $Cs = 16.736$ ppb by wt

$Csed := Ksedw \cdot Cw$ $Csed = 0.054$ g/m^3 or $Csed := Csed \cdot \dfrac{1000}{1.3}$

                                        $Csed = 41.84$ ppb by wt

8.10-1 This is a simple algebraic exercise, so the details will not be given.

8.10-2 The starting point for the liquidus line is

$$x_1^{\mathrm{L}} = \frac{1 - \dfrac{\boldsymbol{g}_2^{\mathrm{L}}(x_1^{\mathrm{L}})}{\boldsymbol{g}_2^{\mathrm{S}}(x_1^{\mathrm{S}})}\exp\left[\dfrac{\Delta\underline{H}_2^{\mathrm{fus}}(T_{m,2})}{RT}\left\{1 - \dfrac{T}{T_{m,2}}\right\}\right]}{\dfrac{\boldsymbol{g}_1^{\mathrm{L}}(x_1^{\mathrm{L}})}{\boldsymbol{g}_1^{\mathrm{S}}(x_1^{\mathrm{S}})}\exp\left[\dfrac{\Delta\underline{H}_1^{\mathrm{fus}}(T_{m,1})}{RT}\left\{1 - \dfrac{T}{T_{m,1}}\right\}\right] - \dfrac{\boldsymbol{g}_2^{\mathrm{L}}(x_1^{\mathrm{L}})}{\boldsymbol{g}_2^{\mathrm{S}}(x_1^{\mathrm{S}})}\exp\left[\dfrac{\Delta\underline{H}_2^{\mathrm{fus}}(T_{m,2})}{RT}\left\{1 - \dfrac{T}{T_{m,2}}\right\}\right]}$$

and for the solidus line is

$$x_1^{\mathrm{S}} = \frac{1 - \dfrac{\boldsymbol{g}_2^{\mathrm{S}}(x_1^{\mathrm{S}})}{\boldsymbol{g}_2^{\mathrm{L}}(x_1^{\mathrm{L}})}\exp\left[-\dfrac{\Delta\underline{H}_2^{\mathrm{fus}}(T_{m,2})}{RT}\left\{1 - \dfrac{T}{T_{m,2}}\right\}\right]}{\dfrac{\boldsymbol{g}_1^{\mathrm{S}}(x_1^{\mathrm{S}})}{\boldsymbol{g}_1^{\mathrm{L}}(x_1^{\mathrm{L}})}\exp\left[-\dfrac{\Delta\underline{H}_1^{\mathrm{fus}}(T_{m,1})}{RT}\left\{1 - \dfrac{T}{T_{m,1}}\right\}\right] - \dfrac{\boldsymbol{g}_2^{\mathrm{S}}(x_1^{\mathrm{S}})}{\boldsymbol{g}_2^{\mathrm{L}}(x_1^{\mathrm{L}})}\exp\left[-\dfrac{\Delta\underline{H}_2^{\mathrm{fus}}(T_{m,2})}{RT}\left\{1 - \dfrac{T}{T_{m,2}}\right\}\right]}$$

a) Regular solution model for the liquid, the solid phase is ideal
the liquidus line is

$$x_1^{\mathrm{L}} = \frac{1 - \exp\left(\dfrac{\Omega(1 - x_1^{\mathrm{L}})^2}{RT}\right)\exp\left[\dfrac{\Delta\underline{H}_2^{\mathrm{fus}}(T_{m,2})}{RT}\left\{1 - \dfrac{T}{T_{m,2}}\right\}\right]}{\exp\left(\dfrac{\Omega(1 - x_1^{\mathrm{L}})^2}{RT}\right)\exp\left[\dfrac{\Delta\underline{H}_1^{\mathrm{fus}}(T_{m,1})}{RT}\left\{1 - \dfrac{T}{T_{m,1}}\right\}\right] - \exp\left(\dfrac{\Omega(x_1^{\mathrm{L}})^2}{RT}\right)\exp\left[\dfrac{\Delta\underline{H}_2^{\mathrm{fus}}(T_{m,2})}{RT}\left\{1 - \dfrac{T}{T_{m,2}}\right\}\right]}$$

and for the solidus line is

$$x_1^{\mathrm{S}} = \frac{1 - \exp\left(-\dfrac{\Omega(x_1^{\mathrm{L}})^2}{RT}\right)\exp\left[-\dfrac{\Delta\underline{H}_2^{\mathrm{fus}}(T_{m,2})}{RT}\left\{1 - \dfrac{T}{T_{m,2}}\right\}\right]}{\exp\left(-\dfrac{\Omega(1 - x_1^{\mathrm{L}})^2}{RT}\right)\exp\left[-\dfrac{\Delta\underline{H}_1^{\mathrm{fus}}(T_{m,1})}{RT}\left\{1 - \dfrac{T}{T_{m,1}}\right\}\right] - \exp\left(-\dfrac{\Omega(x_1^{\mathrm{L}})^2}{RT}\right)\exp\left[-\dfrac{\Delta\underline{H}_2^{\mathrm{fus}}(T_{m,2})}{RT}\left\{1 - \dfrac{T}{T_{m,2}}\right\}\right]}$$

So these nonlinear equations must be solved simultaneously for the liquidus and solidus lines, together with the equations for the second component, and that the sum of the mole fractions in each phase must be unity.

b) Regular solution model for the solid, and the liquid phase is ideal
the liquidus line is

$$x_1^{\mathrm{L}} = \frac{1 - \exp\left(-\dfrac{\Omega(1 - x_1^{\mathrm{S}})^2}{RT}\right)\exp\left[\dfrac{\Delta\underline{H}_2^{\mathrm{fus}}(T_{m,2})}{RT}\left\{1 - \dfrac{T}{T_{m,2}}\right\}\right]}{\exp\left(-\dfrac{\Omega(1 - x_1^{\mathrm{S}})^2}{RT}\right)\exp\left[\dfrac{\Delta\underline{H}_1^{\mathrm{fus}}(T_{m,1})}{RT}\left\{1 - \dfrac{T}{T_{m,1}}\right\}\right] - \exp\left(-\dfrac{\Omega(x_1^{\mathrm{S}})^2}{RT}\right)\exp\left[\dfrac{\Delta\underline{H}_2^{\mathrm{fus}}(T_{m,2})}{RT}\left\{1 - \dfrac{T}{T_{m,2}}\right\}\right]}$$

and for the solidus line is

$$x_1^S = \frac{1 - \exp\left(\frac{\Omega\left(x_1^S\right)^2}{RT}\right)\exp\left[-\frac{\Delta \underline{H}_2^{fus}(T_{m,2})}{RT}\left\{1 - \frac{T}{T_{m,2}}\right\}\right]}{\exp\left(\frac{\Omega\left(1 - x_1^S\right)^2}{RT}\right)\exp\left[-\frac{\Delta \underline{H}_1^{fus}(T_{m,1})}{RT}\left\{1 - \frac{T}{T_{m,1}}\right\}\right] - \exp\left(\frac{\Omega\left(x_1^S\right)^2}{RT}\right)\exp\left[-\frac{\Delta \underline{H}_2^{fus}(T_{m,2})}{RT}\left\{1 - \frac{T}{T_{m,2}}\right\}\right]}$$

So these nonlinear equations must also be solved simultaneously for the liquidus and solidus lines, together with the equations for the second component, and that the sum of the mole fractions in each phase must be unity.

c) Regular solution model for the liquid and the solid phases, but with different values of Ω.
The liquidus line is

$$x_1^L = \frac{1 - \exp\left(\frac{\Omega_L\left(1 - x_1^L\right)^2 - \Omega_S\left(1 - x_1^S\right)^2}{RT}\right)\exp\left[\frac{\Delta \underline{H}_2^{fus}(T_{m,2})}{RT}\left\{1 - \frac{T}{T_{m,2}}\right\}\right]}{\exp\left(\frac{\Omega_L\left(1 - x_1^L\right)^2 - \Omega_S\left(1 - x_1^S\right)^2}{RT}\right)\exp\left[\frac{\Delta \underline{H}_1^{fus}(T_{m,1})}{RT}\left\{1 - \frac{T}{T_{m,1}}\right\}\right] - \exp\left(\frac{\Omega_L\left(x_1^L\right)^2 - \Omega_S\left(x_1^S\right)^2}{RT}\right)\exp\left[\frac{\Delta \underline{H}_2^{fus}(T_{m,2})}{RT}\left\{1 - \frac{T}{T_{m,2}}\right\}\right]}$$

and for the solidus line is

$$x_1^S = \frac{1 - \exp\left(\frac{\Omega_S\left(x_1^S\right)^2 - \Omega_L\left(x_1^L\right)^2}{RT}\right)\exp\left[-\frac{\Delta \underline{H}_2^{fus}(T_{m,2})}{RT}\left\{1 - \frac{T}{T_{m,2}}\right\}\right]}{\exp\left(\frac{\Omega_S\left(1 - x_1^S\right)^2 - \Omega_L\left(1 - x_1^L\right)^2}{RT}\right)\exp\left[-\frac{\Delta \underline{H}_1^{fus}(T_{m,1})}{RT}\left\{1 - \frac{T}{T_{m,1}}\right\}\right] - \exp\left(\frac{\Omega_S\left(x_1^S\right)^2 - \Omega_L\left(x_1^L\right)^2}{RT}\right)\exp\left[-\frac{\Delta \underline{H}_2^{fus}(T_{m,2})}{RT}\left\{1 - \frac{T}{T_{m,2}}\right\}\right]}$$

Again, we have a set of nonlinear equations that must be solved simultaneously for the liquidus and solidus lines, together with the equations for the second component, and that the sum of the mole fractions in each phase must be unity.

8.10-3   (also available as a Mathcad worksheet).

Problem 8.10-3   File: 8-10-3.MCD

$\qquad$ x11 := 0.1 $\qquad$ x12 := 0.9 $\qquad$ T := 225 $\qquad$ $TUC := \dfrac{5000}{2 \cdot 8.314}$ $\qquad$ TUC = 300.698

Given

$$x11 \cdot \exp\left[\frac{5000 \cdot (1 - x11)^2}{8.314 \cdot T}\right] = x12 \cdot \exp\left[\frac{5000 \cdot (1 - x12)^2}{8.314 \cdot T}\right]$$

$$(1 - x11) \cdot \exp\left[\frac{5000 \cdot (x11)^2}{8.314 \cdot T}\right] = (1 - x12) \cdot \exp\left[\frac{5000 \cdot (x12)^2}{8.314 \cdot T}\right]$$

$$v := find(x11, x12) \qquad\qquad v = \begin{bmatrix} 0.111 \\ 0.889 \end{bmatrix}$$

$T := 250$

Given

$$x11 \cdot \exp\left[\frac{5000 \cdot (1 - x11)^2}{8.314 \cdot T}\right] = x12 \cdot \exp\left[\frac{5000 \cdot (1 - x12)^2}{8.314 \cdot T}\right]$$

$$(1 - x11) \cdot \exp\left[\frac{5000 \cdot (x11)^2}{8.314 \cdot T}\right] = (1 - x12) \cdot \exp\left[\frac{5000 \cdot (x12)^2}{8.314 \cdot T}\right]$$

$v := \text{find}(x11, x12)$ $v = \begin{bmatrix} 0.169 \\ 0.831 \end{bmatrix}$

$T := 275$

Given

$$x11 \cdot \exp\left[\frac{5000 \cdot (1 - x11)^2}{8.314 \cdot T}\right] = x12 \cdot \exp\left[\frac{5000 \cdot (1 - x12)^2}{8.314 \cdot T}\right]$$

$$(1 - x11) \cdot \exp\left[\frac{5000 \cdot (x11)^2}{8.314 \cdot T}\right] = (1 - x12) \cdot \exp\left[\frac{5000 \cdot (x12)^2}{8.314 \cdot T}\right]$$

$v := \text{find}(x11, x12)$ $v = \begin{bmatrix} 0.256 \\ 0.744 \end{bmatrix}$

$T := 285$

Given

$$x11 \cdot \exp\left[\frac{5000 \cdot (1 - x11)^2}{8.314 \cdot T}\right] = x12 \cdot \exp\left[\frac{5000 \cdot (1 - x12)^2}{8.314 \cdot T}\right]$$

$$(1 - x11) \cdot \exp\left[\frac{5000 \cdot (x11)^2}{8.314 \cdot T}\right] = (1 - x12) \cdot \exp\left[\frac{5000 \cdot (x12)^2}{8.314 \cdot T}\right]$$

$v := \text{find}(x11, x12)$ $v = \begin{bmatrix} 0.306 \\ 0.694 \end{bmatrix}$

$T := 290$

Given

$$x11 \cdot \exp\left[\frac{5000 \cdot (1 - x11)^2}{8.314 \cdot T}\right] = x12 \cdot \exp\left[\frac{5000 \cdot (1 - x12)^2}{8.314 \cdot T}\right]$$

$$(1 - x11) \cdot \exp\left[\frac{5000 \cdot (x11)^2}{8.314 \cdot T}\right] = (1 - x12) \cdot \exp\left[\frac{5000 \cdot (x12)^2}{8.314 \cdot T}\right]$$

$v := \text{find}(x11, x12)$ $v = \begin{bmatrix} 0.339 \\ 0.661 \end{bmatrix}$

$T := 298$

Given

$$x11 \cdot \exp\left[\frac{5000 \cdot (1 - x11)^2}{8.314 \cdot T}\right] = x12 \cdot \exp\left[\frac{5000 \cdot (1 - x12)^2}{8.314 \cdot T}\right]$$

$$(1 - x11) \cdot \exp\left[\frac{5000 \cdot (x11)^2}{8.314 \cdot T}\right] = (1 - x12) \cdot \exp\left[\frac{5000 \cdot (x12)^2}{8.314 \cdot T}\right]$$

$v := \text{find}(x11, x12)$ $\qquad v = \begin{bmatrix} 0.418 \\ 0.582 \end{bmatrix}$

$T := 300$

Given

$$x11 \cdot \exp\left[\frac{5000 \cdot (1 - x11)^2}{8.314 \cdot T}\right] = x12 \cdot \exp\left[\frac{5000 \cdot (1 - x12)^2}{8.314 \cdot T}\right]$$

$$(1 - x11) \cdot \exp\left[\frac{5000 \cdot (x11)^2}{8.314 \cdot T}\right] = (1 - x12) \cdot \exp\left[\frac{5000 \cdot (x12)^2}{8.314 \cdot T}\right]$$

$v := \text{find}(x11, x12)$ $\qquad v = \begin{bmatrix} 0.458 \\ 0.542 \end{bmatrix}$

8.10-4 (also available as a Mathcad worksheet)

Solid-liquid phase diagram:

Given: $\Omega^S = 10{,}000$, $T_{m,1} = 800$ K , $T_{m,2} = 600$ K ; $\Delta \underline{H}_1^f = 6200$ J/mol ; $\Delta \underline{H}_2^f = 4900$ J/mol .

liquid phase ideal:

$\rightarrow$ solidus line

$$x_1^S = \frac{1 - \boldsymbol{g}_2^S \exp\left\{-\dfrac{\Delta \underline{H}_2^f}{RT}\left(1 - \dfrac{T}{T_{m_2}}\right)\right\}}{\boldsymbol{g}_1^S \exp\left\{-\dfrac{\Delta \underline{H}_1^f}{RT}\left(1 - \dfrac{T}{T_{m_1}}\right)\right\} - \boldsymbol{g}_2^S \exp\left\{\dfrac{\Delta \underline{H}_2^f}{RT}\left(1 - \dfrac{T}{T_{m_2}}\right)\right\}} \tag{1}$$

liquidus line

$$x_1^L = \frac{1 - \dfrac{1}{\boldsymbol{g}_2^S} \exp\left\{\dfrac{\Delta \underline{H}_2^f}{RT}\left(1 - \dfrac{T}{T_{m_2}}\right)\right\}}{\dfrac{1}{\boldsymbol{g}_1^S} \exp\left\{\dfrac{\Delta \underline{H}_1^f}{RT}\left(1 - \dfrac{T}{T_{m1}}\right)\right\} - \dfrac{1}{\boldsymbol{g}_2^S} \exp\left\{\dfrac{\Delta \underline{H}_2^f}{RT}\left(1 - \dfrac{T}{T_{m_2}}\right)\right\}} \tag{2}$$

Start with Equation (1); pick x_1^S , find T so that (1) is satisfied. Use T, x_1^S in (2).

$$g_1^S = \exp\left[\frac{\Omega^S}{RT}\left(x_2^S\right)^2\right]$$

$$g_2^S = \exp\left[\frac{\Omega^S}{RT}\left(x_1^S\right)^2\right]$$

To find solid-solid equilibrium, use

$$\bar{f}_1^{S,I} = \bar{f}_1^{S,II} \rightarrow x_1^{S,I}g_1^{S,I} = x_1^{S,II}g_1^{S,II} \quad \text{and} \quad x_2^{S,I}\cdot g_2^{S,I} = x_2^{S,II}g_2^{S,II}$$

			$\Omega = 10000$		
x	T_S	T_L		Liquid – Liquid Eq.	
0.0001	599.95	599.73	T	x_1^I	x_1^{II}
0.05	573.39	476.34	300	0.021	0.979
0.1	543.92	387.62	350	0.041	0.959
0.2	480.02	350.42	400	0.070	0.930
0.3	418.14	366.34	450	0.111	0.889
0.4	378.88	376.07	500	0.169	0.831
0.5	393.54	372.61	550	0.256	0.744
0.6	458.60	351.32	600	0.458	0.542
0.7	545.01	290.99	575	0.322	0.678
0.8	635.78		601.4		0.5
0.9	722.65				
0.95	762.83	595.06			
0.9999	799.93	799.59			
0.975	781.83	698.52			
0.925	743.08	472.85			

$$T_{uc} = \frac{10000}{2\times 8.314} = 601.40$$

$$x_1^I g_1^I = x_1^{II} g_1^{II}$$

$$\left(1 - x_1^I\right)g_2^I = \left(1 - x_1^{II}\right)g_2^{II}$$
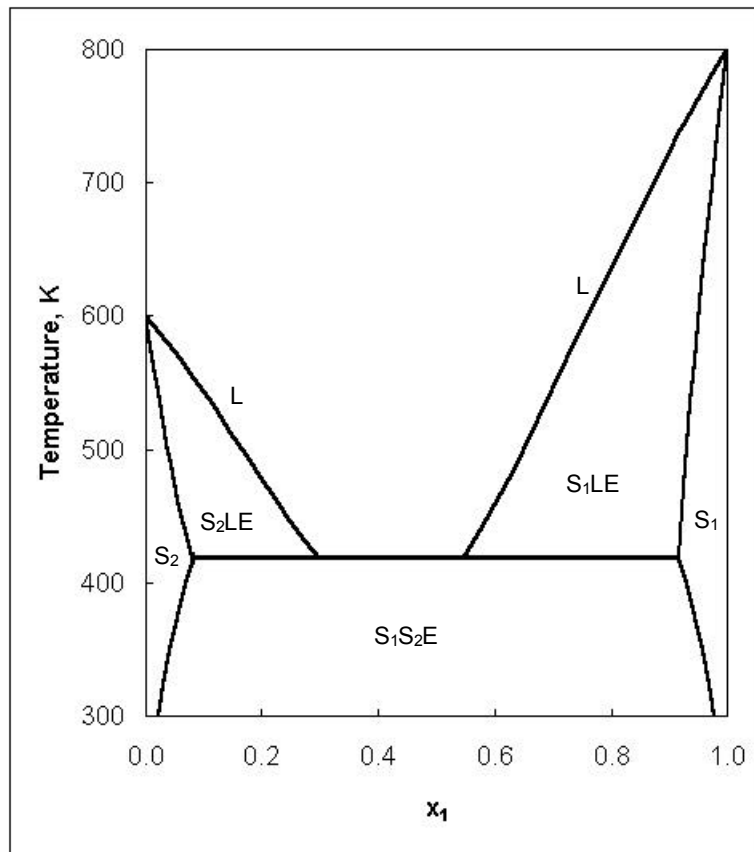
8.10-5

$$\underline{G}^{ex} = x_1 x_2 \Omega \left(1 - x_1 x_2 \frac{\Omega}{RT}\right) \quad \text{so that}$$

$$N\underline{G}^{ex} = \frac{N_1 N_2}{N_1 + N_2} \Omega \left(1 - \frac{N_1 N_2}{(N_1 + N_2)^2} \frac{\Omega}{ZRT}\right) = \frac{N_1 N_2}{N_1 + N_2} \Omega - \frac{N_1^2 N_2^2}{(N_1 + N_2)^3} \frac{\Omega^2}{ZRT}$$

$$\left(\frac{\partial N \underline{G}^{ex}}{\partial N_1}\right)_{T,P,N_2} = \left[\frac{N_2}{N_1 + N_2} - \frac{N_1 N_2}{(N_1 + N_2)^2}\right]\Omega - \left[\frac{2N_1 N_2^2}{(N_1 + N_2)^3} - \frac{3N_1^2 N_2^2}{(N_1 + N_2)^4}\right]\frac{\Omega^2}{ZRT}$$

$$= (x_2 - x_1 x_2)\Omega - \left[2x_1 x_2^2 - 3x_1^2 x_2^2\right]\frac{\Omega^2}{ZRT} = x_2(1 - x_1)\Omega - x_1 x_2^2[2 - 3x_1]\frac{\Omega^2}{ZRT}$$

$$RT \ln \boldsymbol{g}_1 = \left(\frac{\partial N \underline{G}^{ex}}{\partial N_1}\right)_{T,P,N_2} = x_2^2 \Omega - x_1 x_2^2[2 - 3x_1]\frac{\Omega^2}{ZRT}$$

and by symmetry

$$RT \ln \boldsymbol{g}_2 = \left(\frac{\partial N \underline{G}^{ex}}{\partial N_2}\right)_{T,P,N_1} = x_1^2 \Omega - x_2 x_1^2[2 - 3x_2]\frac{\Omega^2}{ZRT}$$

8.10-6 (also available as a Mathcad worksheet).

8.10-6

Treat as freezing point depression problem and use Eqn. 8.5-12.

$$i := 0, 1 .. 9 \qquad x_1 := 1 - 0.1 \cdot i$$

$T_0 := 1410$ $T_1 := 1385$ $T_2 := 1350$ $T_3 := 1316$ $T_4 := 1290$ $T_5 := 1278$

$T_6 := 1261$ $T_7 := 1242$ $T_8 := 1215$ $T_9 := 1090$

$\Delta Cp(T) := 26.606 - 23.932 - 2.469 \cdot 10^{-3} \cdot T + 4.142 \cdot 10^{-5} \cdot T^2$ $R := 8.314$

$\Delta H := 50626$ $Tm := 1410$

$$Term2_i := \frac{1}{R \cdot T_i} \cdot \int_{Tm}^{T_i} \Delta Cp(x) \, dx \qquad Term3_i := \frac{1}{R} \cdot \int_{Tm}^{T_i} \frac{\Delta Cp(x)}{x} \, dx$$

$$Term1_i := \frac{-\Delta H}{8.314 \cdot T_i} \cdot \left(1 - \frac{T_i}{Tm}\right) - Term2_i + Term3_i$$

$$\gamma_i := \frac{1}{x_i} \cdot \exp\left(Term1_i\right)$$

γ_i
1
1.029
1.041
1.074
1.158
1.341
1.592
2.005
2.774
3.809
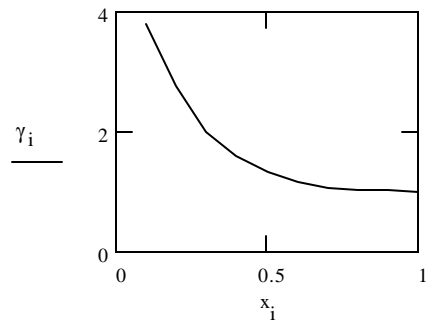
8.11-1   Clearly, it is only water that condenses out at the dew point, since O_2 and N_2 are far above their critical temperatures. Thus, at the dew point

$$P_{H_2O}^{vap} = y_{H_2O}P = P_{H_2O} = \text{ partial pressure of } H_2O \text{ in air.}$$

[In writing this expression, all fugacity coefficients have been assumed equal to unity.]

From the data in Problem 5.12 we have, at the dew point,

$$\ln P_{H_2O}^{vap} = 26.3026 - \frac{5432.8}{273.15 + 25.6} = 7.8086$$

and

$$P_{H_2O}^{vap} = \text{(dew point)} = P_{H_2O} = 2461.8 \text{ Pa}$$

at the air conditions $P_{H_2O}^{vap}(T = 25.6°\text{C}) = 3354.9$

$$\Rightarrow \text{ relative humidity} = \frac{P_{H_2O} = P_{H_2O}^{vap}(T = 20.6°\text{ C})}{P_{H_2O}^{vap}(T = 25.6°\text{C})} \times 100\% = 73.38\%$$

8.11-2   Equilibrium condition for V-L-S equilibrium: $\bar{f}_{H_2O}^V = \bar{f}_{H_2O}^L = \bar{f}_{H_2O}^S$ where

$\bar{f}_{H_2O}^V = y_{H_2O}P_{atm}$

$\bar{f}_{H_2O}^L = $ vapor pressure of liquid water

$\bar{f}_{H_2O}^S = $ vapor (sublimation) pressure of ice.

[Here, again, we have neglected all fugacity coefficient departures from unity.]
Now, in fact, we know that at normal pressures the liquid is the stable phase above 0°C and the solid at temperatures below 0°C. Thus, liquid droplets will stable at saturation conditions above 0°C, and water (ice) crystals will be stable at saturation conditions below 0°C.
At –25°C (248.15 K) and $P = 1/2$ bar, we have, for equilibrium with the liquid

$$y_{H_2O}^{eq, L} = \frac{f_{H_2O}^L}{P_{atm}} = \frac{P^{vap}(\text{water})}{0.5 \text{ bar}} = 1.644 \times 10^{-3}$$

$$[\text{from equating } \bar{f}_{H_2O}^V = \bar{f}_{H_2O}^L\,]$$

For equilibrium with the solid

$$y_{H_2O}^{eq, S} = \frac{P^{vap}(\text{ice})}{0.5 \text{ bar}} = 1.268 \times 10^{-3}$$

$$[\text{from equating } \bar{f}_{H_2O}^V = \bar{f}_{H_2O}^S\,]$$

Thus, if the relative humidity (with respect to equilibrium with the liquid) is only $\left(1.268 \times 10^{-3}/1.644 \times 10^{-3}\right) \times 100\% \sim 77.1\%$ the ice crystals will be stable. At higher relative humidities it is possible to have water vapor in equilibrium with liquid droplets in a metastable state, at lower relative humidities the ice crystals will sublime.

8.11-3   We will assume, since Hydrochloric acid is a strong acid, that the HCl molecule will be completely ionized at all concentrations.
Let $y = $ wt% HCl; $100 - y = $ wt% of H_2O.

$$\text{mol HCl}/100 \text{ grams solution} = \frac{y}{36.5}$$

$$\text{mol } H_2O/100 \text{ grams solution} = \frac{100 - y}{18.0}$$

$$\text{mol } H^+, \text{ Cl}^- \text{ ions}/100 \text{ grams solution} = \frac{2y}{36.5}$$

$$\text{mole fraction of water} = \frac{(100 - y)/18.0}{(100 - y)/18.0 + 2y/36.5} = \frac{2.0278(100 - y)}{2.0278(100 - y) + 2y}$$

Mole fractions for each solution are given in the table below.
Next, we use the partial pressure (vapor-liquid equilibrium) data. For water, we have

$$\bar{f}_W^L = \bar{f}_W^V \Rightarrow x_W \textbf{\textit{g}}_W P_W^{vap} = P_W,$$

where, again, we have neglected all fugacity coefficient corrections. Using, from Problem 5.12, that for $\ln P_W^{vap} = 26.3026 - 5432.8/T$ in Pa; for bar $\ln P_W^{vap} = 14.7898 - 5432.8/T$ and from the problem statement that

$$\ln P_W = 2.3026\left(A - \frac{B}{T} \right)$$

we obtain

$$\ln(x_W \textbf{\textit{g}}_W) - (2.3026A - 1.47898) + \frac{1}{T}(5432.8 - 2.3026B)$$

From which we obtain the following results:

y	x_W	$\ln(x_W \textbf{\textit{g}}_W)$	$x_W \textbf{\textit{g}}_W$	$\textbf{\textit{g}}_W = x_W \textbf{\textit{g}}_W / x_W$	
10	0.9012	–0.19172	0.82554	0.9160	(0.8707)
20	0.8022	–0.53917	0.5832	0.7270	(0.6472)
30	0.7029	–1.16719	0.31124	0.4428	(0.3770)
40	0.6033	–2.12638	0.11927	0.1977	(0.1585)

Note that the activity coefficient for water is significantly less than unity. [Numbers in parentheses are $\textbf{\textit{g}}_W$ calculated assuming HCl not ionized.]

8.11-4   Equilibrium between water in air and water in aqueous solution requires that $\bar{f}_{H_2O}^L = \bar{f}_{H_2O}^V$. Neglecting fugacity coefficient corrections, we have

$$\bar{f}^{L}_{H_2O} = x_{H_2O}\boldsymbol{g}_{H_2O}P^{vap}_{H_2O} = 4.24x_{H_2O}\boldsymbol{g}_{H_2O} \quad \text{bar}$$
$$\underset{\substack{\uparrow \text{entry in table for} \\ 0 \text{ wt\% } Na_2CO_3}}{}$$

$$\bar{f}^{V}_{H_2O} = y_{H_2O}P(\underset{=1}{\underbrace{\frac{f}{P}}}) = y_{H_2O}P = P_{H_2O}$$

$$\Rightarrow \boldsymbol{g}_{H_2O} = \frac{P_{H_2O}}{4.24x_{H_2O}}, \text{ for } P_{H_2O} \text{ in bar}$$

Let W = wt% Na_2CO_3; $MW_{Na_2CO_3} = 106$ g/mol

$$\text{moles } Na_2CO_3/100 \text{ g solution} = \frac{W}{106}$$

$$\text{moles ions}/100 \text{ g solution} = \frac{3W}{106}\left(\begin{matrix}\text{assuming } Na_2CO_3 \text{ is} \\ \text{completely ionized}\end{matrix}\right)$$

$$\text{moles } H_2O/100 \text{ g solution} = \frac{100-W}{18}$$

$$\text{mole fraction water} = \frac{(100-W)/18}{(100-W)/18 + 3W/106} = \frac{100-W}{100-0.4906W}$$

Thus

$$\boldsymbol{g}_{H_2O} = \frac{P_{H_2O}(100-0.4906W)}{4.24(100-W)}$$

Values of $\boldsymbol{g}_{H_2O}$ calculated from above equation are listed below:

W	0	5	10	15	20	25	30
P_{H_2O}(kPa)	4.24	4.16	4.05	3.95	3.84	3.71	3.52
$\boldsymbol{g}_{H_2O}$	1.00	1.007	1.010	1.015	1.021	1.023	1.011
x_{H_2O}	1.0	0.974	0.946	0.918	0.887	0.855	0.821
$\boldsymbol{g}_{H_2O}$ (assuming Na_2CO_3 did not ionize)	1.0	0.990	0.974	0.959	0.944	0.924	0.891

8.11-5 x_{air} = mole fraction of air in water (liquid)

$$x_{air} = \frac{P_{air}}{\underset{\substack{\text{Henry's} \\ \text{law} \\ \text{constant}}}{H}} = \frac{0.1333 \text{ kPa} \times 10^3 \text{ Pa/kPa}}{4.3 \times 10^4 \text{ bar} \times 10^5 \text{ Pa/bar}} \cong 0.3 \times 10^{-7}$$

$\Rightarrow x_{H_2O} = 1$ (Do not have to consider air trapped in water)

At equilibrium

$$\bar{f}^{L}_{H_2O} = \bar{f}^{S}_{H_2O} = \bar{f}^{V}_{H_2O};$$

$$\Rightarrow x_{H_2O}P^{vap}_{H_2O} = P^{sub}_{H_2O} = y_{H_2O}P = P^{vap}_{H_2O} \text{ since } x_{H_2O} = 1$$

[Note: Because of the low pressures involved, we have neglected f/P terms and Poynting corrections.]

For comparison, in an air-free measurement, we have

$$P_{H_2O}^{vap} = P_{H_2O}^{sub} = P_{TP}$$

where P_{TP} is the true triple point temperature.

Since $P_{H_2O}^{vap} = P_{H_2O}^{sub}$ has to be satisfied in both cases, we would obtain the same triple point temperature in both the air-free experiment, and the measurement with air.

In the air-free experiment we measure $P = P_{H_2O}$ and get the triple point pressure. In the experiment with air we measure $P = P_{H_2O} + P_{air}$ and, mistakenly, assume this is the triple point pressure; actually P_{H_2O} is the triple point pressure. The error, ΔP, is equal to the partial pressure of air; here 0.1333 kPa. Thus, we have

$$\% \text{ error} = \frac{\Delta P}{P_{H_2O}^{TP}} \times 100 = \frac{0.1333}{0.6113} \times 100 = 21.8\%$$

[Note: From the Steam Tables, triple point pressure is 0.6113 kPa.]

8.11-6

$$\underline{S}^{ex} = -\left(\frac{\partial \underline{G}^{ex}}{\partial T}\right)_{P,\underline{x}} = -\frac{\partial}{\partial T}\bigg|_{P,\underline{x}} \left\{x_1 \overline{G}_1^{ex} + x_2 \overline{G}_2^{ex}\right\}$$

$$= -\frac{\partial}{\partial T}\bigg|_{P,\underline{x}} RT\{x_1 \ln \gamma_1 + x_2 \ln \gamma_2\}$$

$$= -R\sum x_i \ln \gamma_i - RT\sum x_i \left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{P,\underline{x}}$$

$$\underline{H}^{ex} = -T^2\left[\frac{\partial\left(\underline{G}^{ex}/T\right)}{\partial T}\right]_{P,\underline{x}} = -RT^2 \frac{\partial}{\partial T}\bigg|_{P,\underline{x}} \sum x_i \ln \gamma_i$$

$$= -RT^2 \sum x_i \left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{P,\underline{x}}$$

$$\underline{V}^{ex} = \left(\frac{\partial \underline{G}^{ex}}{\partial P}\right)_{T,\underline{x}} = \frac{\partial}{\partial P}\bigg|_{T,\underline{x}} \sum x_i RT \ln \gamma_i = RT\sum_i x_i \left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,\underline{x}}$$

$$\underline{U}^{ex} = \underline{H}^{ex} - P\underline{V}^{ex} = -RT^2 \sum_i x_i \left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{P,\underline{x}} - PRT\sum_i x_i \left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,\underline{x}}$$

$$= -RT\sum_i x_i \left[\left(\frac{\partial \ln \gamma_i}{\partial \ln T}\right)_{P,\underline{x}} + \left(\frac{\partial \ln \gamma_i}{\partial \ln P}\right)_{T,\underline{x}}\right]$$

$$C_P^{ex} = \left(\frac{\partial \underline{H}^{ex}}{\partial T}\right)_{P,\underline{x}} = -2RT\sum x_i \left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{P,\underline{x}} - RT^2 \sum x_i \left(\frac{\partial^2 \ln \gamma_i}{\partial T^2}\right)_{P,\underline{x}}$$

8.11-7 (a) Since tartaric acid is a weak acid, we will assume it is not ionized. Letting $z =$ grams of tartaric acid per 100 grams of water, we obtain

$$x_T = \frac{\text{mole fraction}}{\text{of tartaric acid}} = \frac{z/150}{z/150 + 100/18} \; ; \; x_W = 1 - x_T \; .$$

At the boiling point we have $x_W \boldsymbol{g}_W P_W^{vap} = P_W = 1.013 \, \text{bar}$. Thus, $\boldsymbol{g}_W = 1.013 / x_W P_W^{vap}$. The results of the computations appear below.

z	x_T	x_W	$\boldsymbol{g}_W$
87	0.0945	0.9055	0.9445
177	0.1752	0.8248	0.8744
272	0.2461	0.7539	0.8105

Thus, solution is not ideal.

(b) Now we use Eqn. (8.7-2)

$$\ln(\boldsymbol{g}_W x_W) = -\frac{\Delta \underline{H}^{fus}(T_m)}{R}\left[\frac{T_m - T_f}{T_m T_f}\right] - \frac{\Delta C_P}{R}\left[1 - \frac{T_m}{T_f} + \ln\frac{T_m}{T_f}\right]$$

From Problem 5.26

$$\begin{array}{l} C_P(\text{liquid}) = 4.22 \; \text{J/g} \, °\text{C} \\ C_P(\text{solid}) = 2.1 \; \text{J/g} \, °\text{C} \end{array} \Rightarrow \Delta C_P = 38.16 \; \text{J/mol} \, °\text{C}$$

Also, from the *Chemical Engineers Handbook* $\Delta \underline{H}^{fus} = 6008.2 \; \text{J/mol}$. Let $y = T_m / T_f$, we obtain

$$\ln(x_W \boldsymbol{g}_W) = \frac{-6008.2}{8.314 \times 273.16}\left[\frac{T_m}{T_f} - 1\right] - \frac{38.16}{8.314}\left[1 - \frac{T_m}{T_f} + \ln\frac{T_m}{T_f}\right]$$

$$\ln(x_W \boldsymbol{g}_W) = -2.6457[y - 1] + 4.590[1 - y + \ln y]$$

Procedure is to use the data tabulated above to obtain the product $x_W \boldsymbol{g}_W$, and then compute y by trial and error. Below are the results of solving the equation above, and also of neglecting the ΔC_P term, i.e., solving

$$\ln(x_W \boldsymbol{g}_W) = -2.6457[y - 1]$$

z	x_w	T_f also ΔT with ΔC_P term	T_f also ΔT without ΔC_P term
87	0.9055	-15.95° C	−15.25° C
177	0.8248	−33.76	−30.03
272	0.7539	−49.99	−42.88

8.11-8 (a) Imagine the separation process to occur continuously, as below:

Mass balance: $0 = 1 - x_1 - x_2$

Energy balance: $0 = \underline{H}_{mix} - x_1\underline{H}_1 - x_2\underline{H}_2 + Q + W$

Entropy balance: $0 = \underline{S}_{mix} - x_1\underline{S}_1 - x_2\underline{S}_2 + \dfrac{Q}{T} + S_{gen}$ ⟋ 0

Subtracting the product of temperature and the entropy balance from the energy balance yields

$$0 = (\underline{H}_{mix} - T\underline{S}_{mix}) - x_1(\underline{H}_1 - T\underline{S}_1) - x_2(\underline{H}_2 - T\underline{S}_2) + W$$

or

$$W = -\{\underline{G}_{mix} - x_1\underline{G}_1 - x_2\underline{G}_2\} = -\Delta\underline{G}_{mix} = -RT\sum_{i=1,\,2} x_i \ln x_i - \underline{G}^{ex}$$

Thus

$$W = -RT[x_1 \ln x_1 + x_2 \ln x_2] - Ax_1x_2$$

and

$$Q = -W[\underline{H}_{mix} - x_1\underline{H}_1 - x_2\underline{H}_2] = -W - \underline{H}^{ex}$$

However,

$$\left.\frac{\P(\underline{G}^{ex}/T)}{\P T}\right|_{P,\,x_i} = -\frac{\underline{H}^{ex}}{T^2} \Rightarrow \underline{H}^{ex} = -T^2 \frac{\P}{\P T}\left(\frac{\underline{G}^{ex}}{T}\right)$$

$$\Rightarrow \underline{H}^{ex} = -T^2 \frac{\P}{\P T}\left\{\frac{Ax_1x_2}{T}\right\} = Ax_1x_2 = \underline{G}^{ex} \Rightarrow \underline{S}^{ex} = 0$$

Therefore

$$Q = -\underline{W} - \underline{H}^{ex} = +RT\sum_{i=1,\,2} x_i \ln x_i + \underline{G}^{ex} - \underline{G}^{ex}$$

or

$$Q = RT\{x_1 \ln x_1 + x_2 \ln x_2\}$$

(b) $W = 0 \Rightarrow RT(x_1 \ln x_1 + x_2 \ln x_2) = -Ax_1x_2$ or

$$T\big|_{W=0} = \frac{-Ax_1x_2}{R[x_1 \ln x_1 + x_2 \ln x_2]}.$$

Upper consolute temperature: $T^{UC} = \dfrac{A}{2R}$

For an equimolar mixture

$$T\big|_{W=0} = \frac{-A(1/2)(1/2)}{R[(1/2)\ln(1/2)]\times 2} = \frac{A}{4R\ln 2} = \frac{T^{UC}}{2\ln 2}$$

and, for this case

$$Q = -R\ln 2 \cdot \frac{T^{UC}}{2\ln 2} = -\frac{1}{2}RT^{UC} = -\frac{A}{4}$$

(c) If A is a function of temperature, then

$$\underline{H}^{ex} = -T^2 \frac{\P}{\P T}\left(\frac{Ax_1x_2}{T}\right)_{P,\underline{x}} = T^2 \frac{Ax_1x_2}{T^2} - Tx_1x_2\left(\frac{\P A}{\P T}\right)_{P,\underline{x}}$$

$$= \underline{G}^{ex} - x_1x_2 T\left(\frac{\P A}{\P T}\right)_{P,\underline{x}}$$

$$W = -RT(x_1 \ln x_1 + x_2 \ln x_2) - Ax_1 x_2$$

as before but

$$Q = RT(x_1 \ln x_1 + x_2 \ln x_2) + x_1 x_2 T \left(\frac{\partial A}{\partial T} \right)_{P,\underline{x}}$$

and, for $W = 0$, we have, as before

$$T = \frac{A/4R}{\ln 2}$$

but T^{UC} is no longer equal to $\dfrac{A}{2R}$.

8.11-9 At equilibrium $\overline{G}_i^{\,\text{I}}(T,P,\underline{x}^{\text{I}}) = \overline{G}_i^{\,\text{II}}(T,P,\underline{x}^{\text{II}})$; $i = 1,\ 2$ and along the equilibrium curve

$$d\overline{G}_i^{\,\text{I}}(T,P,\underline{x}^{\text{I}}) = d\overline{G}_i^{\,\text{II}}(T,P,\underline{x}^{\text{II}}) ; \ i = 1,\ 2$$

Treating *T, P* and one mole fraction as the independent variables in this binary system, we obtain

$$\left. \begin{array}{l}
d\overline{G}_i^{\,\text{I}} = -\overline{S}_i^{\,\text{I}} dT + \overline{V}_i^{\,\text{I}} dP + \left(\dfrac{\partial \overline{G}_i^{\,\text{I}}}{\partial x_1} \right) dx_1 \\[3mm]
d\overline{G}_i^{\,\text{II}} = -\overline{S}_i^{\,\text{II}} dT + \overline{V}_i^{\,\text{II}} dP + \left(\dfrac{\partial \overline{G}_i^{\,\text{II}}}{\partial y_1} \right) dy_1
\end{array} \right\} i = 1,\ 2$$

Equating $d\overline{G}_i^{\,\text{I}}$ and $d\overline{G}_i^{\,\text{II}}$,

$$-\overline{S}_i^{\,\text{I}} dT + \overline{V}_i^{\,\text{I}} dP + \left(\frac{\partial \overline{G}_i^{\,\text{I}}}{\partial x_1} \right)_{T,\,P} dx_1 = -\overline{S}_i^{\,\text{II}} dT + \overline{V}_i^{\,\text{II}} dP + \left(\frac{\partial \overline{G}_i^{\,\text{II}}}{\partial y_1} \right)_{T,\,P} dy_1 ; \ i = 1,\ 2$$

Now multiplying by y_i , summing and rearranging gives

$$-\sum_{i=1}^{2} y_i \left(\overline{S}_i^{\,\text{I}} - \overline{S}_i^{\,\text{II}} \right) dT + \sum y_i \left(\overline{V}_i^{\,\text{I}} - \overline{V}_i^{\,\text{II}} \right) dP$$

$$= \underbrace{\sum y_i \left(\frac{\partial \overline{G}_i^{\,\text{II}}}{\partial y_1} \right)_{T,P} dy_1}_{\substack{=0 \text{ by the Gibbs-} \\ \text{Duhem equation}}} - \sum y_i \left(\frac{\partial \overline{G}_i^{\,\text{I}}}{\partial x_1} \right)_{T,P} dx_1$$

$$\Rightarrow \sum y_i \left(\overline{V}_i^{\,\text{I}} - \overline{V}_i^{\,\text{II}} \right) dP = \sum y_i \left(\overline{S}_i^{\,\text{I}} - \overline{S}_i^{\,\text{II}} \right) dT - \underbrace{\sum y_i \left(\frac{\partial \overline{G}_i^{\,\text{I}}}{\partial x_1} \right)_{T,P} dx_1}_{\substack{\text{Since } x\text{'s and } y\text{'s are mixed,} \\ \text{the Gibbs-Duhem equation} \\ \text{does not apply}}}$$

Since $\overline{G}_i^{\,\text{I}} = \overline{G}_i^{\,\text{II}}$, $\overline{H}_i^{\,\text{I}} - T\overline{S}_i^{\,\text{I}} = \overline{H}_i^{\,\text{II}} - T\overline{S}_i^{\,\text{II}}$ or $\overline{S}_i^{\,\text{I}} - \overline{S}_i^{\,\text{II}} = \left(\overline{H}_i^{\,\text{I}} - \overline{H}_i^{\,\text{II}} \right) / T$.

For vapor-liquid equilibrium, with phase I = liquid, and phase II = vapor, we have, at low and moderate pressures, that

$$\overline{V}_i^{\,\text{II}} \gg \overline{V}_i^{\,\text{I}} , \text{ and } \overline{V}_i^{\,\text{II}} \approx \frac{RT}{P}$$

Therefore

$$-\sum_{i=1}^{2} y_i \frac{RT}{P} dP = \underbrace{\frac{1}{T} \sum_{i=1}^{2} y_i \left(\overline{H}_i^{\mathrm{I}} - \overline{H}_i^{\mathrm{II}} \right) dT}_{\substack{\Delta \underline{H}^{\mathrm{vap}} \text{ for } y_1 \text{ moles} \\ \text{component 1 and} \\ y_2 = 1 - y_1 \text{ moles of} \\ \text{component 2 from solution.}}} - \sum_{i=1}^{2} y_i \left(\frac{\partial \overline{G}_i}{\partial x_1} \right)_{T,P} dx_1$$

$$\underbrace{-\sum_{i=1}^{2} y_i \frac{RT}{P} dP}_{-RTd \ln P}$$

$$\Rightarrow -RTd \ln P = -\frac{1}{T} \Delta \underline{H}^{\mathrm{vap}} dT - \sum_{i=1}^{2} y_i \left(\frac{\partial \overline{G}_i}{\partial x_1} \right)_{T,P} dx_1$$

$$\left(\frac{\partial \ln P}{\partial T} \right)_{\underline{x}} = \frac{\Delta \underline{H}^{\mathrm{vap}}}{RT^2}$$

8.11-10   (a)   Start from the Gibbs-Duhem equation for each phase

$$-\underline{S}^{\mathrm{K}} dT + \underline{V}^{\mathrm{K}} dP + \sum x_i^{\mathrm{K}} d\overline{G}_i^{\mathrm{K}} = 0$$

where K designates the phase, and is equal to I, II or III here. The criterion for equilibrium is

$$\overline{G}_i^{\mathrm{I}} = \overline{G}_i^{\mathrm{II}} = \overline{G}_i^{\mathrm{III}} = \overline{G}_i \text{ (no need to designate phase on } \overline{G}_i \text{)}$$

Along the equilibrium coexistence line

$$d\overline{G}_i^{\mathrm{I}} = d\overline{G}_i^{\mathrm{II}} = d\overline{G}_i^{\mathrm{III}} = d\overline{G}_i$$

Also, the pressures are equal in each phase as are the temperatures. Thus, we have the three equations

$$\underline{V}^{\mathrm{I}} \frac{dP}{dT} + x_1^{\mathrm{I}} \frac{d\overline{G}_1}{dT} + x_2^{\mathrm{I}} \frac{d\overline{G}_2}{dT} = \underline{S}^{\mathrm{I}}$$

$$\underline{V}^{\mathrm{II}} \frac{dP}{dT} + x_1^{\mathrm{II}} \frac{d\overline{G}_1}{dT} + x_2^{\mathrm{II}} \frac{d\overline{G}_2}{dT} = \underline{S}^{\mathrm{II}}$$

$$\underline{V}^{\mathrm{III}} \frac{dP}{dT} + x_1^{\mathrm{III}} \frac{d\overline{G}_1}{dT} + x_2^{\mathrm{III}} \frac{d\overline{G}_2}{dT} = \underline{S}^{\mathrm{III}}$$

However,

$$\underline{G} = \underline{H}^{\mathrm{K}} - T\underline{S}^{\mathrm{K}} = \sum x_i^{\mathrm{K}} \overline{G}_i \Rightarrow T\underline{S}^{\mathrm{K}} = \underline{H}^{\mathrm{K}} - \sum x_i^{\mathrm{K}} \overline{G}_i = \left(\underline{H}^{\mathrm{K}} - \overline{G}_i \right)$$

Using this result gives

$$\underline{V}^{\mathrm{K}} \frac{dP}{dT} + \sum_i x_i^{\mathrm{K}} \left(\frac{d\overline{G}_i}{dT} + \frac{1}{T} \overline{G}_i \right) = \frac{1}{T} \sum x_i^{\mathrm{K}} \overline{H}_i^{\mathrm{K}} \; ; \; K = 1, 2, 3$$

or, in matrix form

$$\begin{bmatrix} \underline{V}^{\mathrm{I}} \\ \underline{V}^{\mathrm{II}} \\ \underline{V}^{\mathrm{III}} \end{bmatrix} \frac{dP}{dT} + \begin{bmatrix} x_1^{\mathrm{I}} \\ x_1^{\mathrm{II}} \\ x_1^{\mathrm{III}} \end{bmatrix} \left(\frac{d\overline{G}_1}{dT} + \frac{1}{T}\overline{G}_1 \right) + \begin{bmatrix} x_2^{\mathrm{I}} \\ x_2^{\mathrm{II}} \\ x_2^{\mathrm{III}} \end{bmatrix} \left(\frac{d\overline{G}_2}{dT} + \frac{\overline{G}_2}{T} \right) = \frac{1}{T} \begin{bmatrix} \sum x_i^{\mathrm{I}} \overline{H}_i^{\mathrm{I}} \\ \sum x_i^{\mathrm{II}} \overline{H}_i^{\mathrm{II}} \\ \sum x_i^{\mathrm{III}} \overline{H}_i^{\mathrm{III}} \end{bmatrix}$$

Thus, we have 3 algebraic equations for the three unknowns

$$\left(\frac{dP}{dT} \right), \ \left(\frac{d\overline{G}_1}{dT} + \frac{\overline{G}_1}{T} \right) \text{ and } \left(\frac{d\overline{G}_2}{dT} + \frac{\overline{G}_2}{T} \right)$$

Using Cramer's rule and solving for $\dfrac{dP}{dT}$ gives

$$\frac{dP}{dT} = \frac{\begin{vmatrix} \dfrac{1}{T}\sum x_i^{\mathrm{I}} \overline{H}_i^{\mathrm{I}} & x_1^{\mathrm{I}} & x_2^{\mathrm{I}} \\ \dfrac{1}{T}\sum x_i^{\mathrm{II}} \overline{H}_i^{\mathrm{II}} & x_1^{\mathrm{II}} & x_2^{\mathrm{II}} \\ \dfrac{1}{T}\sum x_i^{\mathrm{III}} \overline{H}_i^{\mathrm{III}} & x_1^{\mathrm{III}} & x_2^{\mathrm{III}} \end{vmatrix}}{\begin{vmatrix} \underline{V}^{\mathrm{I}} & x_1^{\mathrm{I}} & x_2^{\mathrm{I}} \\ \underline{V}^{\mathrm{II}} & x_1^{\mathrm{II}} & x_2^{\mathrm{II}} \\ \underline{V}^{\mathrm{III}} & x_1^{\mathrm{III}} & x_2^{\mathrm{III}} \end{vmatrix}}$$

This type of relationship was first derived by Gibbs.

(b) The Gibbs Phase Rule is $F = C - P - M + 2$

i)   For liquid-liquid miscibility (only one liquid phase)
$$P = 2 \text{ (vapor, liquid)}, \ C = 2 \text{ and } M = 0$$

$F = 2 - 2 - 0 + 2 = 2$ degrees of freedom.
Thus if, at fixed temperature, the liquid phase mole fraction is varied, the total pressure will change.

ii) liquid-liquid immiscibility (two liquid phases)
$P = 3$ (vapor + 2 liquids)
Thus

$$F = 2 - 3 - 0 + 2 = 1 \text{ degree of freedom}$$

Consequently, at fixed temperature the two phase compositions and the pressure are fixed. Varying the average mole fraction would change the mass distribution between the two phases, but would *not* change the composition of either phase or the total pressure. That is, when two liquid phases and a vapor phase exist in a binary mixture, the equilibrium pressure depends only on temperature and not on average composition.

8.11-11 Types of equilibrium that could occur are:
i)   solid-liquid
ii) liquid-vapor
iii) solid-liquid-vapor
iv) solid-vapor
We will assume
i)   Ideal solutions $\Rightarrow \bar{f}_i^{\mathrm{L}} = x_i P_i^{\mathrm{vap}}$
ii) Ideal gas phase $\Rightarrow \bar{f}_i^{\mathrm{V}} = y_i P$

iii) That oxygen and nitrogen are immiscible in the solid phase. Thus
$\bar{f}_i^S = f_i^S = P_i^{\text{sub}}$.

For vapor-liquid equilibrium, we have $\bar{f}_i^V = \bar{f}_i^L \Rightarrow x_i P_i^{\text{vap}} = y_i P$

For solid-liquid equilibrium we have $\bar{f}_i^S = \bar{f}_i^L \Rightarrow P_i^{\text{sub}} = x_i P_i^{\text{vap}}$

Calculation of solid-liquid equilibrium:

1) Assume N_2 is the solid phase in equilibrium with the liquid

2) Choose T, use data in the problem statement to calculate $P_{H_2}^{\text{sub}}$ and $P_{H_2}^{\text{vap}}$, and

   $x_{N_2} = P_{N_2}^{\text{sub}} \big/ P_{N_2}^{\text{vap}}$

3) Repeat calculation for other values of T

4) Repeat calculation assuming O_2 is the solid phase, and calculating

   $x_{O_2} = P_{O_2}^{\text{sub}} \big/ P_{O_2}^{\text{vap}}$

5) At each composition, determine which solid freezes out by determining which results in the highest melting temperature.

[In this calculation, the tabulated vapor pressure and sublimation pressure data were plotted as $\ln P$ vs $1/T$, and this graph was used for interpolation.] Some results are shown below:

T(K)	$P_{N_2}^{\text{sub}}(T) \big/ P_{N_2}^{\text{vap}}(T)$	$= x_{N_2}$	T(K)	$P_{O_2}^{\text{sub}} \big/ P_{O_2}^{\text{vap}}$	$= x_{O_2}$
34	0.126/0.4467	0.282	45.46	3.8933/5.5733	0.699
38	1.806/4.7867	0.377	47.62	10.560/13.733	0.769
42	15.427/32.2533	0.478	50.0	29.867/34.000	0.878
46	89.827/154.80	0.580	52.6	78.667/84.000	0.937
50	390.93/572.93	0.682	54.35		1.0
54	1356.8/1733.7	0.783			
58	3934.7/4471.2	0.880			
62	9873.3/10136.5	0.974			
63.2		1.0			

Since the sublimation and vapor pressures below the normal melting point are so far below the total system pressure of 1 atm (1.013 bar), we do not have to consider either solid-vapor or solid-liquid-vapor equilibrium.

For the calculation of vapor-liquid equilibrium we use $x_i P_i^{\text{vap}} = y_i P$ and
$\sum x_i P_i^{\text{vap}} = 1.013 \text{ bar}$. Thus

$$P = x_{N_2} P_{N_2}^{\text{vap}} + (1 - x_{N_2}) P_{O_2}^{\text{vap}} \Rightarrow P - P_{O_2}^{\text{vap}} = x_{N_2}\left(P_{N_2}^{\text{vap}} - P_{O_2}^{\text{vap}}\right)$$

Therefore

$$x_{N_2} = \frac{P - P_{O_2}^{\text{vap}}}{P_{N_2}^{\text{vap}} - P_{O_2}^{\text{vap}}}$$

and

$$y_{N_2} = \frac{x_{N_2} P_{N_2}^{\text{vap}}}{P}$$

and the procedure is to choose T, calculate $P_{N_2}^{\text{vap}}$ and $P_{O_2}^{\text{vap}}$, and then x_{N_2} and y_{N_2}. The results are given below:

T	75.5	77.5	80	82.5	85	87.5	90.1	K
$P_{N_2}^{vap}$	1.013	1.333	1.849	2.467	3.284	4.200		bar
$P_{O_2}^{vap}$		0.2187	0.3147	0.4267	0.5867	0.7600	1.013	bar
x_{N_2}	1.0	0.713	0.455	0.288	0.158	0.074	0	
y_{N_2}	1.0	0.938	0.830	0.700	0.512	0.305	0	

Below is the vapor-liquid-solid phase diagram for O_2 and N_2 determined by experiment (B.F. Dodge and A. K. Dunbar, *J. Amer. Chem.*, Soc. **49**, 501 (1927); B. F. Dodge, *Chem. & Met. Eng.* **35**, 622 (1928); M. Ruhemann and B. Ruhemann, "Low Temperature Physics", Cambridge Univ. Press, London, 1937, p. 100; and R.B. Scott, "Crogenic Engineering", Van Nostrand, Princeton, 1959, p. 286). The main difference between this figure and our calculations is that O_2 and N_2 actually form mixed solids on freezing, which we presumed would not occur.

[I am grateful to my former colleague at the University of Delaware, Prof. K. Bischoff for bringing these data to our attention.]
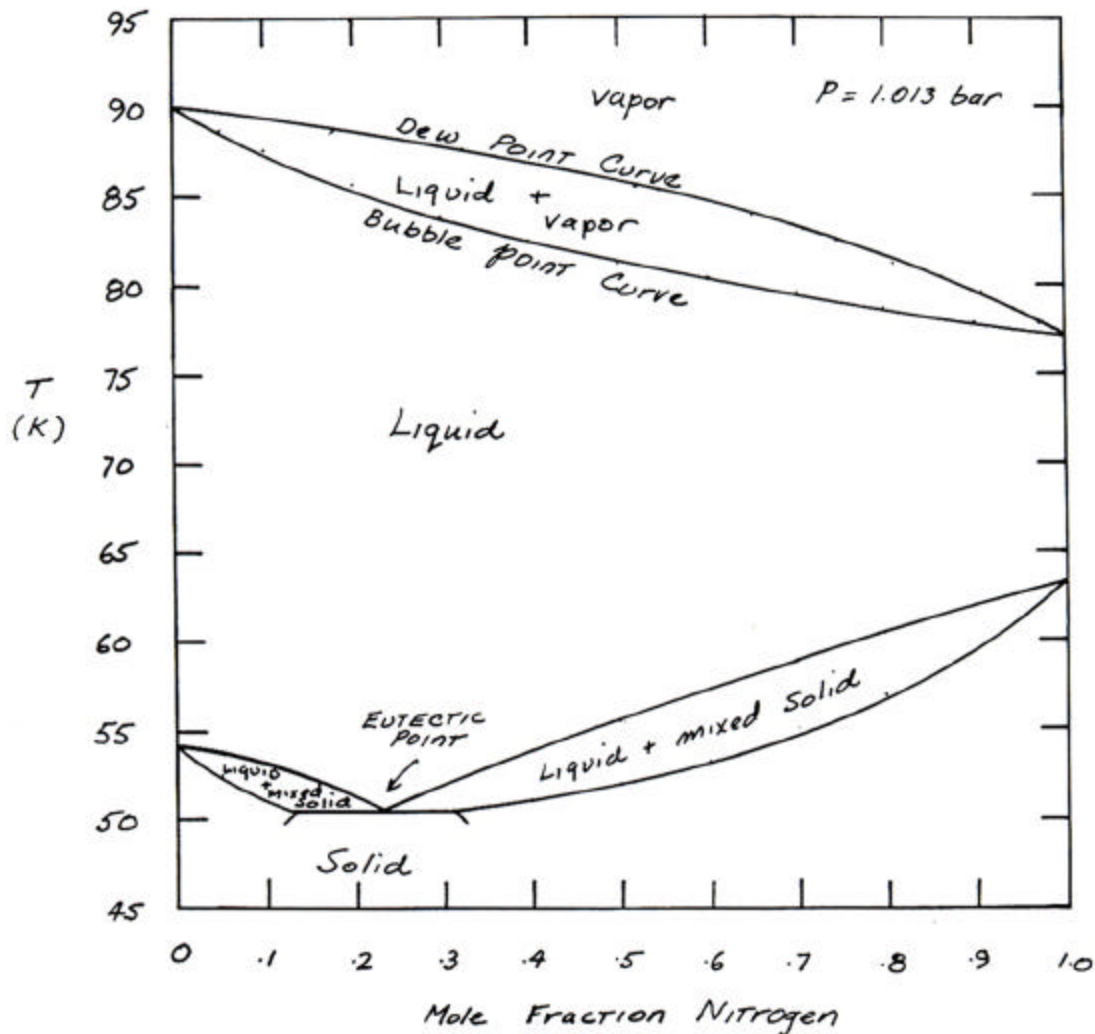
8.11-12 Note: Error in Problem statement in 1st printing vapor pressure of isobutane is 490.9 kPa not 4.909 kPa.

Based on Illustration 8.4-2 this is a problem in vapor-liquid-liquid (3 phase) equilibrium. Also, from Problem 8.9-10, we have that the coexistence pressure is constant over the whole range of average (or total) mole fractions for which two liquid phases exist. From Illustration 8.4-2, one liquid phase is present for $x_{\text{isobutane}} = x_1 \leq 0.1128$ and $x_1 \geq 0.9284$. For *overall* mole fractions in the range $0.1128 \leq x_1 \leq 0.9284$, two liquid phases exist. To compute the V-L-L coexistence pressure in the one-liquid phase region, we use (neglecting fugacity coefficient corrections) $x_1 \boldsymbol{g}_1 P_1^{\text{vap}} + x_2 \boldsymbol{g}_2 P_2^{\text{vap}} = P$ where $P_1^{\text{vap}} = 490.9$ kPa, and $P_2^{\text{vap}} = 0.493$ kPa, and $\boldsymbol{g}_1$ and $\boldsymbol{g}_2$ (or $x_1 \boldsymbol{g}_1$ and $x_2 \boldsymbol{g}_2$) are given in Table in Illustration 8.4-2. Also, the van Laar constants are given there, so $\boldsymbol{g}_1$ and $\boldsymbol{g}_2$ can be computed at other compositions. Results are given below

x_1	$x_1 \boldsymbol{g}_1 P_1^{\text{vap}}$	+	$x_2 \boldsymbol{g}_2 P_2^{\text{vap}}$	P
0	0		1×0.493	0.493 kPa
0.025	0.3068×490.9	+	0.9764×0.493	151.1
0.05	0.5491×490.9	+	0.9555×0.493	270.0
0.075	0.7384×490.9	+	0.9371×0.493	362.9
0.10	0.8843×490.9	+	0.9231×0.493	434.6
0.1128	0.945×490.9	+	0.914×0.493	464.4
↓	↓		↓	↓
0.9284				464.4
0.95	0.9582×490.9	+	0.7325×0.493	470.7
0.975	0.9771×490.9	+	0.4318×0.493	479.9
1	490.9			490.9
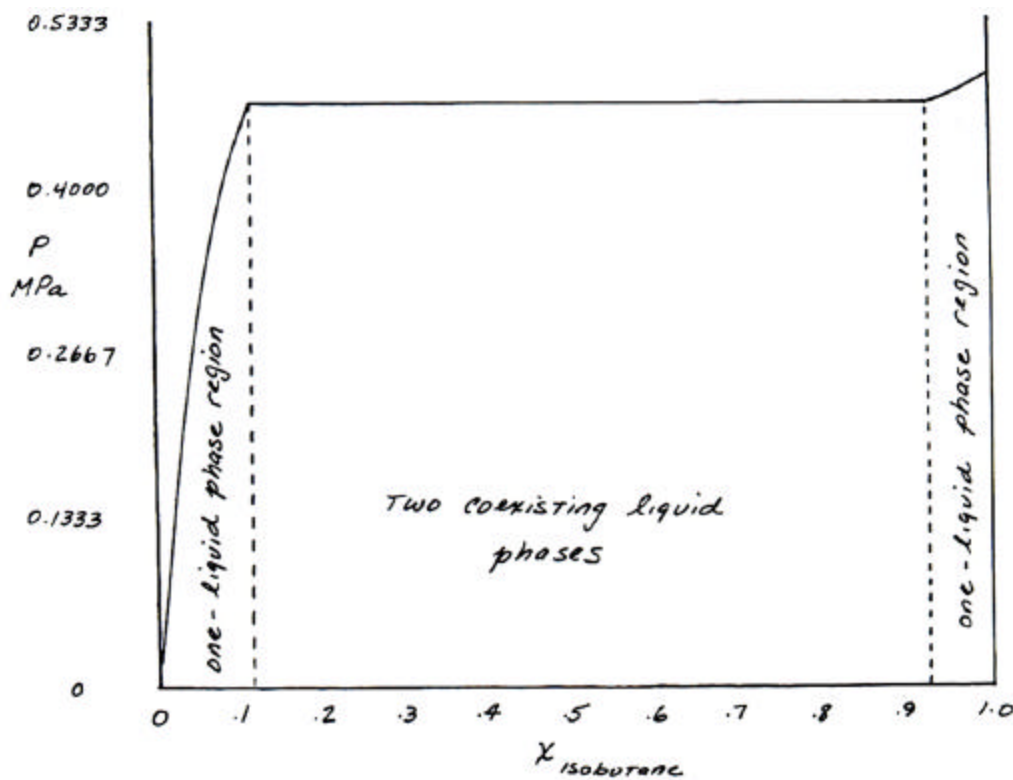
8.11-13 The vapor pressure of water is 1.013 bar at 100°C. To compute the vapor pressure of acetone, we fit the data in the problem statement to $\ln P^{\mathrm{vap}} = A/T + B$ and find $A = -3618.9$, $B = 10.9930$ and $P_{AC}^{\mathrm{vap}}(100°C) = 3.650$ bar.

(a) To compute activity coefficients, we will use the van Laar model with $a = 2.05$, $b = 1.50$, as given in Table 7.5-1. Thus

$$\ln g_{AC} = \frac{a}{\left[1 + a x_{AC}/(b(1 - x_{AC}))\right]^2} = \frac{2.05}{\left[1 + 1.3667(x_{AC}/(1 - x_{AC}))\right]^2}$$
$$\Rightarrow g_{AC} = 1.050 \text{ at } x_{AC} = 0.8$$

and

$$\ln g_W = \frac{b}{\left[1 + b x_W/(a(1 - x_W))\right]^2} = \frac{1.50}{\left[1 + 0.7317(x_W/(1 - x_W))\right]^2}$$
$$\Rightarrow g_W = 2.921 \text{ at } x_W = 0.2$$

At vapor-liquid equilibrium

$$x_W g_W P_W^{\mathrm{vap}} + x_{AC} g_{AC} P_{AC}^{\mathrm{vap}} = P$$

Substituting the results for g_i, P_i^{vap} above yields
$$P = 3.658 \text{ bar}$$

Thus, for all pressure above 3.658 bar only a liquid of composition $x_W = 0.2$, $x_{AC} = 0.8$ will be present.

(b) This calculation is more difficult, since we can not calculate the dew point "pressure" (at fixed temperature) until the liquid phase composition and activity coefficients are known. Thus the problem involves a trial-and-error solution of the equations

$$x_W g_W P_W^{\mathrm{vap}} = y_W P \; ; \; x_{AC} g_{AC} P_{AC}^{\mathrm{vap}} = y_{AC} P, \text{ and } x_{AC} + x_W = 1$$

where x_W, x_{AC} and P are the unknowns (The g_i can be calculated from the x_i using the van Laar equations). By repeated guesses, I find

$$P = 3.601 \text{ bar; } x_W = 0.295 \text{ and } x_{AC} = 0.705$$

Thus, for all pressures below 3.601 bar, only the vapor (of composition $y_W = 0.20$, $y_{AC} = 0.80$) is present.

Note: One should check the conditions of both parts (a) and (b) to the above problem for the possible occurrence of two coexisting liquid phases.

8.11-14 Using the program VLMU with $k_{CO_2-nC_6} = 0.11$ (Table 7.4-1) results in no solution at 140 bar and 75°C. However, trying the bubble point and dew point pressure programs we obtain the following results (at $T = 348.15$ K)

x_{CO_2}	bubble point P, bar	y_{CO_2}	dew point P, bar	y_{CO_2}	dew point P, bar
0.1	12.96	0.001	1.21	0.9	15.06
0.3	37.93	0.05	1.28	0.92	20.25
0.5	64.15	0.1	1.35	0.93	24.64
0.7	89.14	0.3	1.76	0.94	32.02
0.72	91.36	0.4	2.07	0.945	38.56
0.74	93.49	0.5	2.51	0.947	42.62
0.76	95.52	0.6	3.17	0.949	49.39
0.78	97.43	0.7	4.31	0.9495	52.75
0.80	99.17	0.73	4.83		
		0.75	5.25	Program doesn't	
	Program doesn't	0.78	6.03	converge at higher	
	converge at higher	0.80	6.70	CO_2 concentrations	
	CO_2 concentrations	0.82	7.56		

Since the program doesn't converge at higher concentrations of CO_2 along either the bubble point or dew point curves, we have to make an estimate of the CO_2 concentration based on the data above. There are two possibilities: (1) The CO_2

saturation of the liquid at 140 bar is in the retrograde region at somewhere between x_{CO_2} of 0.8 and 0.95 [Note, simple equation of state programs, such as VLMU typically do not converge in the retrograde region, and more sophisticated algorithms and numerical methods must be used]; (2) at 140 bar only the vapor exists, that is, all the hexane vaporizes.

An alternative is to use the activity coefficient approach. We do this here using regular solution theory and corresponding states for the fugacity coefficients. The starting point is the equilibrium condition

$$x_i \boldsymbol{g}_i f_i^{\mathrm{L}} = y_i f_i^{\mathrm{V}}$$

which, for hexane translates to

$$x_{\mathrm{H}} \boldsymbol{g}_{\mathrm{H}} \left(\frac{f}{P}\right)_{\mathrm{sat,\,H}} P_{\mathrm{H}}^{\mathrm{vap}} \exp\left\{\frac{\underline{V}_{\mathrm{H}}^{\mathrm{L}}\left(P - P_{\mathrm{H}}^{\mathrm{vap}}\right)}{RT}\right\} = y_{\mathrm{H}} P\left(\frac{f}{P}\right)_{\mathrm{H}}$$

while for CO_2, which is considerable above its critical point, we have

$$x_{CO_2} \boldsymbol{g}_{CO_2} \left(\frac{f^{\mathrm{L}}(P = 1.013\ \mathrm{bar})}{P_C}\right)_{CO_2} P_{C,\,CO_2} \exp\left\{\frac{\underline{V}_{CO_2}^{\mathrm{L}}(P - 1.013\ \mathrm{bar})}{RT}\right\} = y_{CO_2} P\left(\frac{f}{P}\right)_{CO_2}$$

Also, fitting vapor pressure data for *n*-hexane in "*The Chemical Engineers Handbook*" we find $P_{\mathrm{H}}^{\mathrm{vap}}(T = 75°\mathrm{C}) = 1.226\ \mathrm{bar}$. Also $T = 75°\mathrm{C} = 348.15\ \mathrm{K}$

Next, we have

	T_C(K)	P_C(bar)	$\boldsymbol{d}(\mathrm{cal/cc})^{1/2}$		$\underline{V}^{\mathrm{L}}(\mathrm{cc/mol})$
n-hexane	507.4	29.69	7.3	←Table 7.6-1→	132
CO_2	304.2	73.76	6.0	←Table 8.3-1→	55

	T_r	P_r	$(f/P)_{\mathrm{sat}}$	(f^{L}/P_C)	(f^{V}/P)
n-hexane	0.686	4.715	0.732		~0.08←Fig. 5.4-1
CO_2	1.144	1.898		~1.15	0.65←Fig. 8.3-1

Thus

$$x_{CO_2} \times 1.15 \times 73.76 \times \exp\left\{\frac{55 \times 10^{-6}\ \mathrm{m^3/mol} \times (140 - 1.013)\mathrm{bar}}{348.15\ \mathrm{K} \times 8.314 \times 10^{-5}\ (\mathrm{bar\ m^3})/(\mathrm{mol\ K})}\right\} \boldsymbol{g}_{CO_2} = y_{CO_2} \times 0.650 \times 140$$

$$\Rightarrow x_{CO_2} \boldsymbol{g}_{CO_2} = 0.8238 y_{CO_2}$$

and

$$x_{\mathrm{H}} \times 0.732 \times 1.226 \times \exp\left\{\frac{132 \times 10^{-6} \times (140 - 1.226)}{348.15 \times 8.314 \times 10^{-5}}\right\} \boldsymbol{g}_{\mathrm{H}} = y_{\mathrm{H}} \times 0.08 \times 140$$

$$\Rightarrow x_{\mathrm{H}} \boldsymbol{g}_{\mathrm{H}} = 6.628 y_{\mathrm{H}}$$

The ideal mixture $(\boldsymbol{g}_i = 1)$ solution is

$y_{CO_2} = 0.9696$ $x_{CO_2} = 0.7988$ (Easily solved using

$y_H = 0.0304$ $x_H = 0.2012$ Mathcad)

To obtain a more accurate solution, regular solution theory will now be used to compute the $\boldsymbol{g}_i$'s

$$\ln \boldsymbol{g}_H = \frac{\underline{V}_H^L \boldsymbol{f}_{CO_2}^2 \left(\boldsymbol{d}_H - \boldsymbol{d}_{CO_2} \right)^2}{RT}$$

and

$$\ln \boldsymbol{g}_{CO_2} = \frac{\underline{V}_{CO_2}^L \boldsymbol{f}_H^2 \left(\boldsymbol{d}_H - \boldsymbol{d}_{CO_2} \right)^2}{RT}$$

using the ideal solution as a first guess and iterating, or using Mathcad and solving directly, I obtain the following

$y_{CO_2} = 0.9620$ $x_{CO_2} = 0.7747$ Qualitatively in agreement

$y_H = 0.0380$ $x_H = 0.2253$ with the P-R e.o.s. results.

Note the enormous solubility of carbon dioxide in hexane and, indeed, in reservoir crude! That is why carbon dioxide has been used in enhanced oil recovery (crude oil swells so more is recovered, and viscosity drops so the trapped oil in the earth matrix flows more easily.)

8.11-15 Possibilities: 1 liquid phase
                                        1 vapor phase
                                        2 phases vapor + liquid
                                        2 phases liquid + liquid
                                        3 phases liquid + liquid + vapor
We will assume that only one liquid phase exists and show that this assumption is correct.
From the data in the problem statement
$$P_{EAC}^{vap} = 0.9475 \text{ bar} \text{ and } P_{EOH}^{vap} = 0.8879 \text{ bar}$$
The bubble point pressure of an equimolar mixture is
$$P = \sum x_i \boldsymbol{g}_i P_i^{vap} = 0.5 \exp\left(0.896 \times 0.5^2\right)(0.9475 + 0.8879) = 1.148 \text{ bar}$$

Since the applied pressure is 1.8 bar, no vapor is in equilibrium with an equimolar mixture at the specified temperature of 75°C. Now we have to check to see whether one or two liquids are present at equilibrium. To determine this we start with

$$RT \ln \boldsymbol{g}_i = A x_j^2 \Rightarrow \ln \boldsymbol{g}_i - \frac{A}{RT} x_j^2 = A' x_j^2$$

with $A' = 0.896$ given in the problem statement. Therefore $A = A'RT = 0.896RT$. Now from eqn. 8.4-14 we have that the upper consolute temperature (the highest temperature at which two liquids exist) for the one-constant Margules equation is

$$T_{UC} = \frac{A}{2R} = \frac{0.896\,RT}{2R} = 0.448\,T = 155.97\ \text{K}$$

This temperature is so much below the system temperature of 348.15 K, that the single liquid phase is the stable phase. Therefore, the equimolar mixture at 75 °C and 1.8 bar is stable, and the only phase present.

8.11-16 For an azeotropic mixture, from eqn. (8.1-3)

$$\pmb{g}_i = P / P_i^{vap}$$

$$\pmb{g}_C(x_C = 0.51) = \frac{0.2747}{0.246} = 1.1167$$

$$\pmb{g}_B(x_C = 0.51) = \frac{0.2747}{0.244} = 1.1258$$

Since the two activity coefficients are so close, and the azeotrope occurs near 0.5 mole fraction, so I will use the one-constant Margules equation.

$$\frac{\underline{G}^{ex}(x_C = 0.51)}{RT} = x_C \ln \pmb{g}_C + x_B \ln \pmb{g}_B = 0.51\ln(1.1167) + 0.49\ln(1.1258) = 0.11435$$

$$= A x_C x_B = A(0.51)(0.49) = 0.11435$$

$A = 0.4576$ therefore $\underline{G}^{ex} = 8.314 \times (273.15+40) \times 0.4576 = 1191 x_C x_B$

$$RT \ln \pmb{g}_C = 1191 x_B^2 \quad \text{or} \quad \pmb{g}_C = \exp(0.4576 x_B^2)$$

$$RT \ln \pmb{g}_B = 1191 x_C^2 \quad \text{or} \quad \pmb{g}_B = \exp(0.4576 x_C^2)$$

$$P(x_C) = x_C \exp(0.4576(1 - x_C)^2)0.246 + (1 - x_B) \exp(0.4576 x_C^2)0.244$$

Also

$$y_C(x_C) = \frac{x_C \exp(0.4576(1 - x_C)^2)0.246}{P(x_C)}$$
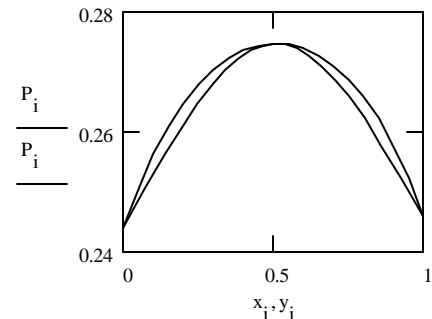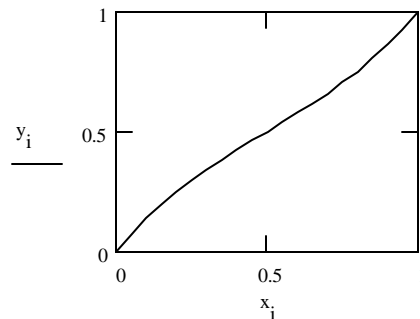
b) The LLE upper consolute temperature is

$$T_{UC} = \frac{A}{2R} = \frac{0.4576 \times 313.15 \times 8.314}{2 \times 8.314} = 71.65\ \text{K}$$

which is much below the freezing point of each compound.

c) Freezing point depression

$$\ln(x_S \boldsymbol{g}_S) = -\frac{\Delta \underline{H}^{fus}(T_{m,\text{solvent}})}{R}\left(\frac{1}{T} - \frac{1}{T_{m,\text{solvent}}}\right) \quad \text{or}$$

$$\frac{1}{T} = \frac{1}{T_{m,\text{solvent}}} - \frac{R}{\Delta \underline{H}^{fus}(T_{m,\text{solvent}})}\ln(x_S \boldsymbol{g}_S) \quad \text{or}$$

$$T = \frac{T_{m,\text{solvent}}}{1 - \dfrac{RT_{m,\text{solvent}}}{\Delta \underline{H}^{fus}(T_{m,\text{solvent}})}\ln(x_S \boldsymbol{g}_S)}$$

For cyclohexane freezing

$$T = \frac{273.15 + 6.6}{1 - \dfrac{8.314 \times (273.15 + 6.6)}{2630}\ln(x_B \boldsymbol{g}_B)} = \frac{279.75}{1 - 0.8844 \ln(x_B \boldsymbol{g}_B)}$$

For benzene freezing

$$T = \frac{273.15 + 5.53}{1 - \dfrac{8.314 \times (273.15 + 5.53)}{9953}\ln(x_C \boldsymbol{g}_C)} = \frac{278.68}{1 - 0.2378 \ln(x_C \boldsymbol{g}_C)}$$

8.11-17

$$j_1 = -\frac{C_1 D_o}{RT}\nabla\left(\boldsymbol{m}^o + RT \ln x_1 \boldsymbol{g}_1\right) = CD\nabla x_1$$
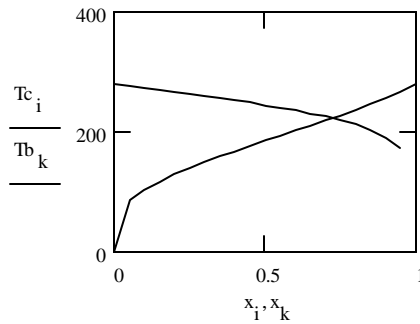
a) $x_1 D_o\left[\nabla \ln x_1 + \nabla \ln \boldsymbol{g}_1\right] = D\nabla x_1 = x_1 D_o\left[\dfrac{1}{x_1} + \dfrac{\partial \ln \boldsymbol{g}_1}{\partial x_1}\right]$

$$D = D_o\left[1 + \frac{\partial \ln \boldsymbol{g}_1}{\partial \ln x_1}\right]$$

$$RT \ln \boldsymbol{g}_1 = A(1 - x_1)^2$$

b)

$$\frac{\partial \ln \boldsymbol{g}_1}{\partial \ln x_1} = x_1 \frac{\partial \ln \boldsymbol{g}_1}{\partial x_1} = -x_1 \frac{\partial \ln \boldsymbol{g}_1}{\partial x_2} = -x_1 \frac{\partial\left(\dfrac{A}{RT}x_2^2\right)}{\partial x_2} = -2Ax_1 x_2$$

$$D = D_o\left[1 + \frac{\partial \ln \boldsymbol{g}_1}{\partial \ln x_1}\right] = D_o\left(1 - \frac{2A}{RT}x_1 x_2\right)$$

c)   1) Infinite dilution $x_1 \to 0$ and $D \to D_o$

2) At LLE critical point $T_{UC} = \dfrac{A}{2R}$ at $x_1 = x_2 = 0.5$

$$D = D_o\left[1 - \frac{2 \times 2 \times R \times T_{UC}}{R \times T_{UC}}\right] = 0$$

3) Negative deviations from Raoult's law $\Rightarrow A$ is negative

$$D = D_o\left(1 - \frac{2A}{RT}x_1 x_2\right) \text{ with } A \text{ negative, } D > D_o$$

8.11-18 (also available as a Mathcad worksheet).

8.11-18

$\gamma\,Pinf := 16$ $\gamma\,Hinf := 6.34$ $PvapP := 20.277$ $PvapH := 28.022$

Using the van Laar equation

$\alpha := \ln(\gamma\,Pinf)$ $\beta := \ln(\gamma\,Hinf)$

$i := 1, 2 .. 99$ $x_i := 0.01 \cdot i$

$$\gamma P_i := \exp\left[\frac{\alpha}{\left[\left(1 + \dfrac{\alpha}{\beta}\dfrac{x_i}{1 - x_i}\right)^2\right]}\right] \qquad \gamma H_i := \exp\left[\frac{\beta}{\left[\left(1 + \dfrac{\beta}{\alpha}\dfrac{1 - x_i}{x_i}\right)^2\right]}\right] \qquad P_i := x_i \cdot PvapP \cdot \gamma P_i + \left(1 - x_i\right) \cdot PvapH \cdot \gamma H_i$$
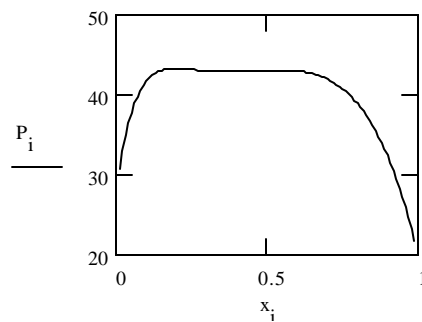
$$yP_i := \frac{\left(x_i \cdot PvapP \cdot \gamma P_i\right)}{P_i}$$
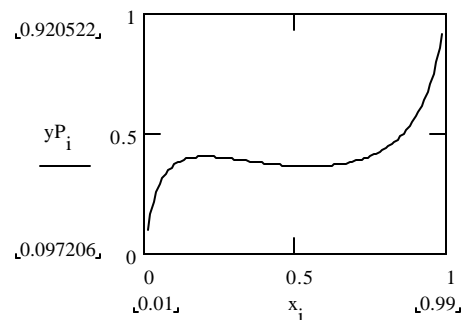
So this system exhibits either azeotropy or LLE. Test for LLE

$x11 := 0.01$ $x12 := 0.90$

Given

$$x11 \cdot \exp\left[\frac{\alpha}{\left(1 + \dfrac{\alpha}{\beta}\dfrac{x11}{1-x11}\right)^2}\right] = x12 \cdot \exp\left[\frac{\alpha}{\left(1 + \dfrac{\alpha}{\beta}\dfrac{x12}{1-x12}\right)^2}\right]$$

$$(1 - x11) \cdot \exp\left[\frac{\beta}{\left(1 + \dfrac{\beta}{\alpha}\dfrac{1-x11}{x11}\right)^2}\right] = (1 - x12) \cdot \exp\left[\frac{\beta}{\left(1 + \dfrac{\beta}{\alpha}\dfrac{1-x12}{x12}\right)^2}\right]$$

$y := \text{find}(x11, x12)$

$x11 := y_0$ $x11 = 0.113$ $x21 := 1 - x11$ $x21 = 0.887$

$x12 := y_1$ $x12 = 0.684$ $x22 := 1 - x12$ $x22 = 0.316$

$x12 = 0.684$

So there is LLE

Note that many of the problems in this chapter can be solved relatively easily with two programs. The first is CHEMEQ which makes the calculation of the chemical equilibrium constant at any temperature very easy. The second is an equation solving program, such as Mathcad, for solving the nonlinear algebraic equation(s) which result. It is advisable that students know how to use both. [I have used Mathcad for many of the problem solutions reported here.]

9.1 From Equation 9.1-18

$$\ln K_a(T = 25° \text{C}) = \frac{-\Delta \underline{G}^{\circ}_{\text{rxn}}(25° \text{C})}{RT} = \frac{-17,740}{8.314 \times 298.15}$$

$$\Rightarrow \ln K_a = -7.1566 \text{ and } K_a(T = 25° \text{C}) = 7.7967 \times 10^{-4}$$

Next using Eqn. 9.1-23b with $\Delta a = 16.736$ J/mol K ; $\Delta b = \Delta c = \Delta d = \Delta e = 0$ gives [Note: Error in problem statement of first printing. $\Delta C_P = 16.736$ J/mol K not kJ/mol K]

$$\ln \frac{K_a(T = 500 \text{ K})}{K_a(T = 298.15 \text{ K})} = \frac{\Delta a}{R} \ln \frac{500}{298.15}$$

$$+ \frac{1}{R}\left[-\Delta \underline{H}^{\circ}_{\text{rxn}}(298.15) + \Delta a \times 298.15\right]\left[500^{-1} - 298.15^{-1}\right]$$

$$= \frac{16.736}{8.314} \ln \frac{500}{298.15}$$

$$+ \frac{1}{8.314}\left[-55,480 + 16.736 \times 298.15\right]\left(\frac{1}{500} - \frac{1}{298.15}\right)$$

$$= 1.0407 + 8.2228 = 9.2635$$

$$\ln K_a(T = 500 \text{ K}) = \ln K_a(T = 298.15) + 9.2635 = -7.1566 + 9.2635 = 2.107$$

$$\Rightarrow K_a(T = 500 \text{ K}) = 8.225$$

Mass Balance Table

Species	In	Out	y_i	$y_i(X = 0.9436)$
IPOH	1	$1-X$	$(1-X)/(1+X)$	0.0290
Prop	0	X	$X/(1+X)$	0.4855
H$_2$	0	X	$X/(1+X)$	0.4855
Total		$1+X$		$\rightarrow$ calculated after X was found below

Now $K_a = \dfrac{a_{H_2}a_{Prop}}{a_{IPOH}} = \dfrac{X^2(P = 1.013 \text{ bar}/1 \text{ bar})}{(1+X)(1-X)} = \dfrac{X^2}{(1-X^2)}$.

$X^2 = K_a(1-X)^2$; $(1+K_a)X^2 = K_a$ or $X = \sqrt{K_a/(1+K_a)}$;

$K_a = 8.225 \Rightarrow X = 0.9436 \Rightarrow 94.36\%$ of alcohol is converted.

9.2 Reaction: $CaC_2O_4 = CaCO_3 + CO$

$$K_a = \frac{a_{CaCO_3}a_{CO}}{a_{CoC_2O_4}} = a_{CO} = P_{CO}$$

$T(°C)$	375	388	403	410	416	418
$P_{diss} = P_{CO}(\text{kPa})$	1.09	4.00	17.86	33.33	78.25	91.18
$K_a = P_{CO}/100$	0.0109	0.0400	0.1786	0.3333	0.7825	0.9181
$\ln K_a$	-4.5282	-32.315	-1.7356	-1.1112	-0.2581	-0.1052
$T(K)$	648.15	661.15	676.15	683.15	689.15	691.15
$-RT\ln K_a = \Delta G^\circ_{rxn}$ kJ / mol CaC_2O_4 reacted	24.401	17.763	9.757	6.3113	1.4788	0.6351

Now $\dfrac{d(\Delta G^\circ_{rxn}/RT)}{dT} = -\dfrac{d\ln K_a}{dT} = -\dfrac{\Delta H^\circ_{rxn}}{RT^2}$ (1)

and $\Delta S^\circ_{rxn} = \dfrac{\Delta H^\circ_{rxn} - \Delta G^\circ_{rxn}}{T}$ (2)

Plot the data for $\ln K_a$ vs. T. It falls on a reasonably straight line of slope ~ 0.106.

i.e., $\dfrac{d\ln K_a}{dT} \sim 0.103$. Thus, $\Delta H^\circ_{rxn} \cong 0.103RT^2$, which follows from Eqn. (1). Once

ΔH°_{rxn} is evaluated, Eqn. (2) can be used to get ΔS°_{rxn}. The results are given below:

$T(°C)$	375°C	403°C	418°C	
ΔH^o_{rxn}	358.7	390.4	409.9	kJ/mol CaC_2O_4 reacted
ΔS^o_{rxn}	0.5159	0.5630	0.5984	kJ/mol K CaC_2O_4 reacted
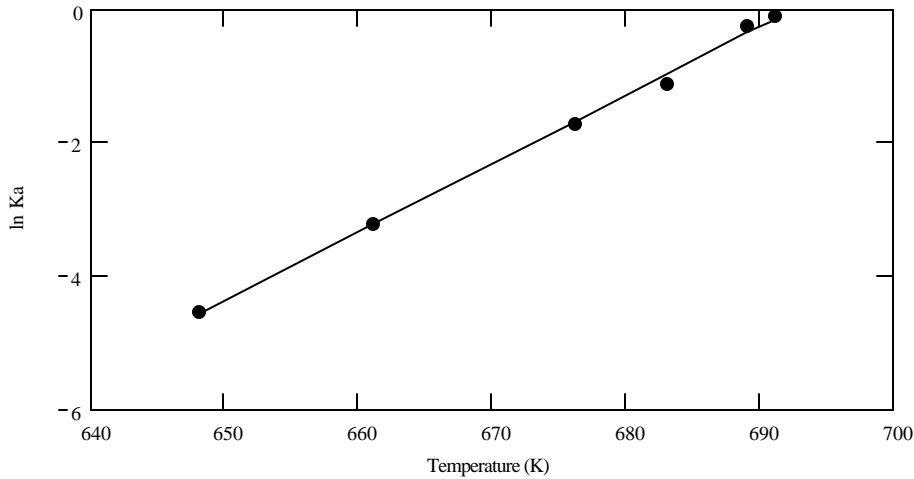
9.3   Reactions: $C + CO_2(g) = 2CO(g)$ (1)

$\qquad\qquad\qquad 2CO(g) = 2C + O_2(g)$ (2)

Mole balance table

Species	Initial	Final	y_i
C	—		
CO_2	1	$1 - X_1$	$(1 - X_1)/(1 + X_1 - X_2)$
CO	0	$2X_1 - 2X_2$	$2(X_1 - X_2)/(1 + X_1 - X_2)$
O_2	0	X_2	$X_2/(1 + X_1 - X_2)$
		$\overline{1 + X_1 - X_2}$	

$$a_i = \frac{y_i P}{1\ \text{bar}} = y_i \ \text{since}\ P = 1\ \text{bar}$$

(a)   From the program CHEMEQ we find that $K_{a,1}(T = 2000\ \text{K}) = 39050$

$\qquad$ at $T = 2000\ \text{K}$ $K_{a,2} = 2.445 \times 10^{-19} \Rightarrow K_{a,2} \sim 0,\ X_2 \sim 0$ and $K_{a,1} = 39050$

$$K_{a,1} = \frac{a_{CO}^2}{a_C a_{CO_2}} = \frac{4(X_1 - X_2)^2}{(1 - X_1)(1 + X_1 - X_2)} \cong \frac{4(X_1)^2}{(1 - X_1)(1 + X_1)} \Rightarrow X_1^2 = \frac{K_{a,1}}{4 + K_{a,1}} = 1$$

$\qquad$ (as one would expect with such a large equilibrium constant)

(b)   At 1000 K using CHEMEQ

$$K_{a,1}(T = 1000 \text{ K}) = 1.835$$

$$K_{a,2}(T = 1000 \text{ K}) = 3.984 \times 10^{-23}$$

$$X_1 = \sqrt{\frac{1.835}{4 + 1.835}} = 0.561$$

Thus, the composition of the gas leaving the graphite bed is

Species	2000 K	1000 K
CO_2	2.594×10^{-5}	0.283
CO	1.0	0.717
O_2	0	0

9.4

$$K_a = \exp\left\{-\frac{\Delta G_{rxn}^o}{RT}\right\} = \exp\left\{\frac{-2866}{8.314 \times 298.15}\right\} = 0.3147$$

$$= \frac{a_{\text{diamond}}}{a_{\text{graphite}}}; \quad \text{where } a_i = \frac{f_i(T,P)}{f_i(T,P = 1 \text{ bar})} = \exp\left\{\frac{\underline{V}_i}{RT}(P - 1 \text{ bar})\right\}$$

$$\uparrow \text{Poynting correction}$$
terms assumed
incompressible solid

$$\frac{a_{\text{diamond}}}{a_{\text{graphite}}} = \frac{\exp\{\underline{V}_{\text{dim}}(P - 1 \text{ bar})/RT\}}{\exp\{\underline{V}_{\text{gr}}(P - 1 \text{ bar})/RT\}} = \exp\left\{\frac{(\underline{V}_{\text{dim}} - \underline{V}_{\text{gr}})(P - 1 \text{ bar})}{RT}\right\}$$

where

$$\underline{V}_{\text{diam}} = \frac{12 \text{ g/mol}}{3.51 \text{ g/cc}} = 3.4188 \text{ cc/mol} = 3.4188 \times 10^{-6} \text{ m}^3/\text{mol}$$

$$\underline{V}_{\text{graph}} = \frac{12 \text{ g/mol}}{2.25 \text{ g/cc}} = 5.3333 \text{ cc/mol} = 5.3333 \times 10^{-6} \text{ m}^3/\text{mol}$$

$$\ln 0.3147 = \frac{(3.4188 - 5.3333)(P - 1) \text{ cc - bar}}{RT} = \frac{-\Delta \underline{G}_{rxn}^o}{RT} = \frac{-2866}{R} \text{ J/mol}$$

$$\Rightarrow P - 1 \text{ bar} = \frac{2866 \text{ J/mol}}{1.9145 \text{ cc/mol}} = 1497.0 \text{ J/cc} = 14970 \text{ bar}$$

or $P = 14971 \text{ bar}$.

Thus for $P < 14971 \text{ bar}$; $\dfrac{a_{\text{diam}}}{a_{\text{graph}}} > K_a$ and graphite is stable phase

for $P > 14971 \text{ bar}$; $\dfrac{a_{\text{diam}}}{a_{\text{graph}}} < K_a$ and diamond is stable phase

$\Rightarrow$ Need a hydraulic press capable of exerting 14971 bar to convert pencil leads to diamonds. (Also, should consider a higher temperature!)

9.5   For convenience, write reaction as $N_2 + O_2 = 2NO_2$

Species balance table

Species	Initial	Final	y_i
O_2	1	$1 - X$	$(1 - X)/4.762$
N_2	$0.79/0.21 = 3.762$	$3.762 - X$	$(3.762 - X)/4.762$
NO	0	$2X$	$2X/4.762$
		$\overline{4.762}$	

Since $P = 1.013$ bar ; $a_i = \dfrac{y_i P}{1 \text{ bar}}$

$$K_a = \frac{y_{NO}^2}{y_{N_2} y_{O_2}} = \frac{(2X)^2}{(1 - X)(3.762 - X)} \quad \text{which has the solution}$$

$$X = \frac{-2.381 + \sqrt{1.9073 + 15.048/K_a}}{(4/K_a) - 1}$$

Using the program CHEMEQ and its data base the following results are obtained (which agree with Figure 9.1-2)

$T(°C)$	1500	1600	1800	2000
K_a	0.9795×10^{-4}	0.1924×10^{-3}	0.5861×10^{-3}	0.1455×10^{-2}
X	0.00954	0.0133	0.0231	0.0361

$T(°C)$	2100	2200	2400	2500
K_a	0.2154×10^{-2}	0.3077×10^{-2}	0.5718×10^{-2}	0.007487
X	0.0438	0.0520	0.0701	0.0796

$T(°C)$	2600	2800	2900	3000
K_a	0.009539	0.01450	0.01732	0.02028
X	0.0893	0.1086	0.118	0.1269

9.6 (a) From Appendix IV

	$\Delta \underline{H}_f^{\circ}$	$\Delta \underline{G}_f^{\circ}$
$Na_2SO_4 \cdot 10H_2O$	–4322.5	–3642.3 kJ/mol
Na_2SO_4	–1382.8	–1265.2
H_2O	–241.8	–228.6

$$\Rightarrow \Delta H_{rxn}(T = 25°C) = (-4322.5) - (-1382.8) - 10(-228.6) = -521.7 \text{ kJ/mol}$$

$$\Delta G_{rxn}(T = 25°C) = -91.1 \text{ kJ/mol}$$

$$\Rightarrow \ln K_a(T = 25°C) = \frac{+91,100}{(8.314 \times 298.15)} = +36.751$$

$$K_a(T = 25°C) = 9.139 \times 10^{15}$$

Now

$$K_a = \frac{a_{Na_2SO_4 \cdot 10H_2O}}{a_{Na_2SO_4} \cdot a_{H_2O}^{10}} = \left(\frac{1 \, bar}{P_{H_2O}}\right)^{10} = 0.9139 \times 10^{15}$$

$$\Rightarrow P_{H_2O}(25° C) = 2.503 \times 10^{-2} \; bar = 0.0253 \; bar$$

(b) At 15°C. Since 15°C is near 25°C we will correct K_a for temperature using only the ΔH_{rxn}^o term, i.e.

$$\ln \frac{K_a(T = 15°C)}{K_a(T = 25°C)} = -\frac{\Delta H_{rxn}^o}{R}\left(\frac{1}{288.15} - \frac{1}{298.15}\right) = 7.3438$$

$$K_a(T = 15° C) = K_a(T = 25° C)\exp(7.304) = 1.358 \times 10^{19}$$

$$P_{H_2O}(15° C) = 1.221 \times 10^{-2} \; bar = 0.01221 \, bar$$

Experimental data (Baxter and Lansing, J.A.C.S. **42**, 419 (1920))
$$P_{H_2O}(0° C) = 0.003693 \; bar$$

$$P_{H_2O}(15° C) = 0.01228 \; bar$$

$$P_{H_2O}(25° C) = 0.0256 \; bar$$

9.7   (also available as a Mathcad worksheet)

$K_a = \dfrac{a_{CS_2}}{a_C a_{S_2}} = \dfrac{y_{CS_2}}{y_{S_2}}$.   Since $a_C = 1$ (solid), and $P = 1 \, bar =$ standard state

pressure.
Species balance table:

Species	Initial	Final	y_i	$K_a = X/(1-X)$
C	—	—	—	
S_2	1	$1-X$	$(1-X)$	$\Rightarrow$ or
CS_2	0	X	X	$X = K_a/(1+K_a)$
		1		

Using CHEMEQ I find $K_a(750°C) = 8.478$ and $K_a(1000°C) = 6.607$. Therefore $X(750°C) = 0.894$ and $X(1000° C) = 0.869$. $X = y_{CS_2}$ is the percentage equilibrium conversion of sulfur.

9.8   (a) $Ba(NO_3)_2$ solution

$$I = \frac{1}{2}\sum z_i^2 C_i = \frac{1}{2}\left\{(2)^2 C_{Ba} + (1)^2 C_{NO_3} + (1)^2 C_{Ag} + (1)^2 C_{Cl}\right\}$$

$$= \frac{1}{2}\left\{4C_{Ba} + C_{NO_3} + C_{Ag} + C_{Cl}\right\}$$

but $C_{Ag} = C_{Cl} = C_{AgCl}$; $C_{Ba} = C_{Ba(NO_3)_2}$; $C_{NO_3} = 2C_{Ba(NO_3)2}$

$$I = \frac{1}{2}\left\{4C_{Ba(NO_3)_2} + 2C_{Ba(NO_3)_2} + 2C_{AgCl}\right\} = 3C_{Ba(NO_3)_2} + C_{AgCl}$$

$C_{Ba(NO_3)_2}$	C_{AgCl}	I	$\sqrt{I}$	$\ln K_s$, where $K_s = C_{AgCl}^2$
2.111×10^{-4}	0.1309×10^{-4}	6.4639×10^{-4}	2.542×10^{-2}	-22.4873
7.064×10^{-4}	0.1339×10^{-4}	21.3259×10^{-4}	4.618×10^{-2}	-22.4420
44.02×10^{-4}	0.1450×10^{-4}	132.21×10^{-4}	11.498×10^{-2}	-22.2827
56.0×10^{-4}	0.1467×10^{-4}	168.147×10^{-4}	12.967×10^{-2}	-22.2594
(mol/liter)	(mol/liter)			

(b) $La(NO_3)_2$ solution

Using similar analysis to that above yields $I = 6C_{La(NO_3)_3} + C_{AgCl}$.

$C_{La(NO_3)_2}$	C_{AgCl}	I	$\sqrt{I}$	$\ln K_s$, where $K_s = C_{AgCl}^2$
1.438×10^{-4}	0.1317×10^{-4}	8.7597×10^{-4}	2.9597×10^{-2}	-22.4751
5.780×10^{-4}	0.1367×10^{-4}	34.8167×10^{-4}	5.9006×10^{-2}	-22.4006
16.6×10^{-4}	0.1432×10^{-4}	99.7432×10^{-4}	9.9872×10^{-2}	-22.3077
28.07×10^{-4}	0.1477×10^{-4}	168.568×10^{-4}	12.983×10^{-2}	-22.2458
(mol/liter)	(mol/liter)			

$\sqrt{I}$ $(mol/liter)^{\frac{1}{2}}$
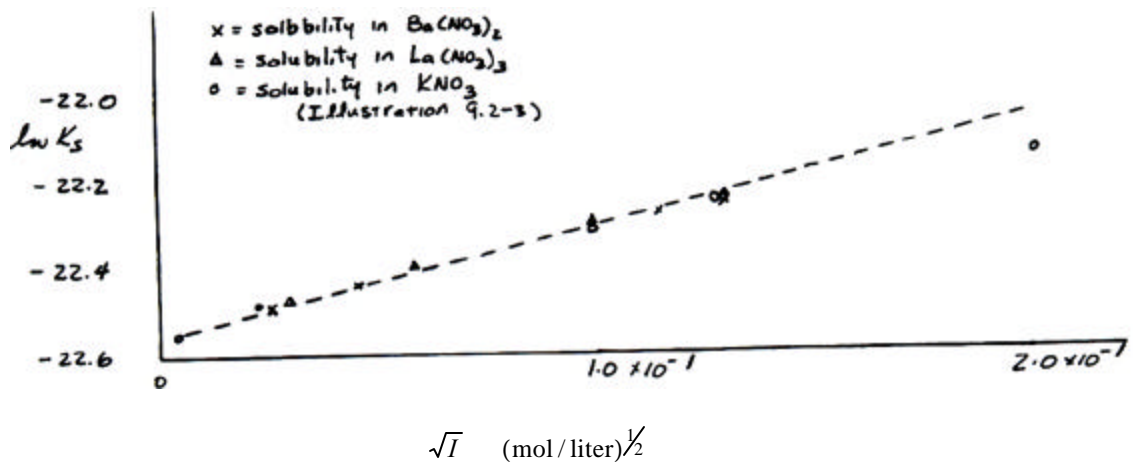
Except for the single point or high ionic strength (AgCl in KNO_3), all the data fall on a straight line.

9.9   For $BaSO_4 = Ba^{++} + SO_4^{--}$, we have

$$I = \frac{1}{2}\sum z_i^2 M_i \cong \frac{1}{2}\left\{2^2 C_{Ba^{++}} + 2^2 C_{SO_4^{-}}\right\} = 4C_{BaSO_4} = 4S$$

where $S = $ solubility of $BaSO_4$ in moles/liter

also $K_s = C_{Ba^{++}}C_{SO_4^{-}} = S^2$. Note we have neglected the difference between M
and C. Thus

$T(°C)$	a(Table 7.6)	S	$K_s = S^2$	$\sqrt{I} = 2\sqrt{S}$
5	1.140	15.6×10^{-6}	2.43×10^{-10}	7.9×10^{-3}
10	1..149	16.7	2.789	8.173
15	1.158	18.3	3.349	8.556
20	1.167	19.8	3.920	8.900
25	1.178	21.6	4.666	9.295
		(mol/liter)	$(mol/liter)^2$	$(mol/liter)^{1/2}$

Now $K_s = \dfrac{K_a(1\,molal)^{n_+ + n_-}}{g_{\pm}^{n_+ + n_-}}$ and $K_s = \dfrac{K_s^{\circ}}{g_{\pm}^{n_+ + n_-}}$. $K_s^{\circ} = K_a(1\,molal)^{n_+ + n_-}$ or

$K_a = \dfrac{K_s^{\circ}}{(1\,molal)^{n_+ + n_-}}$ and

$$\ln K_s = \ln K_s^{\circ} - \ln_{\pm}^{n_+ + n_-}$$
$$= \ln K_s^{\circ} + \left(n_{Ba^{++}} + n_{SO_4^{-}}\right)\left|z_{Ba^{++}}z_{SO_4^{-}}\right|a\sqrt{I}$$
$$= \ln K_s^{\circ} + 2\cdot(2\times2)a\sqrt{I} = \ln K_s^{\circ} + 16a\sqrt{I}$$

or $K_s^{\circ} = K_s \exp\left(-16a\sqrt{S}\right) = S^2 \exp\left(-16a\sqrt{S}\right)$.

Note that K_a is the equilibrium constant for the reaction

$$BaSO_4(s) = Ba^{++}(aq,\ ideal\ 1\ molal) + SO_4^{--}(aq,\ ideal\ 1\ molal)$$
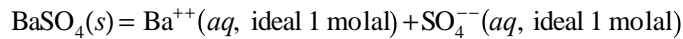
and $\dfrac{\Delta G_{rxn}}{T} = -R\ln K_a$. Thus we have

$T(°C)$	K_s°	$\ln K_s^{\circ}$	$\dfrac{\Delta G_{rxn}}{T} = -R\ln K_a$	ΔH_{rxn}	ΔG_{rxn}	ΔS_{rxn}
5	2.261×10^{-10}	−22.2100	184.654	20490	51,362	−110.99
10	2.587	−22.0754	183.535	21234	51,968	−108.54
15	3.094	−21.8964	182.047	21991	52,457	−105.73
20	3.607	−21.7430	180.771	22760	52,993	−103.13
25	4.275	−21.5731	179.359	23543	53,476	−100.40
	$(mol/lit)^2$		$\left(\dfrac{J}{mol\,K}\right)$	(J/mol)	(J/mol)	(J/mol)

$\Delta G_{rxn}/T$ is essentially a linear function of T as can be seen by plotting the data. Also, from the plot we have

$$\frac{\P(\Delta G_{rxn}/T)}{\P T} \sim \frac{\Delta(\Delta G_{rxn}/T)}{\Delta T} \sim -0.26485 \text{ J/mol K}^2$$

However

$$\frac{\P(G/T)}{\P T} = -\frac{H}{T^2} \Rightarrow \Delta H_{rxn} = -T^2 \frac{\P(\Delta G_{rxn}/T)}{\P T} = T^2(0.26485)$$

Finally

$$\Delta S = \frac{\Delta H - \Delta G}{T} \Rightarrow \Delta S_{rxn} = \frac{\Delta H_{rxn} - \Delta G_{rxn}}{T}$$

Both ΔH_{rxn} and ΔS_{rxn} are given in the table on previous page.

9.10 (also available as a Mathcad worksheet)

(a) Using the program CHEMEQ, the following results are obtained

$$\text{rxn 1} \quad C_3H_8 + 3H_2O = 3CO + 7H_2$$
$$\text{rxn 2} \quad C_3H_8 + 6H_2O = 3CO_2 + 10H_2$$
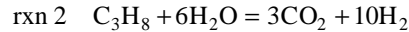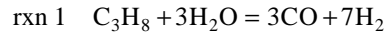
rxn	K_a	K_a	ΔH^o_{rxn}	ΔG^o_{rxn}	ΔH^o_{rxn}	ΔG^o_{rxn}
	1000 K	1100 K	1000 K	1000 K	1100 K	1100 K
1	0.1343×10^{12}	0.4806×10^{14}	537.260	–213.030	538.140	–288.11
2	0.3332×10^{12}	0.3851×10^{14}	432.380	–220.590	436.440	–286.09

All energies in kJ/mol of C_3H_8

(b) $K_{a,1} = \dfrac{a_{H_2}^7 a_{CO}^3}{a_{C_3H_8} a_{H_2O}^3}$ and $K_{a,2} = \dfrac{a_{H_2}^{10} a_{CO_2}^3}{a_{C_3H_8} a_{H_2O}^6}$ where, since $P = 1$ bar

$$a_i = \frac{y_i P}{1 \text{ bar}} = y_i.$$

Species balance table

Species	In	Out	y_i
C_3H_8	1	$1 - X_1 - X_2$	$(1 - [X_1 + X_2])/\Sigma$
H_2O	10	$10 - 3X_1 - 6X_2$	$(10 - 3X_1 - 6X_2)/\Sigma$
CO	0	$3X_1$	$3X_1/\Sigma$
CO_2	0	$3X_2$	$3X_2/\Sigma$
H_2	0	$7X_1 + 10X_2$	$(7X_1 + 10X_2)/\Sigma$
		$\Sigma = 11 + 6(X_1 + X_2)$	

Thus

$$K_{a,1} = \frac{27 X_1^3 (7X_1 + 10X_2)^7}{(1 - X_1 - X_2)(10 - 3X_1 - 6X_2)^3 (11 + 6X_1 + 6X_2)^6}$$

$$K_{a,2} = \frac{27 X_2^3 (7 X_1 + 10 X_2)^{10}}{(1 - X_1 - X_2)(10 - 3 X_1 - 6 X_2)^6 (11 + 6 X_1 + 6 X_2)^6}$$

Also

$$\frac{K_{a,1}}{K_{a,2}} = \frac{X_1^3 (10 - 3 X_1 - 6 X_2)^3}{X_2^3 (7 X_1 + 10 X_2)^3}$$

In view of the very large numerical values of the equilibrium constants, we expect $X_1 + X_2 \sim 1$. Using this approximation we get

$$K_{a,1} = \frac{27 X_1^3 (7 + 3 X_2)^7}{(1 - X_1 - X_2)(7 - 3 X_2)^3 (17)^6} \; ; \; K_{a,2} = \frac{27 X_2^3 (7 + 3 X_2)^{10}}{(1 - X_1 - X_2)(7 - 3 X_2)^6 (17)^6}$$

and

$$\frac{K_{a,1}}{K_{a,2}} = \frac{X_1^3 (7 - 3 X_2)^3}{X_2^3 (7 + 3 X_2)^3} \Rightarrow \left(\frac{K_{a,1}}{K_{a,2}}\right)^{1/3} = \frac{X_1 (7 - 3 X_2)}{X_2 (7 + 3 X_2)} = \frac{(1 - X_2)(7 - 3 X_2)}{X_2 (7 + 3 X_2)}$$

Note that this last equation is a simple quadratic equation for X_2 given $K_{a,1}$ and $K_{a,2}$. Also, then $X_1 = 1 - X_2$.

(c) at 1000 K: $X_1 = 0.527$; $X_2 = 0.473$

at 1100 K: $X_1 = 0.603$; $X_2 = 0.397$

Thus we obtain

Species	y_i(1000 K)	y_i(1100 K)
C_3H_8	0	0
H_2O	0.328	0.342
CO	0.093	0.106
CO_2	0.083	0.070
H_2	0.495	0.482

9.11 (also available as a Mathcad worksheet)

Reaction: $SO_2 + \dfrac{1}{2} O_2 = SO_3$
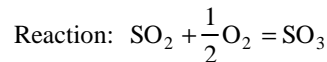
Species balance table

Species	Initial	Final	y_i
SO_2	1	$1-X$	$\dfrac{1-X}{3.38-0.5X}$
O_2	$\dfrac{1}{2}$	$\dfrac{1}{2}(1-X)$	$\dfrac{1/2(1-X)}{3.38-0.5X}$
N_2	$\dfrac{1}{2}\times\dfrac{0.79}{0.21}=1.88$	1.88	$\dfrac{1.88}{3.38-0.5X}$
SO_3	0	X	$\dfrac{X}{3.38-0.5X}$

$$3.38-\frac{1}{2}X$$

Since $P=1.013$ bar ; $a_i=\dfrac{y_iP}{1\ \text{bar}}=1.013y_i$

$$K_a=\frac{a_{SO_3}}{a_{SO_2}a_{O_2}^{1/2}}=\frac{y_{SO_3}}{y_{SO_2}y_{O_2}^{1/2}}=\frac{X(3.38-0.5X)^{1/2}}{1.013^{1/2}(1-X)^{3/2}(0.5)^{1/2}}$$

The chemical equilibrium constant for this problem was calculated using the program CHEMEQ and then the problem was solved using Mathcad. The results appear below

$T(°C)$	K_a	X	y_{SO_2}	y_{O_2}	y_{SO_3}
0	1.016×10^{14}	~1	~0	~0	0.3472
100	0.8625×10^{9}	~1	~0	~0	0.3472
200	0.1012×10^{7}	0.9998	6.148×10^{-5}	3.074×10^{-5}	0.3472
300	0.1265×10^{5}	0.9967	0.001139	0.000569	0.3459
400	0.5903×10^{3}	0.9750	0.008635	0.0004317	0.3371
500	0.6188×10^{2}	0.8935	0.0363	0.0182	0.3046
600	0.1104×10^{2}	0.7090	0.0962	0.0481	0.2343
700	0.2847×10^{1}	0.4569	0.1723	0.0862	0.1450
800	0.9566	0.2467	0.2313	0.1157	0.0757
900	0.3951	0.1252	0.2637	0.1319	0.0377
1000	0.1863	0.0655	0.2792	0.1396	0.0196
1100	0.09969	0.0366	0.2866	0.1433	0.0109
1200	0.05862	0.0220	0.2903	0.1451	0.00652
1300	0.03722	0.0141	0.2923	0.1462	0.00418
1400	0.02518	0.0096	0.2934	0.1467	0.00285
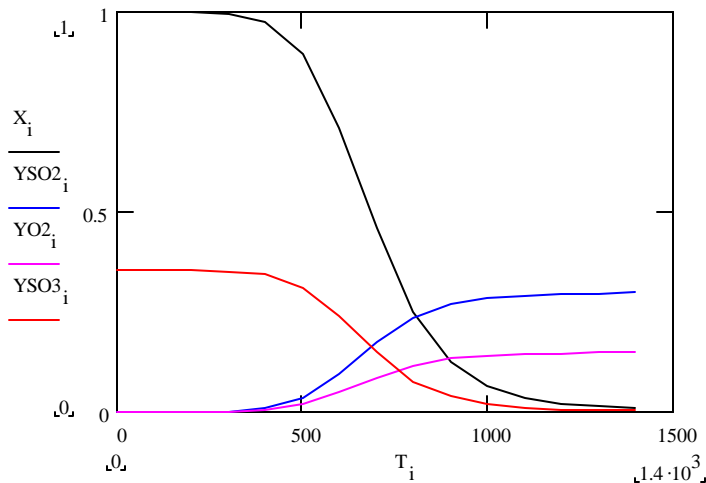
9.12 Reaction: $C_2H_4 + Cl_2 = C_2H_4Cl_2$

However, $C_2H_4Cl_2$ is a liquid at 50°C — 2 phase reaction!

Some physical property data

Species	Normal boiling point	$P^{vap}(50°C)$	T_C	P_C bar
$C_2H_4Cl_2$	83.47°C	0.288 bar		
C_2H_4	–88.63°C	122.5 bar‡	9.2°C	50.36
Cl_2	–34.6°C	14.87 bar		

‡Since ethylene is above its critical temperature, its "liquid-phase" vapor-pressure will have to be estimated if we are to do the vapor-liquid equilibrium calculation. However, since we need only a moderate extrapolation (from $T = 9.2°C$ to $T = 50°C$), we will do an extrapolation of the vapor-pressure data, and not use Shair's correlation. Using vapor-pressure equation in the *Handbook of Chemistry and Physics*, we find $P^{vap}(50°C) \sim 122.5$ bar for ethylene.

Note: To be consistent, all vapor pressure data for this problem have been taken from the *Handbook of Chemistry and Physics*. The data differs, in many cases by $\pm 20\%$ from *The Chemical Engineers' Handbook*. I believe the latter may be more accurate.

Species balance table

Species	Initial	Final	
C_2H_4	1	$1-X$	$= y_{C_2H_4}V + x_{C_2H_4}L$
Cl_2	1	$1-X$	$= y_{Cl_2}V + x_{Cl_2}L$
$C_2H_4Cl_2$	0	X	$= y_{C_2H_4Cl_2}V + x_{C_2H_4Cl_2}L$

Also, since $P = 1$ bar , $a_i = \dfrac{y_i P}{1 \text{ bar}} = y_i$ for species whose standard state is a vapor.

Note: An obvious first guess is that no $C_2H_4Cl_2$ is present in the vapor phase, and no Cl_2 or C_2H_4 is present in the liquid phase. Since the standard states of

C_2H_4 and Cl_2 are as pure vapors and $C_2H_4Cl_2$ is as a liquid, this would result in an equilibrium relation of the form

$$K_a = \frac{a_{C_2H_4Cl_2}}{a_{C_2H_4}a_{Cl_2}} = \frac{1}{1/2 \cdot 1/2} = 4$$

which clearly can not be true! Therefore, to obtain the correct solution to this problem we must consider the possibility that all species may be present in all phases!

In the table above, L and V are the total number of moles in the liquid and vapor phases, respectively. $L + V = 1$

Phase equilibrium: $\bar{f}_1^V = \bar{f}_i^L \Rightarrow y_i P = x_i g_i P_i^{vap}$

Chemical equilibrium: (standard state: C_2H_4 and Cl_2 = vapor; $C_2H_4Cl_2$ = pure liquid)

$$K_a = \frac{x_{C_2H_4Cl_2} g_{C_2H_4Cl_2}}{y_{C_2H_4} y_{Cl_2}}$$

Now using data in Appendices II and IV, and Eqn. 9.1-23b we obtain

$K_a(T = 50^\circ C) \sim 1.1 \times 10^{23}$ a huge number.

$$\Rightarrow \left(y_{C_2H_4Cl_2} y_{Cl_2}\right) \times 1.1 \times 10^{23} = x_{C_2H_4Cl_2} g_{C_2H_4Cl_2}$$

$\Rightarrow$ Reaction goes, essentially, to completion.

Vapor-liquid equations

$$y_{C_2H_4Cl_2} = x_{C_2H_4Cl_2} g_{C_2H_4Cl_2}(0.284); \quad y_{C_2H_4} = x_{C_2H_4} g_{C_2H_4}(121); \quad y_{Cl_2} = x_{Cl_2} g_{Cl_2}(14.68)$$

Now going back to chemical equilibrium relation

$$\left(x_{C_2H_4} g_{C_2H_4}\right)\left(x_{Cl_2} g_{Cl_2}\right) \times (14.68)(121)\left(1.1 \times 10^{23}\right) = x_{C_2H_4Cl_2} g_{C_2H_4Cl_2}$$

Since, for this system, we expect all the activity coefficients to be of reasonable size (less than, say, 10), it is clear that the only solution is $x_{C_2H_4Cl_2} \sim 1$, $x_{C_2H_4} = x_{Cl_2} = 0$ [actually, these latter mole fractions will be of the order 10^{-13}]

Plugging these values back into the vapor-liquid equilibrium equation, we find $\sum y_i < 1$. $\Rightarrow$ No vapor phase!

Thus, the solution to this problem is that there is no vapor phase present at equilibrium, only a liquid phase. The reaction goes to completion in the liquid phase, so that

$$x_{C_2H_4Cl_2} = 1, \quad x_{C_2H_4} = 0, \quad x_{Cl_2} = 0.$$

9.13 $\quad \overline{G}_i = \underline{G}_i + RT \ln g_i x_i = \underline{G}_i + RT \ln g_i^+ x_i^+$ where

x_i = apparent mole fraction = $\dfrac{N_i^\circ}{\sum N_j^\circ}$

x_i^+ = actual mole fraction = $\dfrac{N_i}{\sum N_j}$

In the model, $g_i^+ = 1$, since the ternary mixture is ideal.

$$\Rightarrow g_i = \frac{x_i^+}{x_i} = \frac{N_i}{N_A + N_B + N_{B_2}} \times \frac{N_A + N_B^\circ}{N_i^\circ} = \frac{N_i}{N_i^\circ} \times \frac{N_A + N_B^\circ}{N_A + N_B + N_{B_2}}$$

$$\Rightarrow \boldsymbol{g}_A = \frac{N_A + N_B{}^{\circ}}{N_A + N_B + N_{B_2}} \quad \text{and} \quad \boldsymbol{g}_B = \frac{N_B}{N_B{}^{\circ}} = \frac{N_A + N_B{}^{\circ}}{N_A + N_B + N_{B_2}}$$

Now consider the chemical equilibrium:

	Initial Number moles	Final number moles	Mole fraction x_i
A	N_A	N_A	$\dfrac{N_A}{N_A + N_B^{\circ} - N_{B_2}}$
B	N_B°	$N_B^{\circ} - 2X$	$\dfrac{N_B^{\circ} - 2N_{B_2}}{N_A + N_B^{\circ} - N_{B_2}}$
B_2	—	X	$\dfrac{N_{B_2}}{N_A + N_B^{\circ} - N_{B_2}}$

$$N_A + N_B^{\circ} - X$$
$$= N_A + N_B^{\circ} - N_{B_2}$$

$$K_a = \frac{a_{B_2}}{a_B^2} = \frac{N_{B_2}\left(N_A + N_B^{\circ} - N_{B_2}\right)}{\left(N_B^{\circ} - 2N_{B_2}\right)^2}$$

Solving this equation gives

$$N_{B_2} = \frac{\left(N_B^{\circ} + N_A/k\right) - \sqrt{\left(N_B^{\circ} + N_A/k\right)^2 - 4K_A\left(N_B^{\circ}\right)^2/k}}{2}$$

where $k = 4K_a + 1$, and

$$\frac{2kN_{B_2}}{N_A + N_B^{\circ}} = x_a + kx_B - \left(kx_B^2 + 2kx_a x_B + x_a^2\right)^{1/2}$$

$$= 2kx_a + 2kx_B - \boldsymbol{d} = 2k - \boldsymbol{d}$$

and $\boldsymbol{d} = (2k-1)x_a + kx_B + \left(kx_B^2 + 2kx_a x_B + x_a^2\right)^{1/2}$

Also we obtain

$$N_{B_2} = \frac{\left(N_A + N_B^{\circ}\right)}{2k}[2k - \boldsymbol{d}]; \quad N_B = N_B^{\circ} - \frac{\left(N_A + N_B^{\circ}\right)}{k}[2k - \boldsymbol{d}]$$

$$N_A + N_B + N_{B_2} = \left(N_A + N_B{}^{\circ}\right)\left(\frac{\boldsymbol{d}}{2k}\right) \quad \text{and} \quad \frac{N_A + N_B{}^{\circ}}{N_A + N_B + N_{B_2}} = \frac{2k}{\boldsymbol{d}}$$

Thus

$$\boldsymbol{g}_A = \frac{N_A + N_B^{\circ}}{N_A + N_B + N_{B_2}} = \frac{2k}{\boldsymbol{d}} \quad \text{and}$$

$$\boldsymbol{g}_B = \frac{N_B\left(N_A + N_B^{\circ}\right)}{N_B^{\circ}\left(N_A + N_B + N_{B_2}\right)}$$

$$= \left[1 - \frac{(2k - \boldsymbol{d})}{x_B k}\right]\frac{2k}{\boldsymbol{d}} = \frac{2}{x_B \boldsymbol{d}}\left\{\left(x_A^2 + 2kx_A x_B + kx_B^2\right)^{1/2} - x_A\right\}$$

9.14 (also available as a Mathcad worksheet)

Reactions: $C_2H_5OH + \dfrac{1}{2}O_2 = CH_3CHO + H_2O$ rxn 1

$C_2H_5OH = CH_3CHO + H_2$ rxn 2
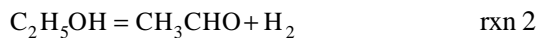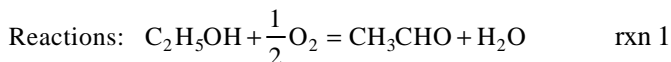
Species balance table:

Species	In	Out
C_2H_5OH	1	$1 - X_1 - X_2$
O_2	0.75	$0.75 - 0.5X_1$
N_2	$\dfrac{0.79}{0.21} \times 0.75 = 2.8214$	2.8214
H_2O	0	X_1
CH_3CHO	0	$X_1 + X_2$
H_2	0	X_2
Σ		$4.571 + \dfrac{1}{2}X_1 + X_2$

Using the program CHEMEQ we obtain

$K_{a,1} = 7.228 \times 10^{13}$ aerobic reaction

$K_{a,2} = 6.643$ is greatly favored!

With these values of the equilibrium constant we obtain $X_1 \sim 1$ and $X_2 \cong 0$ [all ethyl alcohol used up in first reaction].   Therefore, $y_{C_3H_5OH} \sim 0$, $y_{O_2} \sim 0.049$, $y_{N_2} \sim 0.556$, $y_{H_2O} \sim 0.197$, $y_{CH_3CHO} \sim 0.197$ and $y_{H_2} \sim 0$.

9.15 (also available as a Mathcad worksheet)

$C_3H_8 = C_3H_6 + H_2$ rxn 1

$C_3H_8 = C_2H_4 + CH_4$ rxn 2
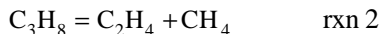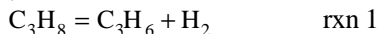
Species balance table

Species	Initial	Final	y_i
C_3H_8	1	$1 - X_1 - X_2$	$\dfrac{1 - X_1 - X_2}{1 + X_1 + X_2}$
C_3H_6	0	X_1	$\dfrac{X_1}{1 + X_1 + X_2}$
H_2	0	X_1	$\dfrac{X_1}{1 + X_1 + X_2}$
C_2H_4	0	X_2	$\dfrac{X_2}{1 + X_1 + X_2}$
CH_4	0	X_2	$\dfrac{X_2}{1 + X_1 + X_2}$
Σ		$1 + X_1 + X_2$	

In general, we have $a_i = \dfrac{y_i P}{1 \text{ bar}}$, thus

$$K_{a,1} = \frac{a_{C_3H_6}a_{H_2}}{a_{C_3H_8}} = \frac{y_{C_3H_6}y_{H_2}}{y_{C_3H_8}}\left(\frac{P}{1\,\text{bar}}\right) = \frac{P}{1\,\text{bar}}\frac{X_1^2}{(1-X_1-X_2)(1+X_1+X_2)}$$

Similarly

$$K_{a,2} = \frac{a_{C_2H_4}a_{CH_4}}{a_{C_3H_8}} = \frac{P}{1\,\text{bar}}\frac{X_2^2}{(1-X_1-X_2)(1+X_1+X_2)}$$

Also $\dfrac{K_{a,2}}{K_{a,1}} = \dfrac{X_2^2}{X_1^2}$, so define $\alpha = \dfrac{X_2}{X_1} = \sqrt{\dfrac{K_{a,2}}{K_{a,1}}}$. Thus

$$K_{a,1} = \frac{(P/1\,\text{bar})X_1^2}{(1-(1+\alpha)X_1)(1+(1+\alpha)X_1)} = \frac{(P/1\,\text{bar})X_1^2}{1-(1+\alpha)^2 X_1^2}$$

(a) Constant pressure case: $P/1\,\text{bar} = 1$

$$\Rightarrow X_1 = \sqrt{\frac{K_{a,1}}{1+\left(K_{a,1}^{1/2}+K_{a,2}^{1/2}\right)^2}} \quad\text{and}\quad X_2 = \sqrt{\frac{K_{a,2}}{1+\left(K_{a,1}^{1/2}+K_{a,2}^{1/2}\right)^2}}$$

Results are given in table below.

(b) Constant volume case: Assume gas is ideal

$$PV = NRT \Rightarrow P_f = \frac{N_f}{N_i}\frac{T_f}{T_i} = \left[(1+X_1+X_2)\frac{T}{298.15}\right]\text{bar}$$

or

$$P_f = \frac{[1+(1+\alpha)X_1]T}{298.15}$$

$$\Rightarrow K_{a,1} = \frac{[1+(1+\alpha)X_1](T/298.15)X_1^2}{[1+(1+\alpha)X_1][1-(1+\alpha)X_1]} = \frac{X_1^2 T}{298.15[1-(1+\alpha)X_1]}$$

$$\Rightarrow X_1 = \frac{298.15}{T}K_{a,1}^{1/2}\left\{\sqrt{\left[K_{a,1}^{1/2}+K_{a,2}^{1/2}\right]^2 + \frac{4T}{298.15}} - \left[K_{a,1}^{1/2}+K_{a,2}^{1/2}\right]\right\}$$

$$\Rightarrow X_2 = \frac{298.15}{T}K_{a,2}^{1/2}\left\{\sqrt{\left[K_{a,1}^{1/2}+K_{a,2}^{1/2}\right]^2 + \frac{4T}{298.15}} - \left[K_{a,1}^{1/2}+K_{a,2}^{1/2}\right]\right\}$$

Results are given in table below.

				$T(\text{K})$			
	1000	1200	1400	1500	1600	1800	2000
$K_{a,1}$	2.907	38.88	246.0	512.6	972.4	2809	6511
$K_{a,2}$	534.3	2581	7754	11950	17350	31900	50870

Part a

$y_{C_3H_8}$	0	0	0	0	0	0	0
$y_{C_3H_6} = y_{H_2}$	0.034	0.055	0.076	0.086	0.096	0.114	0.132
$y_{C_2H_4} = y_{CH_4}$	0.465	0.445	0.424	0.414	0.404	0.386	0.368

Part b

$y_{C_3H_8}$	0.003	0.001	0.000	0.000	0.000	0.000	0.000
$y_{C_3H_6} = y_{H_2}$	0.034	0.055	0.076	0.086	0.096	0.114	0.132
$y_{C_2H_4} = y_{CH_4}$	0.464	0.445	0.424	0.414	0.404	0.386	0.368
P bar	6.69	8.045	9.389	10.061	10.732	12.074	13.416

As usual, all equilibrium constant were computed using the program CHEMEQ and Mathcad.

9.16 (also available as a Mathcad worksheet)

Reaction: $N_2 + O_2 = 2NO$

Species balance table

Species	Initial	Final	y_i
N_2	1	$1 - X$	$\dfrac{1-X}{2}$
O_2	1	$1 - X$	$\dfrac{1-X}{2}$
NO	0	$2X$	X
Σ		2	

Since $P = 1$ bar , $a_i = \dfrac{y_i P}{1 \text{ bar}} = y_i$. Thus

$$K_a = \frac{a_{NO}}{a_{N_2} a_{O_2}} = \frac{4X^2}{(1-X)^2}$$

or

$$K_a^{1/2} = \frac{2X}{1-X} \Rightarrow X = \frac{\sqrt{K_a}}{2 + \sqrt{K_a}} \tag{1}$$

Now, the energy balance for the adiabatic reactor, Eqn. (9.7-10b) is

$$0 = \sum (N_i)_{\text{in}} \int_{T_{\text{in}}}^{T_{\text{out}}} C_{P,i} dT + \Delta \underline{H}_{\text{rxn}}(T_{\text{out}}) X$$

or

$$X = -\frac{\displaystyle\int_{T_{\text{in}}}^{T_{\text{out}}} \{C_{P,N_2} + C_{P,O_2}\} dT}{\Delta \underline{H}_{\text{rxn}}(T_{\text{out}})} \tag{2}$$

Using the program CHEMEQ and the data in Appendix II, together with eqns. (1 and 2), the following results are obtained.

$T(K)$	K_a	$\Delta \underline{H}_{rxn}$	X^{eq}	X^{energy}
		(kJ/mol)		
2800	0.008002	162.26	0.0428	0.0955
2820	0.008406	161.38	0.0438	0.0865
2840	0.008822	160.48	0.0449	0.0773
2860	0.009251	159.54	0.0459	0.0681
2880	0.009691	158.58	0.0469	0.0587
2900	0.01014	157.58	0.0479	0.0493
2920	0.01060	156.55	0.0490	0.0397
2940	0.01108	155.49	0.0500	0.0300
2960	0.01156	154.39	0.0510	0.0201
2980	0.01206	153.26	0.0521	0.0101
3000	0.01256	152.10	0.0531	0.0

The solution is $T \sim 2902.5$ K and $X = 0.0482$ so that $y_{NO} = 0.0482$, $y_{N_2} = y_{O_2} = 0.4759$.

9.17 Suppose we start with 1 mole of hydrogen and z moles of nitrogen. The species balance table is:

Species	Initial	Final	y_i
H_2	1	$1 - 3X$	$\dfrac{1 - 3X}{1 + z - 2X}$
N_2	z	$z - X$	$\dfrac{z - X}{1 + z - 2X}$
NH_3	0	$2X$	$\dfrac{2X}{1 + z - 2X}$
		$\Sigma = 1 + z - 2X$	

and

$$K_a = \frac{\left(P_{NH_3}/1\,\text{bar}\right)^2}{\left(P_{N_2}/1\,\text{bar}\right)\left(P_{H_2}/1\,\text{bar}\right)^3} = \frac{y_{NH_3}^2}{y_{N_2} y_{H_2}^3}\left(\frac{1\,\text{bar}}{P}\right)^2$$

$$\Rightarrow K_a \left(\frac{P}{1\,\text{bar}}\right)^2 = \frac{4 X^2 (1 + z - 2X)^2}{(z - X)(1 - 3X)^3} \tag{1}$$

Note: We are assuming P is low enough that no f/P corrections are needed!

Now we want to know how X changes with z, so we will look at the derivative dX/dz at constant T and P. Starting from Eqn. (1) we obtain

$$0 = \frac{8X(1+z-2X)^2}{(z-X)(1-3X)^3}\frac{dX}{dz} + \frac{8X^2(1+z-2X)}{(z-X)(1-3X)^3}\left(1-2\frac{dX}{dz}\right)$$

$$-\frac{4X^2(1+z-2X)^2}{(z-X)^2(1-3X)^3}\left(1-\frac{dX}{dz}\right) - \frac{12X^2(1+z-2X)^2}{(z-X)(1-3X)^4}\left(-3\frac{dX}{dz}\right)$$

$$\Rightarrow \frac{dX}{dz} = \frac{[1/(z-X)]-[2/(1+z-2X)]}{(2/X)-[4/(1+z-2X)]+[1/(z-X)]+[9/(1-3X)]}$$

where X must be equal to, or smaller than, the smallest of $1/3$ and z.

For $y_{N_2} = 0.5 = \frac{z-X}{1+z-2X} \Rightarrow z = 1$. Let $z = 1 + \delta$ where δ may be either $+$ or $-$.

$$\frac{dX}{dz} = \frac{[1/(1+\delta-X)]-[2/(2-2X+\delta)]}{(2/X)-[4/(2-2X+\delta)]+[1/((1-X)+\delta)]+[9/(1-3X)]}$$

Since $X \le 1/3$, the denominator is always positive, so we need only look at the numerator to determine the sign of dX/dz.

$$\text{Num} = \frac{1}{1+\delta-X} - \frac{1}{1-X+(\delta/2)}$$

Now do Taylor series expansions in $\frac{\delta}{1-X}$ and $\frac{\delta}{2(1-X)}$.

$$\text{Num} = \frac{1}{1-X}\left(1-\frac{\delta}{1-X}\right) - \frac{1}{1-X}\left(1-\frac{\delta}{2(1-X)}\right) = \frac{-\delta}{2(1-X)^2}$$

Thus, the sign of dX/dz is the same as the sign of $(-\delta)$. If $\delta > 0$, i.e., more N_2 is added than is required for $y_{N_2} = 0.5$, $dX/dz < 0$, so that NH_3 decomposes, and N_2 is produced.

If, however, $\delta < 0$, i.e., less N_2 is added than is needed for $y_{N_2} = 0.5$, the addition of N_2 causes more NH_3 to be formed.

Note: If, instead of N_2 addition at constant pressure, the nitrogen was added at constant total volume, so that partial pressure of either species were unaffected, and the partial pressure of N_2 increased, then, from

$$K_a = \frac{\left(P_{NH_3}/1\ \text{bar}\right)^2}{\left(P_{H_2}/1\ \text{bar}\right)\left(P_{H_2}/1\ \text{bar}\right)^3}$$

it is clear that the reaction would always go in the direction of increased ammonia production. This is an important distinction between reactions at constant volume and at constant pressure in this case.

9.18 (also available as a Mathcad worksheet)

Reactions: $C_4H_{10} = C_4H_8 + H_2$ rxn 1
$\qquad\qquad C_4H_8 = C_4H_6 + H_2$ rxn 2
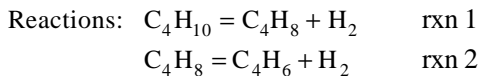
Species balance table

Species	Initial	Final	y_i
C_4H_{10}	1	$1 - X_1$	$\dfrac{1 - X_1}{1 + X_1 + X_2}$
C_4H_8	0	$X_1 - X_2$	$\dfrac{X_1 - X_2}{1 + X_1 + X_2}$
C_4H_6	0	X_2	$\dfrac{X_2}{1 + X_1 + X_2}$
H_2	0	$X_1 + X_2$	$\dfrac{X_1 + X_2}{1 + X_1 + X_2}$
Σ		$1 + X_1 + X_2$	

Since pressure $= 1\,\text{bar}$, $a_i = \dfrac{y_i P}{1\,\text{bar}} = y_i$. Thus

$$K_{a,1} = \frac{y_{C_4H_8} y_{H_2}}{y_{C_4H_{10}}} = \frac{(X_1 - X_2)(X_1 + X_2)}{(1 - X_1)(1 + X_1 + X_2)}$$

$$\Rightarrow K_{a,\,1}\left(1 + X_2 - X_1^2 - X_1 X_2\right) = X_1^2 - X_2^2 \qquad (1)$$

and

$$K_{a,2} = \frac{y_{C_4H_6} y_{H_2}}{y_{C_4H_8}} = \frac{X_2(X_1 + X_2)}{(X_1 - X_2)(1 + X_1 + X_2)}$$

$$\Rightarrow K_{a,2}\left(X_1 + X_1^2 - X_2 - X_2^2\right) = X_1 X_2 + X_2^2 \qquad (2)$$

Using CHEMEQ (for equilibrium constants) and Mathcad (for solution) I obtain

T	$K_{a,1}$	$K_{a,2}$	X_1	X_2	$y_{C_4H_{10}}$	$y_{C_4H_8}$	$y_{C_4H_6}$	y_{H_2}
900	0.9731	0.1191	0.724	0.147	0.147	0.308	0.079	0.466
1000	5.814	0.5575	0.951	0.464	0.020	0.202	0.192	0.586

9.19 This problem can be solved graphically, as shown here, or analytically as seen in the Mathcad worksheet.

Reaction: $H_2 + \dfrac{1}{2}O_2 = H_2O$
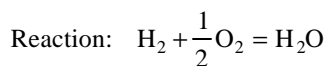
Using the program CHEMEQ, the equilibrium constant can be computed at each temperature. The results are given on the next page. Also, since $P = 1.013\,\text{bar}$ $a_i = \dfrac{y_i P}{1\,\text{bar}} = y_i \times 1.013$.

(a)   Stoichiometric amount of pure oxygen

Species	In	Out	y_i
H_2	1	$1-X$	$\dfrac{2(1-X)}{3-X}$
O_2	0.5	$\dfrac{1}{2}(1-X)$	$\dfrac{1-X}{3-X}$
H_2O	0	X	$\dfrac{2X}{3-X}$
Σ		$\dfrac{1}{2}(3-X)$	

$$\Rightarrow K_a = \frac{a_{H_2O}}{a_{H_2} a_{O_2}^{1/2}(1.013)^{1/2}} = \frac{2X}{3-X} \cdot \frac{3-X}{2(1-X)} \cdot \frac{(3-X)^{1/2}}{(1-X)^{1/2}(1.013)^{1/2}}$$

$$= \frac{X(3-X)^{1/2}}{(1-X)^{3/2}(1.013)^{1/2}}$$

or

$$K_a(1-X)^{3/2}(1.013)^{1/2} - X(3-X)^{1/2} = 0$$

This will be solved using Mathcad.
From the energy balance we obtain the following

$T(K)$	X_{Eng} (Part a)	X_{Eng} (Part b)	X_{Eng} (Part c)
1000	0.129	0.194	0.509
1200	0.167	0.226	0.658
1300			0.734
1400	0.207	0.279	0.811
1500			0.899
1600	0.246	0.333	0.968
1800	0.286	0.388	1.127
2000	0.328	0.443	
2200	0.370	0.500	
2400	0.412	0.557	
2600	0.455	0.615	
2800	0.498	0.674	
3000	0.542	0.733	
3200	0.585	0.792	
3400	0.629	0.852	
3600	0.674	0.911	

and, from Eqn. (9.7-10b), we get

$$X = -\sum_{i=1}^{C} (N_i)_{in} \frac{\displaystyle\int_{T_{in}}^{T_{ed}} C_{P,i}\, dT}{\Delta \underline{H}_{rxn(T_{ed})}}$$

where $\displaystyle\sum_{i=1}^{C}(N_i)_{in}C_{P,i} = C_{P,H_2} + \frac{1}{2}C_{P,O_2}$ and $T_{in} = 298.15 \text{ K}$.

(b) 100% excess oxygen

Species	In	Out	y_i
H_2	1	$1-X$	$\dfrac{1-X}{2-0.5X}$
O_2	1	$1-\dfrac{1}{2}X$	$\dfrac{1-0.5X}{2-0.5X}$
H_2O	0	X	$\dfrac{X}{2-0.5X}$
		$\overline{\quad 2-\dfrac{1}{2}X \quad}$	

$\Rightarrow K_a(1-X)(1-0.5X)^{1/2} - X(2-0.5X)^{1/2} = 0$ and, for energy balance

$$\sum_{i=1}^{C}(N_i)_{in}C_{P,i} = C_{P,N_2} + C_{P,O_2}$$

(c) 100% excess oxygen in air

Species	In	Out	y_i
H_2	1	$1-X$	$\dfrac{1-X}{5.762-0.5X}$
O_2	1	$1-0.5X$	$\dfrac{1-0.5X}{5.762-0.5X}$
N_2	$\dfrac{0.79}{0.21}\times 1 = 3.762$	3.762	$\dfrac{3.762}{5.762-0.5X}$
H_2O	0	X	$\dfrac{X}{5.762-0.5X}$
		$\overline{\quad 5.762-0.5X \quad}$	

$\Rightarrow K_a(1-X)(1-0.5X)^{1/2} - X(5.762-0.5X)^{1/2} = 0$

and

$$\sum_{i=1}^{C}(N_i)_{in}C_{P,i} = C_{P,H_2} + C_{P,O_2} + 3.762\,C_{P,N_2}$$

From the intersections of the equilibrium and energy balance curves, we obtain the following solutions [curves on following page] (or directly by solving the equations using MATHCAD)

(a) $T_{ad} = 3535 \text{ K}$ $y_{H_2} = 0.291$

   $X = 0.659$ $y_{O_2} = 0.146$

                     $y_{H_2O} = 0.563$

(b) $T_{ad} = 3343 \text{ K}$ $y_{H_2} = 0.104$

   $X = 0.835$ $y_{O_2} = 0.368$

                     $y_{H_2O} = 0.528$

(c) $T_{ad} = 1646 \text{ K}$ $y_{H_2} \sim 0$

      $X \cong 1.0$ $y_{O_2} = 0.095$

                              $y_{H_2O} = 0.190$

                              $y_{N_2} = 0.715$

Letters denote parts a, b or c of problem.
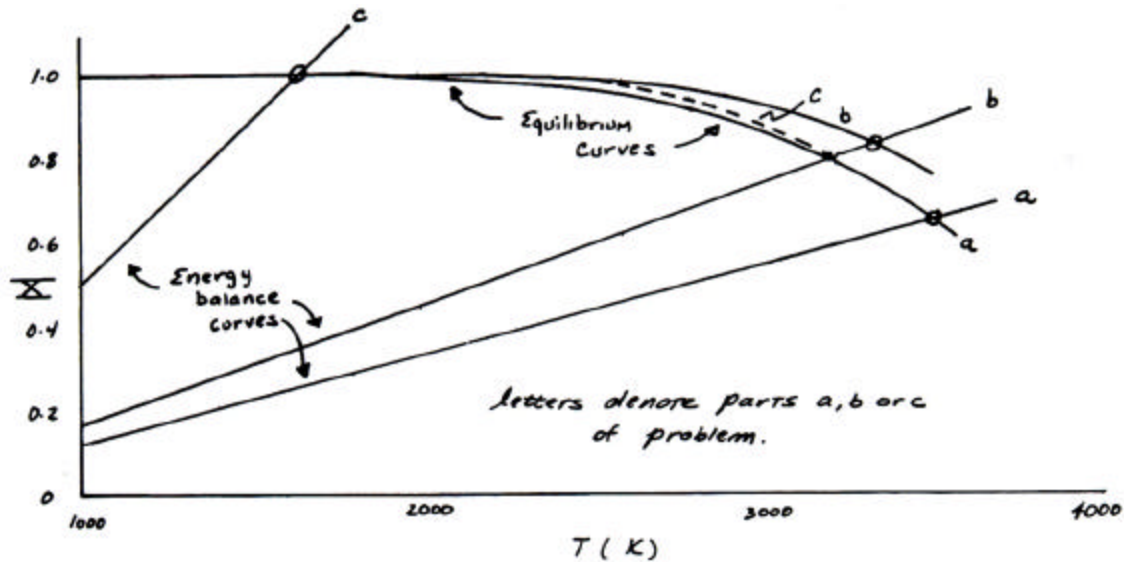
9.20   Using the data in the problem statement, Tables 2.4 and A6.1, I find

$$K_{a,1}(750 \text{ K}) = \frac{a_{CaOSiO_2} a_{CO_2}}{a_{CaCO_3} a_{SiO_2}} = 148.1 = a_{CO_2} = \frac{y_{CO_2} P}{1 \text{ bar}}, \qquad (1)$$

since the activity of all the solids are unity.

$$K_{a,2}(750 \text{ K}) = \frac{a_{SiO_2}^3 a_{Fe_3O_4} a_{CO}}{a_{FeO\cdot SiO_2}^3 a_{CO_2}} = 0.0277 = \frac{a_{CO}}{a_{CO_2}} = \frac{y_{CO}}{y_{CO_2}}, \qquad (2)$$

and

$$K_{a,3}(750 \text{ K}) = \frac{a_{Fe_3O_4} a_{SiO_2}^3}{a_{FeOSiO_2}^3 a_{O_2}^{1/2}} = 0.8973 \times 10^{14} = \frac{1}{a_{O_2}^{1/2}} = \left(\frac{1 \text{ bar}}{y_{O_2} P}\right)^{1/2}$$

$$\Rightarrow \frac{y_{O_2} P}{1 \text{ bar}} = 1.242 \times 10^{-28} \qquad (3)$$

From eqn. (2) we have

$\dfrac{y_{CO}}{y_{CO_2}} \sim 0.0277$, while from spectroscopic observations $\dfrac{y_{CO}}{y_{CO_2}} \cong 10^{-4}$

Also, from eqn. (1), $P_{CO_2} \sim 148$ bar , while from the probe, the total atmospheric pressure is only between 75 and 105 bar. Finally, from Eqn. (3), we conclude there is no O_2 in the atmosphere, compared to a trace from spectroscopic observations.

Conclusions? Somewhat ambiguous!

Calculations and data are not in quantitative agreement, but are certainly in qualitative agreement. Consider the uncertainty in all the measurements, the atmospheric model is undoubtedly a reasonable one, and can not be rejected.

9.21 (a) The condition for chemical equilibrium is

$$K_a^V = \exp\left(\frac{-\Delta \underline{G}_{rxn}^V}{RT}\right) = \frac{a_{EB}^V}{a_S^V a_H^V} \text{ ; vapor phase} \qquad (1)$$

or

$$K_a^L = \exp\left(\frac{-\Delta \underline{G}_{rxn}^L}{RT}\right) = \frac{a_{EB}^L}{a_S^L a_H^L} \text{ ; liquid phase} \qquad (2)$$

where $\Delta \underline{G}_{rxn}^i$ is the standard state Gibbs free energy change on reaction in phase i.

The phase equilibrium requirements are

$$\bar{f}_{EB}^L = \bar{f}_{EB}^V, \ \bar{f}_S^L = \bar{f}_S^V \text{ and } \bar{f}_H^L = \bar{f}_H^V \qquad (3)$$

From problem statement $\Delta \underline{G}_{rxn}^V = -83.0$ kJ/mol , and $K_i^V = 3.482 \times 10^{14}$. This implies that the reaction will go, essentially, to completion in the gas phase. Now $\underline{G} = \underline{H} - T\underline{S}$, and for most liquids neither $\Delta \underline{H}^{vap}$ or $T\Delta \underline{S}^{vap}$ is more than several kJ/mol. Also, since, for hydrogen, the vapor is the stable phase, $\underline{G}_{H_2}^L > \underline{G}_{H_2}^V$. Therefore, it seems likely that $\Delta \underline{G}_{rxn}^L$ will be of about the same size and sign as $\Delta \underline{G}_{rxn}^V$. Consequently, the liquid phase chemical equilibrium constant will also be large, and the hydrogenation reaction will essentially go to completion in the liquid phase.

$\Rightarrow$ mole fraction of styrene will be very small in both phases. The problem then reduces to determining the solubility of the excess hydrogen in the liquid ethyl benzene, and determining the amount of ethyl benzene in the vapor. Thus, the equations to be solved are

$$\bar{f}_{EB}^L = \bar{f}_{EB}^V \Rightarrow x_{EB} \gamma_{EB} f_{EB}^L = y_{EB} P$$

and

$$\bar{f}_H^L = \bar{f}_H^V \Rightarrow x_H \gamma_H f_H^L = y_H P$$

Here we have assumed that the vapor phase is ideal.

As a first guess, we will assume that very little hydrogen is dissolved in the liquid phase. Thus, $\gamma_{EB} = 1$, $\phi_{EB} = 1$, and, using regular solution theory

$$\ln \gamma_H = \frac{\underline{V}_H^L (\delta_{EB} - \delta_H)^2}{RT} = \frac{3.1 \text{ cc/mol} \times (8.8 - 3.25)^2 \text{ cal/cc} \times 4.184 \text{ J / cal}}{8.314 \text{ J/mol K} \times 298.15 \text{ K}} = 0.1612$$

$$\Rightarrow \gamma_H = 1.175$$

Next we have to estimate the fugacity of hydrogen in the liquid phase. An obvious way to proceed is to use Shair's correlation, in Sec. 8.5. However, hydrogen was not used in developing this correlation, and Prausnitz warns against its use for light gases such as hydrogen and helium; since experimental data are not available, we have little choice but to use this

correlation. Note, however, that for hydrogen, $T_C = 33.2$ K and $P_C = 12.97$ bar, so that $T_r = T/T_C = 8.98$, which is off the scale of Fig. 8.3-1. If we extrapolate this correlation to $T_r = 8.98$ (a very serious assumption), then we obtain $\left(f^L/P_C\right)_{1.013\ \text{bar}} \sim 4$, and

$$f^L(1.013\ \text{bar, }25°\text{C}) = 4 \times 12.97\ \text{bar} = 51.88\ \text{bar}$$

[Note the the Poynting pressure correction of this result to 3 bar total pressure is negligible.]
As a first guess, we will assume that the gas-phase is essentially pure hydrogen. Therefore,

$$x_H = \frac{y_H P}{\gamma_H f_H^L} = \frac{3\ \text{bar}}{1.175 \times 51.88\ \text{bar}} = 0.049\ ,\ \text{and}\ x_{EB} = 1 - x_H = 0.951\ .$$

Using the vapor pressure data for ethyl benzene, plotted in the form of $\ln P^{\text{vap}}$ vs $1/T$, we find that $P_{EB}^{\text{vap}} = 1.273$ kPa at 25°C.

$$y_{EB} = \frac{x_{EB} \gamma_{EB} P_{EB}^{\text{vap}}}{P} = \frac{0.951 \times 1 \times 1.273}{3 \times 100\ \text{kPa}} \cong 0.004$$

and $y_H = 0.996$ [Since the gas phase is almost pure hydrogen, as assumed, there is no need to iterate to a solution].

$$\begin{aligned} x_H &= 0.049 & y_H &= 0.996 \\ \Rightarrow x_{EB} &= 0.951\ \text{and}\ y_{EB} = 0.004 \\ x_S &\cong 0 & y_S &\cong 0.0 \end{aligned} \quad \begin{aligned} &\text{at } T = 25°\text{C} \\ &\text{and } P = 3\ \text{bar} \end{aligned}$$

An alternative calculation is to use the Peng-Robinson equation of state. The critical properties of hydrogen are given in Table 4.6-1. The values for ethylbenzene are $T_C = 617.2$ K, $P_C = 36$ bar, $\omega=0.302$, and $T_B=409.3$ K. There is no binary interaction parameters for hydrogen with other components in Table 7.4-1, so we will assume that its value is zero. Using the isothermal flash calculation in the program VLMU we obtain the following results

$$\begin{aligned} x_H &= 0.0018 & y_H &= 0.9952 \\ x_{EB} &= 0.9982\ \text{and}\ y_{EB} = 0.0048 \\ x_S &\cong 0 & y_S &\cong 0.0 \end{aligned} \quad \begin{aligned} &\text{at } T = 25°\text{C} \\ &\text{and } P = 3\ \text{bar} \end{aligned}$$

This may be a more accurate calculation than using regular solution theory which required an extrapolation of the Prausnitz-Shair correlation.. However, the result is based on the assumption that $k_{ij} = 0$. It would be better to have some experimental data to get a better estimate of this parameter.

(b) At 150°C and 3 bar.
Using the data in the Problem statement, Appendices II and IV we find $K_a(T = 150°\text{C}) = 3.1 \times 10^8$. So again we can presume that all the styrene in the vapor and liquid phases is converted to ethyl benzene.
As a first approximation (iteration), we will assume that the liquid phase is essentially pure ethyl benzene. Thus we obtain

$$\gamma_H = \exp\left\{ \frac{3.1(3.25 - 8.8)^2}{1.987 \times 423.15} \right\} = 1.12$$

Here again, we find, extrapolating Fig. 8.3-1, that

$$f_H^L \sim 51.88\ \text{bar} \Rightarrow x_H = \frac{3}{51.88 \times 1.12} = 0.052$$

and $x_{EB} = 1 - 0.052 = 0.948$.
Now, however, $P_{EB}^{\text{vap}} \sim 1.303$ bar

$$\Rightarrow y_{EB} = \frac{1.303 \times 0.948}{3} = 0.412$$

Now using these values for another iteration, we obtain

$$x_H = 0.029 \quad y_H = 0.586 \quad T = 150° C$$
$$x_{EB} = 0.971 \quad y_{EB} = 0.414 \quad 3 \text{ bar}$$
$$x_{ST} \sim 0 \quad y_{ST} = 0.0$$

Again using the Peng-Robinson equation of state, the program VLMU and the assumption that $k_{ij} = 0$, we obtain the following

$$x_H = 0.0016 \quad y_H = 0.5034 \quad T = 150° C$$
$$x_{EB} = 0.9984 \quad y_{EB} = 0.4966 \quad 3 \text{ bar}$$
$$x_{ST} \sim 0 \quad y_{ST} = 0.0$$

In both parts a and b we see that the results of the equation of state calculation are in qualitative, but not quantitative agreement with the Prausnitz-Shair correlation. However, the latter predicts much higher solubilities of hydrogen in the liquid phase. The equation of state calculation is much easier to do (given the availability of the program VLMU). If some experimental data were available for hydrogen solubility in ethylbenzene (or other aromatics), the value of k_{ij} could be adjusted to reproduce that data. Then we would have more confidence in the equation of state predictions for the problem here. If such experimental data were available, it is not clear how one would adjust the Prausnitz-Shair correlation to match that such data.

9.22 (a) Energy balance on a fixed mass of gas

$$\frac{dU}{dt} = \dot{Q} - P \cancel{\frac{dV}{dt}}^{0} + \cancel{\dot{W}}^{0} \Rightarrow \dot{Q} = \left(\frac{\partial U}{\partial t}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial t}\right)_V$$

but $C_V = \dfrac{\dot{Q}}{\left(\dfrac{\partial T}{\partial t}\right)_V} = \left(\dfrac{\partial U}{\partial T}\right)_V$.

Now $U = \sum N_i \overline{U}_i = \sum N_i \underline{U}_i$, since we will assume the gas is ideal at the temperatures and pressures encountered here. Also $N_i = N_{i,0} + \nu_i X$ and $\underline{U}_i(T) = \underline{U}_i(T_R) + \int_{T_R}^{T} C_V dT$ where T_R is some convenient reference temperature.

$$C_{V,eff} = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\right)_V \sum N_i \underline{U}_i = \sum \left(\frac{\partial N_i}{\partial T}\right)_V \underline{U}_i + \sum N_i \left(\frac{\partial \underline{U}_i}{\partial T}\right)_V$$

$$= \sum \nu_i \underline{U}_i \left(\frac{\partial X}{\partial T}\right)_V + \sum N_i C_{V,i} = \Delta \underline{U}_{rxn}(T) \left(\frac{\partial X}{\partial T}\right)_V + \sum N_i C_{V,i}(T)$$

where $\Delta \underline{U}_{rxn} = \sum \nu_i \underline{U}_i$ = internal energy change on reaction.
Species balance table

Species	In	Out	y_i
N_2O_4	1	$1-X$	$\dfrac{1-X}{1+X}$
NO_2	0	$2X$	$\dfrac{2X}{1+X}$
Σ		$1+X$	

$$K_a = \frac{a_{NO_2}^2}{a_{N_2O_4}} = \frac{\left(y_{NO_2} P/1\text{ bar}\right)^2}{\left(y_{N_2O_4} P/1\text{ bar}\right)} = \frac{y_{NO_2}^2 P}{y_{N_2O_4}(1\text{ bar})} = \frac{4X^2(P/1\text{ bar})}{(1-X)(1+X)}$$

By the ideal gas law $PV = NRT \Rightarrow \dfrac{P}{NT} = \dfrac{P_0}{N_0 T_0}$ where the subscript $_0$ denotes the initial

conditions

$$\Rightarrow P = P_0\left(\frac{N}{N_0}\right)\left(\frac{T}{T_0}\right) = \frac{1.013\text{ bar}(1+X)T}{300}$$

$$\Rightarrow K_a = \frac{4X^2(1+X)T \cdot 1.013}{(1-X)(1+X)T_0} = \frac{4 \cdot 1.013 \cdot X^2 T}{(1-X)T_0}$$

$$\text{or } \frac{X^2}{1-X} = \frac{T_0 K_a}{4 \cdot 1.013 \cdot T} = \alpha \qquad X^2 - \alpha(1-X) = 0$$

$$X + \alpha X - \alpha = 0 \Rightarrow X = \frac{\alpha}{2}\left\{\sqrt{1+\frac{4}{\alpha}} - 1\right\} \qquad\qquad (1)$$

$$\left(\frac{dX}{dT}\right)_V = \frac{d}{dT}\left[\frac{\alpha}{2}\left\{\sqrt{1+\frac{4}{\alpha}}-1\right\}\right] = \left[X - \frac{1}{\sqrt{1+(4/\alpha)}}\right]\frac{d\ln\alpha}{dT}$$

but $\dfrac{d\ln\alpha}{dT} = \dfrac{d\ln K_a}{dT} - \dfrac{1}{T} = \dfrac{\Delta \underline{U}_{rxn}}{RT^2}$. Also

$$\Delta \underline{U}_{rxn} = \sum \nu_i \underline{U}_i = \sum \nu_i (\underline{H}_i - RT) = \Delta \underline{H}_{rxn} - RT\sum \nu_i \qquad\qquad (2)$$

$$\sum \nu_i = 1 \Rightarrow \Delta \underline{U}_{rxn} = \Delta \underline{H}_{rxn} - RT$$

$$\Rightarrow C_{V,eff} = (1-X)C_{V,N_2O_4} + XC_{V,NO_2} + \frac{(\Delta\underline{U}_{rxn})^2}{RT^2}\left[X - \frac{1}{\sqrt{1+(4/\alpha)}}\right] \qquad (3)$$

First two terms give the composition (mole fraction) – weighted heat capacity of the individual components; the last term is the enhancement of the heat capacity due to the chemical reaction. This term has one $\Delta\underline{U}_{rxn}$ dependence since that amount of energy is absorbed as the reaction equilibrium shifts, and a second $\Delta\underline{U}_{rxn}$ dependence, since this determines the extent of a shift in the equilibrium with temperature.

(b) Using CHEMEQ and the data in Appendix II (for C_P^*), $\ln K_a$ was determined at each temperature along with C_V for both NO_2 and N_2O_4. Then, from Eqns. (1) and (3) X and $C_{V,eff}$ as well. These are tabulated and plotted below.

T (K)	α	X	P (bar)	C_{V,NO_2}	C_{V,N_2O_4}	$C_{V,eff}$
300	0.044275	0.1891	1.205	37.11	78.83	410.5
350	1.0016	0.6177	1.912	38.94	84.47	546.9
400	10.0613	0.9163	2.588	40.65	89.55	195.9
450	58.883	0.9835	3.014	42.22	94.06	69.11
500	236.25	0.9958	3.370	43.67	98.01	49.23
550	721.36	0.9986	3.712	45.00	101.39	46.49
600	1796.25	0.9994	4.051	46.23	104.20	46.71
700	7220.4	0.99986	4.727	48.36	108.12	48.45
					J/mol K	
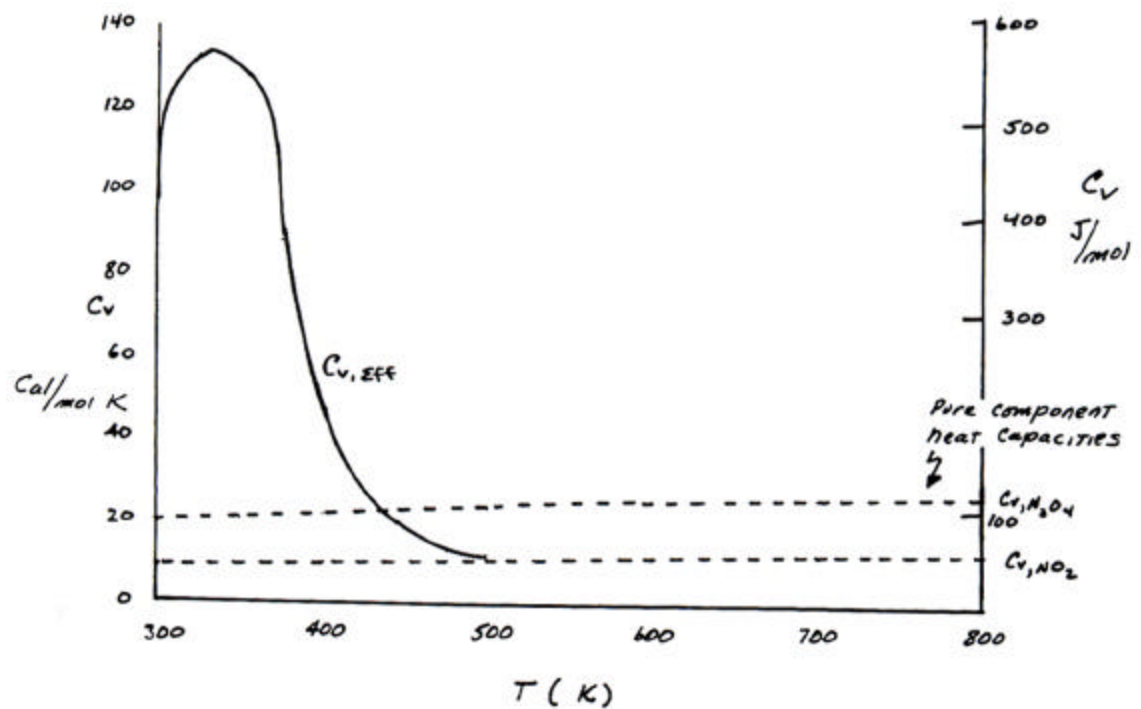
9.23 This is a very difficult problem. I used the NASA chemical equilibrium program, referenced in Sec. 9.4, in the solution of this problem. I will describe here how this problem could be solved without this program.

First we need to identify the independent chemical reactions among the components. Starting from

$2C + 2H = HCCH$

$2O = O_2$ and first using

$C + O = CO$ $2H = HCCH - 2C$

$2H + O = H_2O$ to eliminate H, and then

$C + 2O = CO_2$ $O = \dfrac{1}{2}O_2$

$2H = H_2$ to eliminate O

yields

$$C + \frac{1}{2}O_2 = CO$$

$$HCCH + \frac{1}{2}O_2 = H_2O + 2C$$

$$C + O_2 = CO_2$$

$$HCCH = H_2 + 2C$$
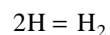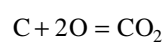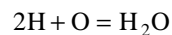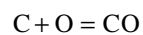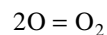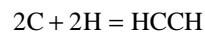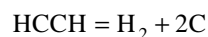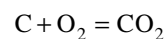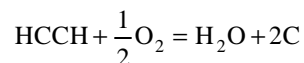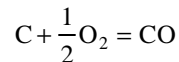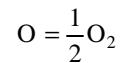
From Fig. 9.1-2 we have that K_a for the reaction $C + (1/2)O_2 = CO$ is very large over the whole temperature range (i.e., $K_a = O(10^{10})$ at 1000 K and $O(10^6)$ at 3000 K). Since O_2 is present in excess, this implies that their will be no solid carbon present. Thus, we will eliminate C using the reaction equation $C = CO - (1/2)O_2 \Rightarrow$

1) $HCCH + \dfrac{3}{2}O_2 = H_2O + 2CO$

2) $\quad CO + \dfrac{1}{2}O_2 = CO_2$

3) $\quad HCCH + O_2 = H_2 + 2CO$
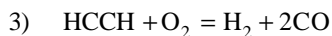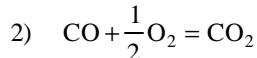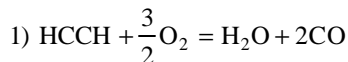
The three equations above form a set of independent reactions that can be used for the description of this reaction system. In fact, since eqns. (1) and (3) are both expected to go to completion, I used the following reaction sequence for the description of this system:

$$HCCH + \dfrac{5}{2}O_2 = H_2O + 2CO_2 \quad rxn\ 1$$

$$CO + \dfrac{1}{2}O_2 = CO_2 \qquad\qquad rxn\ 2$$

$$H_2 + \dfrac{1}{2}O_2 = H_2O \qquad\qquad rxn\ 3$$
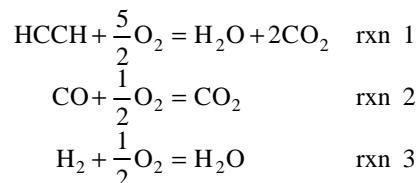
The first step in the numerical solution of this problem is the calculation of the equilibrium constants and heats of reaction for the reactions above. Using the program CHEMEQ I obtained:

T	3000	3100	3200	3300	3400	
$\Delta H_{rxn,1}$	−1310	−1320	−1332	−1345	−1361	kJ
$K_{a,1}$	1.59×10^{16}	2.90×10^{15}	5.82×10^{14}	1.27×10^{14}	2.97×10^{13}	
$\Delta H_{rxn,2}$	256.2	251.2	245.5	238.8	221.0	kJ
$K_{a,2}$	0.3246	0.4507	0.6092	0.8027	1.033	
$\Delta H_{rxn,3}$	261.9	264.9	266.9	269.9	273.5	kJ
$K_{a,3}$	0.0476	0.0668	0.0922	0.1252	0.1675	

T	3500	3600	3700	3800	3900	
$\Delta H_{rxn,1}$	−1378	−1398	−1419	−1444	−1470	kJ
$K_{a,1}$	7.45×10^{12}	1.98×10^{12}	5.54×10^{11}	1.633×10^{11}	5.006×10^{10}	
$\Delta H_{rxn,2}$	222.2	212.1	200.6	187.6	173.0	kJ
$K_{a,2}$	1.299	1.598	1.926	2.274	2.633	
$\Delta H_{rxn,3}$	277.6	282.2	287.5	293.5	300.2	kJ
$K_{a,3}$	0.2213	0.2891	0.3738	0.4793	0.6098	

Clearly, with such a large value of the equilibrium constant, reaction (1) must go essentially to completion. I will assume it does. Thus, the reaction stoichiometry is

$$HCCH + \dfrac{5}{2}O_2 = H_2O + 2CO_2 \quad X_1 = 1$$
$$CO_2 = CO + \dfrac{1}{2}O_2 \qquad X_2 = ?$$
$$H_2O = H_2 + \dfrac{1}{2}O_2 \qquad X_3 = ?$$

Note: These reactions are the inverses of reactions 2 and 3 above.
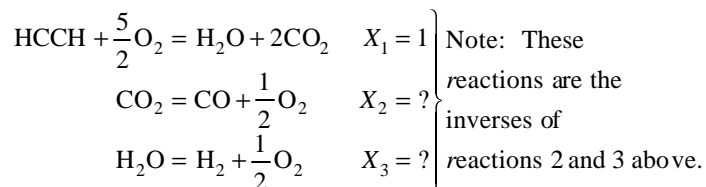
Species	Initially	After rxn 1 goes to completion	Equilibrium	y_i
HCCH	1	0	0	0
O_2	$\dfrac{15}{4}$	$\dfrac{5}{4}$	$\dfrac{5}{4}+\dfrac{1}{2}X_2+\dfrac{1}{2}X_3$	$\left(\dfrac{5}{4}+\dfrac{1}{2}X_2+\dfrac{1}{2}X_3\right)\Big/\Sigma$
CO_2	0	2	$2-X_2$	$\dfrac{2-X_2}{\Sigma}$
H_2O	0	1	$1-X_3$	$\dfrac{1-X_3}{\Sigma}$
H_2	0	0	X_3	$\dfrac{X_3}{\Sigma}$
CO	0	0	X_2	$\dfrac{X_2}{\Sigma}$

$$\Sigma = \frac{17}{4}+\frac{1}{2}(X_2+X_3)$$

$$\Rightarrow \left(K_{a,2}\right)^{-1} = \frac{a_{CO}a_{O_2}^{1/2}}{a_{CO_2}} = \frac{y_{CO}\,y_{O_2}^{1/2}}{y_{CO_2}}$$

$$= \frac{X_2[(5/4)+(1/2)X_2+(1/2)X_3]^{1/2}}{(2-X_2)[(17/4)+(1/2)X_2+(1/2)X_3]^{1/2}} \qquad (1)$$

(where for simplicity I have assumed that the standard state and atmospheric pressures were the same) and

$$\left(K_{a,3}\right)^{-1} = \frac{a_{H_2}a_{O_2}^{1/2}}{a_{H_2O}} = \frac{y_{H_2}\,y_{O_2}^{1/2}}{y_{H_2O}} = \frac{X_3[(5/4)+(1/2)X_2+(1/2)X_3]^{1/2}}{(1-X_3)[(17/4)+(1/2)X_2+(1/2)X_3]^{1/2}} \qquad (2)$$

where the equilibrium constants $K_{a,2}$ and $K_{a,3}$ are the ones whose numerical values are given in the table above.

Instead of solving these nonlinear algebraic equations, I used the NASA Gibbs free energy minimization program to find the equilibrium mole fractions. Since this package uses a different set of thermodynamic data, the computed mole fractions do not agree with eqns. (1 and 2) and the table of equilibrium constants given above. The results are:

T (K)	3000	3200	3400	3600	3800	4000
y_{CO}	0.1530	0.2126	0.2605	0.2940	0.3154	0.3284
y_{CO_2}	0.2777	0.2017	0.1395	0.0945	0.0642	0.0442
y_{H_2}	0.0153	0.0254	0.0384	0.0539	0.0705	0.0869
y_{H_2O}	0.2001	0.1818	0.1616	0.1404	0.1193	0.0995
y_{O_2}	0.3539	0.3785	0.4000	0.4173	0.4307	0.4410
X_2			1.3017	1.5126	1.6609	1.7614
X_3			0.1920	0.2771	0.3710	0.4658
ΔH_{rxn}(kJ)			−1006	−987.8	−997.0	−1025
T_{AD} $\int_{T_{in}}^{} C_P dT$ (kJ)	616.3	691.2	775.7	871.9	981.1	1106

In the table above, the mole fractions were computed using the NASA program, X_2 and X_3 were then computed from the mole fractions using

$$y_{H_2} = X_3/\Sigma \text{ and } y_{CO} = X_2/\Sigma$$

where $\Sigma = \dfrac{17}{4} + \dfrac{1}{2}(X_2 + X_3)$. ΔH_{rxn} and the integral $\displaystyle\int_{T_{in}}^{T_{AD}} C_P dT$ were computed using Eqn. (9.1-19a) and the ΔH_{rxn} data in Table A6.1 and C_P data in Table 2.4. Also,

$$\Delta \underline{H}_{rxn}(T) = \Delta \underline{H}_{rxn,1}(T) + X_2 \Delta \underline{H}_{rxn,2}(T) + X_3 \Delta \underline{H}_{rxn,3}(T)$$

and

$$\int_{T_{in}}^{T_{AD}} \left(C_{P,HCCH} + \frac{15}{4} C_{P,O_2} \right) dT = \int_{T_{in}}^{T_{AD}} C_P dT .$$

Finally, from eqn. (9.7-10a) we have, at the adiabatic reaction (flame) temperature that

$$0 = \sum_{i=1}^{C} (N_i)_{in} \int_{T_{in}}^{T_{AD}} C_{P,i} dT + \sum_{j=1}^{M} \Delta H_{rxn,j}(T_{AD}) X_j$$

or, in the notation here

$$\int_{T_{in}}^{T_{AD}} C_P dT + \Delta H_{rxn}(T_{AD}) = 0$$

Plotting up the results in the previous table, i.e. $\displaystyle\int_{T_{in}}^{T_{AD}} C_P dT$ vs T and ΔH_{rxn} vs T, leads to the solution

$$T_{AD} = 3830 \text{ K} \qquad X_2 = 1.680 \qquad X_3 = 0.387$$
$$y_{CO_2} = 0.0606, \qquad y_{CO} = 0.3180, \qquad y_{H_2O} = 0.1160$$
$$y_{H_2} = 0.0732 \qquad \text{and} \qquad y_{O_2} = 0.4322.$$

Comment: The solution above considered only O_2, H_2O, CO_2, CO, H_2 and HCCH as possible reaction species. At the high temperatures involved here, other reactions and other species are possible. This is obvious in the results below. The dashed lines result from the chemical equilibrium program of NASA with only the species mentioned above as allowed species, and the solid lines result from the Chemical Equilibrium Program with all species allowed.
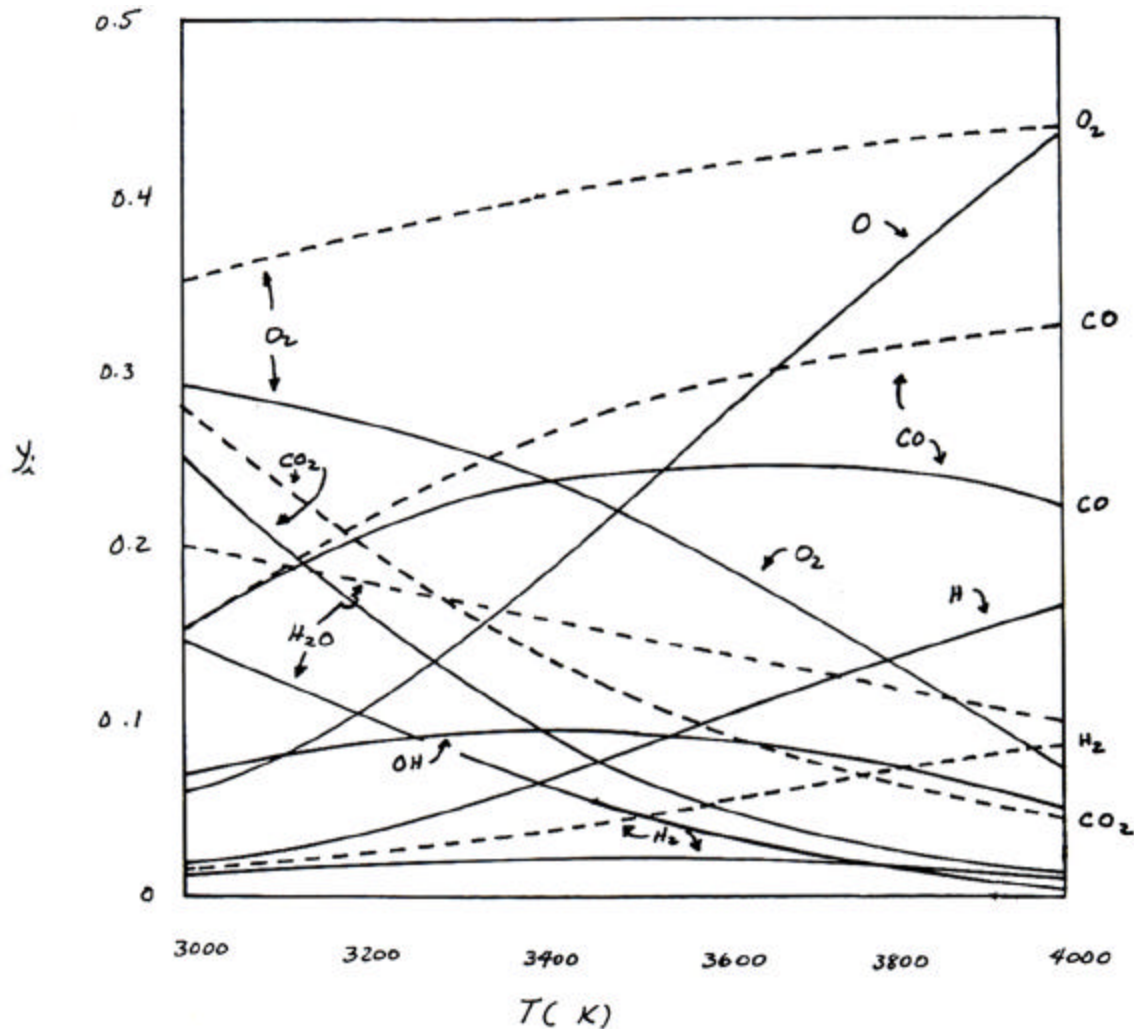
Note how different the two solutions are!

The actual (unrestricted) solution has O and H (not ions, but atoms) as important reaction products, but these species have not even been considered in the adiabatic reaction temperature calculation. The conclusion is that restricting over consideration to just the species in the problem statement is unjustified!

9.24   (also available as a Mathcad worksheet)
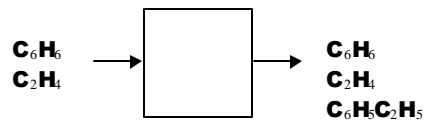
Using the program CHEMEQ we obtain that at 600 K, $K_a = 345.0$ and $\Delta H_{rxn} = -103.94$ kJ/mol for the reaction

$$C_6H_6(g) + C_2H_4(g) = C_6H_5C_2H_5(g).$$
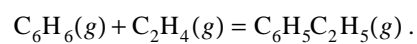
To find the extent of reaction we use

Species	Initial	Final	y_i	a_i
C_6H_6	1	$1-X$	$\dfrac{1-X}{2-X}$	$\left(\dfrac{1-X}{2-X}\right)\left(\dfrac{P}{1\ \text{bar}}\right)$
C_2H_4	1	$1-X$	$\dfrac{1-X}{2-X}$	$\left(\dfrac{1-X}{2-X}\right)\left(\dfrac{P}{1\ \text{bar}}\right)$
$C_6H_5C_3H_5$	0	X	$\dfrac{X}{2-X}$	$\left(\dfrac{X}{2-X}\right)\left(\dfrac{P}{1\ \text{bar}}\right)$
		$\overline{2-X}$		

$$K_a = 345.0 = \frac{a_{C_6H_5C_2H_5}}{a_{C_6H_6}\cdot a_{C_2H_4}} = \frac{[X/(2-X)](P/1\ \text{bar})}{[(1-X)/(2-X)]^2(P/1\ \text{bar})^2}$$

$$= \frac{X(2-X)}{(1-X)^2(P/1\ \text{bar})}$$

Now $P = P_{\text{initial}} \times \dfrac{\text{Total of moles}}{\text{Initial \# of moles}} = 1.013\ \text{bar} \times \dfrac{2-X}{2} =$

$$\Rightarrow K_a = 345.0 = \frac{2\cdot X \cdot (2-X)}{1.013\cdot(1-X)^2(2-X)} = \frac{2\cdot X}{1.013\cdot(1-X)^2}$$

which has the solution $X = 0.927$ and $P = 0.5434\ \text{bar}$.
Heat which must be *removed* to keep reactor isothermal is
$$0.927 \times 103,940 = 96,352\ \text{J (removed)}\ .$$

9.25 The two "reactions" are $HI(g) = \dfrac{1}{2}H_2(g) + \dfrac{1}{2}I_2(g)$ and $I_2(g) = I_2(s)$.

Using the data in the *Chemical Engineer's Handbook* we have

$$\Delta G^{\circ}_{\text{rxn},1} = 1.95\,\text{kcal} = 8.159\ \text{kJ} \qquad \Delta G^{\circ}_{\text{rxn},2} = -4.63\,\text{kcal} = \text{-19.37 kJ}$$

$$K_{a,1} = \exp\left\{\frac{-\Delta G^{\circ}_{\text{rxn},1}}{RT}\right\} = 3.72\times 10^{-2} = \frac{a_{H_2}^{1/2}a_{I_2}^{1/2}}{a_{HI}}$$

$$K_{a,2} = \exp\left\{\frac{-\Delta G^{\circ}_{\text{rxn},2}}{RT}\right\} = 2478.3 = \frac{a_{I_2}(s)}{a_{I_2}(g)}$$

Solid precipitation of one tiny crystal is just like a dew-point problem, that is, at the pressure at which the first bit of solid appears the vapor composition is unchanged. Therefore, the first step is to compute the vapor composition due to reaction 1 only.

Species	Initial	Final	y_i	a_i
HI	1	$1-X$	$1-X$	$\dfrac{(1-X)P}{1\ \text{atm}}$
H_2	0	$\dfrac{1}{2}X$	$\dfrac{1}{2}X$	$\dfrac{(1/2)XP}{1\ \text{atm}}$
I_2	0	$\dfrac{1}{2}X$	$\dfrac{1}{2}X$	$\dfrac{(1/2)XP}{1\ \text{atm}}$
Σ		$\overline{1}$		

Note: standard state pressure in the *Chemical Engineers Handbook* is 1 atm.

$$\Rightarrow 3.72 \times 10^{-2} = \frac{\left[(1/2)X(P/1\text{ atm})^{1/2}\right]^2}{\left[(1-X)(P/1\text{ atm})\right]} = \frac{X}{2(1-X)} = K_{a,1}$$

or

$$x = \frac{2K_{a,1}}{2K_{a,1}+1} = 0.069248 \quad \text{(independent of pressure!)}$$

Thus at all pressures (low enough that nonideal vapor phase corrections can be ignored) we have

$$y_{H_2} = y_{I_2} = 0.03462 \; ; \; y_{HI} = 0.93075$$

which is the composition of the vapor when the first precipitation of solid I_2 occurs.

Now consider the second reaction:

$$a_{I_2(s)} = 1 \qquad\qquad a_{I_2(g)} = y_{I_2}\left(\frac{P}{1\text{ atm}}\right)$$

$$\Rightarrow K_{a,2} = 2478.3 = \frac{1}{y_{I_2}(P/1\text{ atm})} \Rightarrow P = \frac{1\text{ atm}}{K_{a,2}\,y_{I_2}}$$

$$P = \frac{1\text{ atm}}{0.03462 \times 2478.3} = 0.01166\text{ atm} = 0.01181\text{ bar.}$$

Thus, if $P > 0.01181$ bar precipitation of solid I_2 will occur.

9.26 (a) $2NaHCO_3(s) = NaCO_3(s) + CO_2(g) + H_2O(g)$
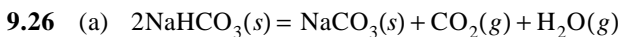
$$K_a = \frac{a_{NaCO_3}a_{CO_2}a_{H_2O}}{a_{NaHCO_3^2}} \text{ but } \left.\begin{array}{l} a_{NaHCO_3} = 1 \\ a_{NaCO_3} = 1 \end{array}\right\}\text{solids}$$

$$\Rightarrow K_a = a_{H_2O}a_{CO_2} = \frac{P_{H_2O}}{1\text{ bar}} \cdot \frac{P_{CO_2}}{1\text{ bar}}$$

but $P_i = y_i P = \dfrac{N_i}{N}P$ where $N =$ total moles in gas phase, $N_i =$ moles of i in gas phase and

$N_{H_2O} = N_{CO_2} \Rightarrow P_{H_2O} = P_{CO_2} = \dfrac{1}{2}P$.

Therefore

$$K_a = \left[\frac{(1/2)P}{1\text{ bar}}\right]^2$$

and

$$K_a(30°C) = \left[\frac{(1/2)\times 0.826\text{ kPa}}{100\text{ kPa}}\right]^2 = 1.706 \times 10^{-5}$$

$$K_a(110°C) = \left[\frac{(1/2)\times 166.97\text{ kPa}}{100\text{ kPa}}\right]^2 = 0.697$$

$$\ln K_a(30°C) = -10.979; \; \ln K_a(110°C) = -0.3610$$

Now

$$\ln \frac{K_a(T_2)}{K_a(T_1)} = \ln K_a(T_2) - \ln K_a(T_1) = -\frac{\Delta H_{rxn}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$ (1)

This assumes that ΔH_{rxn} is independent of T, the only assumption we can make with the limited data in the problem statement

$$\Rightarrow \Delta H_{rxn} = 128.2 \text{ kJ}$$

(b) Going back to Eqn. (1) above we have

$$K_a(T) = K_a(T = 30^\circ C)\exp\left(-\frac{\Delta H_{rxn}}{R}\left(\frac{1}{T} - \frac{1}{303.15}\right)\right) = 1.706 \times 10^{-5} \exp\left(-15420\left(\frac{1}{T} - \frac{1}{303.15}\right)\right)$$

$$\ln K_a = -10.9788 - \frac{15420}{T} + 50.8659 = 39.8871 - \frac{15420}{T}$$

(c) $P_{CO_2} = 1.0 \text{ bar} \Rightarrow P_{H_2O} = 1.0 \text{ bar}$ $P = 2.0 \text{ bar}$

$$\Rightarrow K_a(T) = \left[\frac{(1/2)\times 2.0}{1}\right]^2 = 1$$

$$\Rightarrow T = 386.6 \text{ K} = 113.45^\circ C \text{ for } P_{CO_2} = 1 \text{ bar}.$$

9.27 Reaction $C + 2H_2 = CH_4$

Using the program CHEMEQ we have $K_a(T = 1000 \text{ K}) = 0.09838$

Species	Initial (gas)	Final (gas)	y_i
C			
H_2	1	$1-2X$	$\dfrac{1-2X}{1-X}$
CH_4	0	X	$\dfrac{X}{1-X}$
Σ		$1-X$	

$$K_a = \frac{a_{CH_4}}{a_C a_{H_2}^2} = \frac{a_{CH_4}}{a_{H_2}^2} = \frac{XP}{(1-X)1\text{ bar}} \cdot \frac{(1-X)^2}{(1-2X)^2}\left(\frac{1\text{ bar}}{P}\right)^2$$

$$0.1004 = \frac{X(1-X)}{(1-2X)^2}\frac{1\text{ bar}}{P} = \frac{X(1-X)}{(1-2X)^2}$$

The solutions to this equation are $X = 0.0769$ and $X = 0.9231$.

With such a small value of the equilibrium constant, the $X = 0.0769$ solution is the correct one.

This implies $y_{H_2} = 0.917$ and $y_{CH_4} = 0.083$

This is (probably within experimental and calculational error) essentially the same as the equilibrium composition. Therefore, the reaction process is thermodynamically limited, not mass transfer limited. Consequently increasing the equilibration time by slowing the hydrogen flow will have no effect on the process.

9.28 (also available as a Mathcad worksheet)
Reactions

$$C + H_2O = CO + H_2$$
$$C + 2H_2O = CO_2 + 2H_2$$
$$CO_2 + C = 2CO$$
$$CO + H_2O = CO_2 + H_2$$
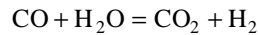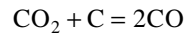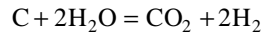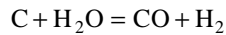
For simplicity, let's write reactions 1, 2 and 4 in reverse

$$CO + H_2 = C + H_2O$$
$$CO_2 + 2H_2 = C + 2H_2O$$
$$CO_2 + C = 2CO$$
$$CO_2 + H_2 = CO + H_2O$$
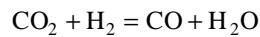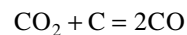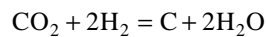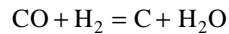
Now need to identify the independent chemical reactions.
Start by writing

$$
\begin{array}{ll}
C + O = CO & \text{Eliminate} \\
2H + O = H_2O & \text{reaction 4} \\
C + 2O = CO_2 & \text{since no} \\
2H = H_2 & \text{H present}
\end{array}
\Rightarrow
\begin{array}{l}
C + O = CO \\
H_2 + O = H_2O \\
C + 2O = CO_2
\end{array}
$$
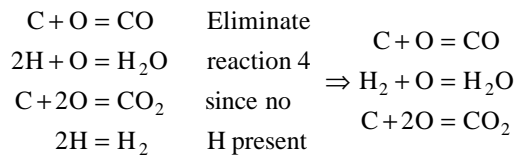
Now use $O = \dfrac{1}{2}CO_2 - \dfrac{1}{2}C$ to eliminate O since no atomic oxygen present.

$$C + \frac{1}{2}CO_2 = \frac{1}{2}C + CO$$
$$H_2 + \frac{1}{2}CO_2 = \frac{1}{2}C + H_2O$$

or

$$
\left.
\begin{array}{l}
C + CO_2 = 2CO \\
2H_2 + CO_2 = C + 2H_2O
\end{array}
\right\}
\begin{array}{l}
\text{This is one set of} \\
\text{independent reactions.}
\end{array}
$$

Add these two

$$2H_2 + C + 2CO_2 = 2CO + C + 2H_2O \Rightarrow H_2 + CO_2 = CO + H_2O$$

We will use

$$
\left.
\begin{array}{l}
H_2 + CO_2 = CO + H_2O \\
2H_2 + CO_2 = C + 2H_2O
\end{array}
\right\}
\begin{array}{l}
\text{as the} \\
\text{independent reactions.}
\end{array}
$$
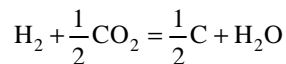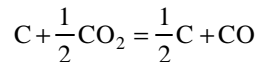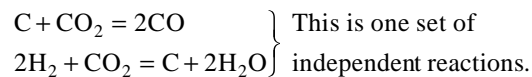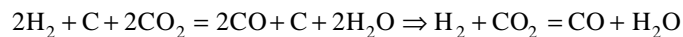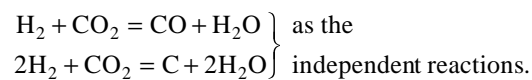
Species	Initial	Final	y_i	a_i
CO_2	1	$1 - X_1 - X_2$	$\dfrac{1 - X_1 - X_2}{\Sigma}$	$\left[\dfrac{1 - X_1 - X_2}{\Sigma}\right]\dfrac{P}{1\,\text{bar}}$
H_2	1	$1 - X_1 - 2X_2$	$\dfrac{1 - X_1 - 2X_2}{\Sigma}$	$\left[\dfrac{1 - X_1 - 2X_2}{\Sigma}\right]\dfrac{P}{1\,\text{bar}}$
CO	0	X_1	$\dfrac{X_1}{\Sigma}$	$\left[\dfrac{X_1}{\Sigma}\right]\dfrac{P}{1\,\text{bar}}$
H_2O	0	$X_1 + 2X_2$	$\dfrac{X_1 + 2X_2}{\Sigma}$	$\left[\dfrac{X_1 + 2X_2}{\Sigma}\right]\dfrac{P}{1\,\text{bar}}$
C	0	(X_2)	0	0

(not in gas phase)

$$\Sigma = 2 - X_2$$

$$K_{a,1} = \frac{a_{CO}a_{H_2O}}{a_{CO_2}a_{H_2}} = \frac{X_1(X_1 + 2X_2)}{(1 - X_1 - X_2)(1 - X_1 - 2X_2)}$$

$$K_{a,2} = \frac{(a_C = 1)a_{H_2O}^2}{a_{H_2}^2 a_{CO_2}} = \frac{(X_1 + 2X_2)^2(2 - X_2)}{(1 - X_1 - 2X_2)^2(1 - X_1 - X_2)}\frac{1\,\text{bar}}{P}$$

Using the program CHEMEQ, I find the following

$T(\text{K})$	$K_{a,1}$	$K_{a,2}$
600	0.3665×10^{-1}	758.6
700	0.1110	48.43
800	0.2493	5.950
900	0.4596	1.137
1000	0.7387	0.2974

(a) No carbon deposits $X_2 = 0$

$$K_{a,1} = \frac{X_1^2}{(1 - X_1)^2} \quad \text{and} \quad K_{a,2} = \frac{X_1^2 \cdot 2}{(1 - X_1)^3}\frac{1\,\text{bar}}{P}$$

Solving these equations, I find

$T(\text{K})$	600	700	800	900	1000
$P(\text{bar})$	1.151×10^{-4}	6.111×10^{-3}	0.126	1.357	9.237

If the pressure for a given temperature is above the pressure calculated, carbon will deposit.

(b)   Exactly 30% of carbon is deposited $X_2 = 0.3$

$$K_{a,1} = \frac{X_1(X_1 + 0.6)}{(0.7 - X_1)(0.4 - X_1)} \text{ and } K_{a,2} = \frac{(x_1 + 0.6)^2(1.7)}{(0.7 - X_1)(0.4 - X_1)^2} \frac{1 \text{ bar}}{P}$$

T(K)	600	700	800	900	1000
X_1	0.0157	0.0410	0.0750	0.1104	0.1427
P(bar)	0.0084	0.170	1.972	15.266	85.419

9.29   The reaction the engineer is concerned about is
$Ti(s) + SiO_2(s) = TiO_2(s) + Si(s)$
This is equivalent to the first reaction in the problem statement minus the second reaction. Therefore
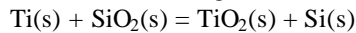
$$\Delta \underline{G}^o_{rxn} = -674 - (-644)\frac{kJ}{mol} = -30\frac{kJ}{mol} = -30,000\frac{J}{mol}$$

and the equilibrium constant for this reaction is

$$K_a = \exp\left(-\frac{\Delta \underline{G}^o_{rxn}}{R \cdot T}\right) = \exp\left(\frac{30000}{8.314 \cdot 1273}\right) = 17.02$$

Consequently, as the engineer fears, the titanium purity will be effected by high temperature contact with silicon dioxide.

9.30   From Eqns. (9.1-8 and 9.9-6) we have that
$$nFE^o = RT \ln K_a = -\Delta G^o_{rxn}$$

Consequently, by measuring the zero-current cell potential we obtain the standard state Gibbs free energy change on reaction (if all the ions are in their standard states). Now if we continue further and measure how the zero-current standard state cell potential varies as a function of temperature, we have

$$nF\left(\frac{\partial E^o}{\partial T}\right)_P = -\left(\frac{\partial \Delta G^o_{rxn}}{\partial T}\right)_P \equiv \Delta S^o_{rxn}$$

Consequently by knowing the zero-current, standard state cell potential

and its temperature derivative we can calculate ΔH^o_{rxn} from

$$\Delta G^o_{rxn} = \Delta H^o_{rxn} - T\Delta S^o_{rxn} \text{ or } \Delta H^o_{rxn} = \Delta G^o_{rxn} + T\Delta S^o_{rxn}$$

Similarly starting from $nFE = -\Delta G_{rxn}$ and the measured zero-current potentials, we can calculate the enthalpy and entropy changes for the reaction when the ions are not in their standard states.

9.31   The chemical reaction is
$CH_3\text{-}CHOH\text{-}CH_3 = CH_3\text{-}CO\text{-}CH_3 + H_2$
Assuming we start with pure acetone, the mass balance table with all species as vapors (given the high temperature and low pressure) is
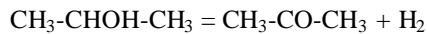
Species	in	out	y	a
i-prop	1	1-X	(1-X)/(1+X)	(1-X)×95.9/(1+X))×100
acetone	0	X	X/(1+X)	X×95.9/(1+X))×100
hydrogen	0	X	X/(1+X)	X×95.9/(1+X))×100
Σ		1+X		

But $X = .564$, so $a_{i\text{-}P} = 0.2673$, and $a_{ace} = a_H = 0.3458$. Therefore

$$K_a = \frac{a_{ace}a_H}{a_{i\text{-}P}} = \frac{0.3458 \times 0.3458}{0.2673} = 0.4474 = \exp\left(-\frac{\Delta \underline{G}^o_{rxn}}{RT}\right)$$

$$-0.8043 = -\frac{\Delta \underline{G}^o_{rxn}}{RT}; \quad \text{so } \Delta \underline{G}^o_{rxn} = 8.314 \times 452.2 \times 0.8043 = 3023.8 \frac{J}{mol}$$

9.32   The reactions are
         $C_6H_6 + H_2 = 1,3\text{-cyclohexadiene}$
         $C_6H_6 + 2H_2 = \text{cyclohexene}$
         $C_6H_6 + 3H_2 = \text{cyclohexane}$

The Gibbs free energy of formation data needed to solve this problem

$$\Delta \underline{G}^o_f(\text{benzene}) = 124.5 \ \frac{kJ}{mol} \qquad \Delta \underline{G}^o_f(\text{cyclohexene}) = 106.9 \ \frac{kJ}{mol}$$

$$\Delta \underline{G}^o_f(\text{cyclohexane}) = 26.9 \ \frac{kJ}{mol} \quad \Delta \underline{G}^o_f(1,3-\text{cyclohexdiene}) = 178.97 \ \frac{kJ}{mol}$$

The Gibbs free energy of formation for 1,3-cyclohexadiene is not available in Appendix IV, Perry's The Chemical Engineer's Handbook or the Handbook of Chemistry and Physics. The value was found using data on the WWW site http://webbook.nist.gov/chemistry. This Web site contains the National Institute of Standards and Technology (NIST) chemistry data book. The values found on this Web site are

$$\Delta \underline{H}^o_f(1,3-\text{cyclohexdiene, 298.15 K}) = 71.41 \ \frac{kJ}{mol}$$

$$\underline{S}(1,3-\text{cyclohexdiene, 298.15 K}) = 197.3 \ \frac{J}{mol \cdot K}$$

$$\underline{S}(C, \text{graphite, 298.15 K}) = 5.88 \ \frac{J}{mol \cdot K}$$

$$\underline{S}(H_2, \text{298.15 K}) = 130.68 \ \frac{J}{mol \cdot K}$$

Note that these entropies are with respect to the entropy equal to zero for the pure component and 0 K. Also, the entropy change of reaction at 0 K is zero for all reactions. Therefore

$$\Delta \underline{S}^o_f(1,3-\text{cyclohexdiene, 298.15 K}) =$$
$$\underline{S}(1,3-\text{cyclohexdiene, 298.15 K}) - 6 \cdot \underline{S}(C, \text{298.15 K}) - 4 \cdot \underline{S}(H_2, \text{298.15 K})$$
$$= 197.3 - 6 \cdot 5.88 - 4 \cdot 130.68 = -360.75 \frac{J}{mol \cdot K}$$
$$\Delta \underline{G}^o_f(1,3-\text{cyclohexdiene, 298.15 K}) = \Delta \underline{H}^o_f - T\Delta \underline{S}^o_f = 71410 - 298.15 \cdot (-360.75)$$
$$= 178967 \frac{J}{mol} = 178.97 \frac{kJ}{mol}$$

The mass balance table assuming all the organics are present only in the liquid phase, and that the hydrogen is present in great excess to keep its partial pressure fixed at 1 bar. Also, since all the organics are so similar, we will

assume they form an ideal liquid mixture, and that there is no hydrogen in the liquid phase. Mass balance table for liquid phase:

Species	In	Out	x	activity
Benzene	1	$1-X_1-X_2-X_3$	$1-X_1-X_2-X_3$	$1-X_1-X_2-X_3$
1,3-cyclohex	0	X_1	X_1	X_1
cyclohexene	0	X_2	X_2	X_2
cyclohexane	0	X_3	X_3	X_3
Total		1		

The equilibrium relations are

$$K_{a,1} = \frac{a_{1,3-\text{cyc}}}{a_{\text{benz}} a_{H_2}} = \frac{X_1}{1-X_1-X_2-X_3} = \exp\left(-\frac{(178970-124500)}{8.314 \times 298.15}\right)$$

$$= \exp(-21.973) = 2.866 \times 10^{-10}$$

$$K_{a,2} = \frac{a_{\text{cychene}}}{a_{\text{benz}} a_{H_2}^2} = \frac{X_2}{1-X_1-X_2-X_3} = \exp\left(-\frac{(106900-124500)}{8.314 \times 298.15}\right)$$

$$= \exp(7.1002) = 1212.2$$

$$K_{a,3} = \frac{a_{\text{cychane}}}{a_{\text{benz}} a_{H_2}^3} = \frac{X_3}{1-X_1-X_2-X_3} = \exp\left(-\frac{(26900-124500)}{8.314 \times 298.15}\right)$$

$$= \exp(39.374) = 1.2587 \times 10^{17}$$

By examining the values of the equilibrium constants, or more directly by taking ratios of these equations, we see that X_3 is about equal to unity. Then by taking the ratio of the first of these equations to the third, we have

$$\frac{X_1}{X_3} = \frac{2.866 \times 10^{-10}}{1.2587 \times 10^{17}} = 2.27 \times 10^{-27} \approx X_1$$

and by taking the ratio of the second of these equations to the third

$$\frac{X_2}{X_3} = \frac{1212.2}{1.2587 \times 10^{17}} = 9.63 \times 10^{-15} \approx X_2$$

This suggests that $X_3 \sim 1$, X_2 is of the order or 10^{-17}, and X_1 is of order 10^{-27}. Thus the benzene will react to form essentially all cyclohexane.

9.33   The process is
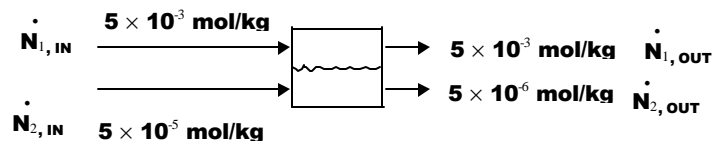
Assume all other component concentrations are unchanged since the glucose concentration is so low. The mass balance is

$$\dot{N}_{1,in} + \dot{N}_{2,in} = \dot{N}_{1,out} + \dot{N}_{2,out}$$

If $\dot{\boldsymbol{d}}$ is the rate of glucose transported, then

$$\left(\dot{N}_G\right)_{1,out} = \left(\dot{N}_G\right)_{1,in} + \dot{\boldsymbol{d}}$$

$$\left(\dot{N}_G\right)_{2,out} = \left(\dot{N}_G\right)_{2,in} - \dot{\boldsymbol{d}}$$

The energy balance is

$$0 = \left(\sum \dot{N}_i \overline{H}_i\right)_{1,in} + \left(\sum \dot{N}_i \overline{H}_i\right)_{2,in} - \left(\sum \dot{N}_i \overline{H}_i\right)_{1,out} - \left(\sum \dot{N}_i \overline{H}_i\right)_{2,out} + \dot{Q} + \dot{W}$$

and the entropy balance is

$$0 = \left(\sum \dot{N}_i \overline{S}_i\right)_{1,in} + \left(\sum \dot{N}_i \overline{S}_i\right)_{2,in} - \left(\sum \dot{N}_i \overline{S}_i\right)_{1,out} - \left(\sum \dot{N}_i \overline{S}_i\right)_{2,out} + \frac{\dot{Q}}{T} + \dot{S}_{gen}$$

The kidney operates reversibly, and minimum work implies $\dot{S}_{gen} = 0$.

Subtracting T times the entropy balance form the energy balance gives

$$0 = \left(\sum \dot{N}_i \overline{G}_i\right)_{1,in} + \left(\sum \dot{N}_i \overline{G}_i\right)_{2,in} - \left(\sum \dot{N}_i \overline{G}_i\right)_{1,out} - \left(\sum \dot{N}_i \overline{G}_i\right)_{2,out} + \dot{W}$$

or

$$\dot{W} = \left(\sum \dot{N}_i \overline{G}_i\right)_{1,out} + \left(\sum \dot{N}_i \overline{G}_i\right)_{2,out} - \left(\sum \dot{N}_i \overline{G}_i\right)_{1,in} - \left(\sum \dot{N}_i \overline{G}_i\right)_{2,in}$$

$$= \left(\dot{N}_G \overline{G}_G\right)_{1,out} + \left(\dot{N}_G \overline{G}_G\right)_{2,out} - \left(\dot{N}_G \overline{G}_G\right)_{1,in} - \left(\dot{N}_G \overline{G}_G\right)_{2,in}$$

$$= \left(\left(\dot{N}_G\right)_{1,in} + \dot{\boldsymbol{d}}\right)\left(\overline{G}_G\right)_{1,out} + \left(\left(\dot{N}_G\right)_{2,in} - \dot{\boldsymbol{d}}\right)\left(\overline{G}_G\right)_{2,out} - \left(\dot{N}_G \overline{G}_G\right)_{1,in} - \left(\dot{N}_G \overline{G}_G\right)_{2,in}$$

Now since the concentrations are very low, and have not changed significantly,

$$\left(\overline{G}_G\right)_{1,in} = \left(\overline{G}_G\right)_{1,out} \quad \text{and} \quad \left(\overline{G}_G\right)_{2,in} = \left(\overline{G}_G\right)_{2,out}$$

Therefore

$$\dot{W} = \dot{\boldsymbol{d}}\left[\left(\overline{G}_G\right)_1 - \left(\overline{G}_G\right)_2\right]$$

(since, from the previous equation, we can eliminate the subscripts in and out). Then

$$\frac{\dot{W}}{\dot{\boldsymbol{d}}} = \left[\left(\overline{G}_G\right)_1 - \left(\overline{G}_G\right)_2\right] = RT \ln\left(\frac{\left(\overline{f}_G\right)_1}{\left(\overline{f}_G\right)_2}\right)$$

Now assuming ideal solutions (or that the activity coefficients of glucose in blood and urine are the same)

$$\frac{\dot{W}}{\dot{\boldsymbol{d}}} = RT \ln\left(\frac{\left(\overline{f}_G\right)_1}{\left(\overline{f}_G\right)_2}\right) = RT \ln\left(\frac{\left(x_G\right)_1}{\left(x_G\right)_2}\right) = RT \ln\left(\frac{\left(C_G\right)_1}{\left(C_G\right)_2}\right)$$

where we have assume that both blood and urine, being mostly water, have about the same molar concentration. Therefore

$$\frac{\dot{W}}{\dot{\boldsymbol{d}}} = RT \ln\left(\frac{\left(C_G\right)_1}{\left(C_G\right)_2}\right) = RT \ln\left(\frac{5 \times 10^{-3}}{5 \times 10^{-5}}\right) = RT \ln(100)$$

$$= 8.314 \frac{J}{mol\ K} \times 310.1\ K \times \ln(100) = 11873 \frac{J}{mol} = 11.873 \frac{kJ}{mol}$$

Note that body temperature is $98.6^\circ F = 310.1\ K$

9.34 (also available as a Mathcad worksheet).

9.34

Given:

$$T := 298.15 \cdot K \qquad M_1 := 0.0001 \cdot \frac{mole}{liter} \qquad M_2 := 0.01 \cdot \frac{mole}{liter}$$

$$\alpha := 1.178 \cdot \left(\frac{mole}{liter}\right)^{-\frac{1}{2}} \qquad R := 8.31451 \cdot \frac{joule}{K \cdot mole}$$

Using eqn 9.9-10 and the Debye-Huckel limiting law of eqn 7.11-15:

$$\ln(\gamma) = -\alpha \cdot 4 \cdot \sqrt{4 \cdot M_{CuSO4}}$$

$$\gamma\left(M_{CuSO4}\right) := \exp\left(-\alpha \cdot 8 \cdot \sqrt{M_{CuSO4}}\right)$$

$$\Delta G_{2moles} := 2 \cdot R \cdot T \cdot \ln\left(\frac{M_1}{M_2}\right) + 2 \cdot R \cdot T \cdot \ln\left(\frac{\gamma\left(M_1\right)}{\gamma\left(M_2\right)}\right)$$

The change is Gibb's Free Energy calculated above is for two moles of electrons (n=2). The number of moles of electrons in this problem is calculated below:

$$n := 2 \cdot \left(\frac{0.01 \cdot mole - 0.0001 \cdot mole}{2}\right) \qquad n = 9.9 \cdot 10^{-3} \quad \cdot mole$$

$$\Delta G := \left(\frac{n}{2}\right) \cdot \Delta G_{2moles}$$

$$Wmax := \Delta G \qquad \text{(for a process at constant temperature and pressure)}$$

$$Wmax = {}^{-}92.204 \quad \cdot joule$$

9.35 (also available as a Mathcad worksheet).
From the Steam Tables $\qquad P^{vap} = 12.349$ kPa
From CHEMEQ $\qquad K_a = 171.2$
H_{NH3} (from problem statement) = 384.5 kPa/mole fraction

The solution at various pressures is

P (kPa)	X	f
0.10	0.0899	0
0.25	0.2017	0
0.50	0.3467	0
1.00	0.5478	0
2.00	0.7868	0
4.00	1.0322	0
6.00	1.1670	0
8.00	1.2559	0
10.00	1.3204	0
12.00	1.3701	0
14.00	1.4099	0
16.00	1.4429	0
18.00	1.4707	0
18.40	1.4757	2.02×10^{-05}
18.50	1.4797	0.0114
19.00	1.4996	0.0680
20.00	1.5339	0.1589
25.00	1.6437	0.3989
30.00	1.7063	0.5068
35.00	1.7488	0.5713
40.00	1.7806	0.6162
50.00	1.8267	0.6792
60.00	1.8602	0.7261
70.00	1.8869	0.7661
80.00	1.9093	0.8030
90.00	1.9291	0.8388
100.00	1.9472	0.8745
104.50	1.9449	0.8908

9.36 (also available as a Mathcad worksheet).

9.36

Rxn: C8H18 + 25/2*O2 = 9*H2O + 8*CO2
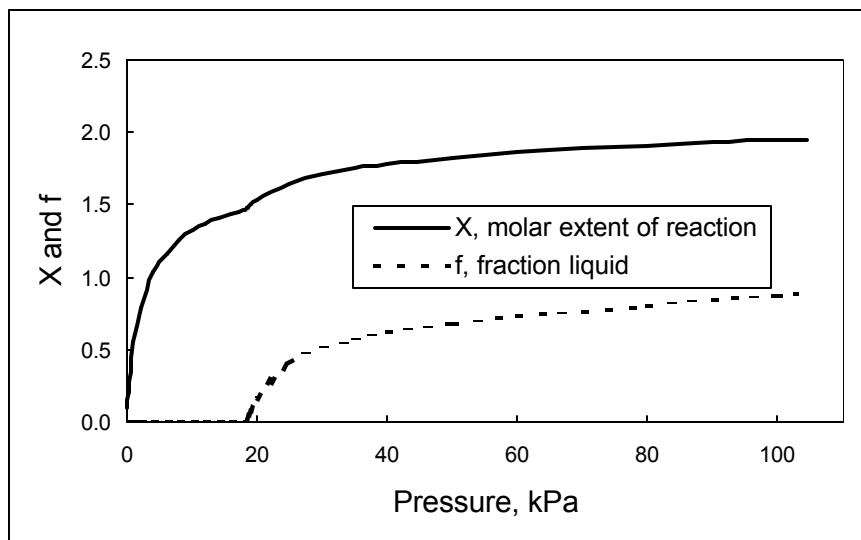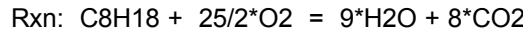
Given:

$$\Delta Hf_{N2} := 0 \cdot \frac{joule}{mole} \qquad \Delta Hf_{O2} := 0 \cdot \frac{joule}{mole} \qquad \Delta Hf_{C8H18} := -255100 \cdot \frac{joule}{mole}$$

$$\Delta Hf_{CO2} := -393500 \cdot \frac{joule}{mole} \qquad \Delta Hf_{H2O} := -285800 \cdot \frac{joule}{mole}$$

$$Cp_{CO2}(T) := 22.243 \cdot \left(\frac{joule}{mole \cdot K}\right) + 5.977 \cdot 10^{-2} \cdot T \cdot \left(\frac{joule}{mole \cdot K^2}\right) - 3.499 \cdot 10^{-5} \cdot T^2 \cdot \left(\frac{joule}{mole \cdot K^3}\right) + 7.464 \cdot 10^{-9} \cdot T^3 \cdot \left(\frac{joule}{mole \cdot K^4}\right)$$

$$Cp_{N2}(T) := 28.883 \cdot \left(\frac{joule}{mole \cdot K}\right) - 0.157 \cdot 10^{-2} \cdot T \cdot \left(\frac{joule}{mole \cdot K^2}\right) + 0.808 \cdot 10^{-5} \cdot T^2 \cdot \left(\frac{joule}{mole \cdot K^3}\right) - 2.871 \cdot 10^{-9} \cdot T^3 \cdot \left(\frac{joule}{mole \cdot K^4}\right)$$

$$Cp_{H2O}(T) := 32.218 \cdot \left(\frac{joule}{mole \cdot K}\right) + 0.192 \cdot 10^{-2} \cdot T \cdot \left(\frac{joule}{mole \cdot K^2}\right) + 1.055 \cdot 10^{-5} \cdot T^2 \cdot \left(\frac{joule}{mole \cdot K^3}\right) - 3.593 \cdot 10^{-9} \cdot T^3 \cdot \left(\frac{joule}{mole \cdot K^4}\right)$$

Mass Balance Table:

Species	In	Out
C8H18	1	0
O2	25/2	0
N2	(25/2)*(0.71/0.21) = 42.26	42.26
CO2	0	8
H2O	0	9
Total	55.76	59.26

$$Nin_{C8H18} := 1 \cdot mole \qquad Nin_{O2} := \frac{25}{2} \cdot mole \qquad N_{N2} := 42.26 \cdot mole$$

$$Nout_{CO2} := 8 \cdot mole \qquad Nout_{H2O} := 9 \cdot mole$$

Energy Balance at Steady State:

$$0 = \sum_{i=1}^{k} N_i \cdot H_i + Q - \int PdV + W \qquad \text{(where Hi is the partial molar enthalpy of species i)}$$

Assuming no heat flow, no change in volume of the engine, and an ideal gas mixture yields:

$$W = \sum_{i=1}^{k} N_i \cdot H_i \qquad \text{(where is Hi is the molar enthalpy of species i)}$$

At 150 C:

$$H_{N2} := \Delta Hf_{N2} + \int_{298.15\cdot K}^{423.15\cdot K} Cp_{N2}(T)\,dT$$

$$H_{H2O} := \Delta Hf_{H2O} + \int_{298.15\cdot K}^{423.15\cdot K} Cp_{H2O}(T)\,dT$$

$$H_{CO2} := \Delta Hf_{CO2} + \int_{298.15\cdot K}^{423.15\cdot K} Cp_{CO2}(T)\,dT$$

$$W := Nout_{CO2}\cdot H_{CO2} + Nout_{H2O}\cdot H_{H2O} + N_{N2}\cdot \left(H_{N2} - \Delta Hf_{N2}\right) - Nin_{C8H18}\cdot \Delta Hf_{C8H18} - Nin_{O2}\cdot \Delta Hf_{O2}$$

$$W = -5.233 \bullet 10^6 \ \cdot joule$$

This work obtained is per mole of n-octane.

9.37 (also available as a Mathcad worksheet).

9.37

Given:

$$T1 := 298.15\cdot K \qquad P1 := 10^5 \cdot Pa \qquad T2 := 650\cdot K \qquad P2 := 10^6\cdot Pa \qquad R := 8.31451\cdot \frac{joule}{K\cdot mole}$$

$$\Delta G_{C3H8} := -24300\cdot \frac{joule}{mole} \qquad \Delta G_{CH4} := -50500\cdot \frac{joule}{mole} \qquad \Delta G_{C2H4} := 68500\cdot \frac{joule}{mole}$$

(at 298.15 K)

$$\Delta H_{C3H8} := -104700\cdot \frac{joule}{mole} \qquad \Delta H_{CH4} := -74500\cdot \frac{joule}{mole} \qquad \Delta H_{C2H4} := 52500\cdot \frac{joule}{mole}$$

Mass Balance Table:

Species	In	Out	y
C3H8	1	1-X	(1-X)/(1+X)
CH4	0	X	X/(1+X)
C2H4	0	X	X/(1+X)

Calculation of mole fractions and activities:

$$yC3H8(X) := \frac{1-X}{1+X} \qquad\qquad yCH4(X) := \frac{X}{1+X} \qquad\qquad yC2H4(X) := \frac{X}{1+X}$$

$$aC3H8(X,P) := yC3H8(X) \cdot \frac{P}{10^5 \cdot Pa} \qquad\qquad aCH4(X,P) := yCH4(X) \cdot \frac{P}{10^5 \cdot Pa}$$

$$aC2H4(X,P) := yC2H4(X) \cdot \frac{P}{10^5 \cdot Pa}$$

$$\Delta G_{rxn} := \Delta G_{C2H4} + \Delta G_{CH4} - \Delta G_{C3H8} \qquad\qquad \Delta G_{rxn} = 4.23 \cdot 10^4 \cdot mole^{-1} \cdot joule$$

$$\Delta H_{rxn} := \Delta H_{C2H4} + \Delta H_{CH4} - \Delta H_{C3H8} \qquad\qquad \Delta H_{rxn} = 8.27 \cdot 10^4 \cdot mole^{-1} \cdot joule$$

$$Ka_{298.15} := \exp\left(-\frac{\Delta G_{rxn}}{R \cdot T1}\right) \qquad\qquad Ka_{298.15} = 3.885 \cdot 10^{-8}$$

Part (a): $X := 10^{-4}$ (initial guess)

Given $Ka_{298.15} = \dfrac{aC2H4(X,P1) \cdot aCH4(X,P1)}{aC3H8(X,P1)}$ $Xa := Find(X)$ $Xa = 1.971 \cdot 10^{-4}$

$yC3H8(Xa) = 1$ $yC2H4(Xa) = 1.971 \cdot 10^{-4}$ $yCH4(Xa) = 1.971 \cdot 10^{-4}$

Part (b):

From equation 9.1-22b:

$$Ka_{650} := Ka_{298.15} \cdot \exp\left[-\frac{\Delta H_{rxn}}{R} \cdot \left(\frac{1}{T2} - \frac{1}{T1}\right)\right] \qquad\qquad Ka_{650} = 2.704$$

$X := .5$ (initial guess)

Given $Ka_{650} = \dfrac{aC2H4(X,P1) \cdot aCH4(X,P1)}{aC3H8(X,P1)}$ $Xb := Find(X)$ $Xb = 0.854$

$yC3H8(Xb) = 0.079$ $yC2H4(Xb) = 0.461$ $yCH4(Xb) = 0.461$

Part (c):

$X := .5$ (initial guess)

Given $Ka_{650} = \dfrac{aC2H4(X, P2) \cdot aCH4(X, P2)}{aC3H8(X, P2)}$ $Xc := Find(X)$ $Xc = 0.461$

$yC3H8(Xc) = 0.369$ $yC2H4(Xc) = 0.316$ $yCH4(Xc) = 0.316$

9.38   (also available as a Mathcad worksheet).

9.38

$R := 8.31451 \cdot \dfrac{joule}{K \cdot mole}$ $G_{rxn} := -2400 \cdot \dfrac{joule}{mole}$ $T := 298.15 \cdot K$ $V := 4 \cdot liter$

$a_A(x_A, \gamma_A) := x_A \cdot \gamma_A$ $a_B := 1$

$a_C(x_A, \gamma_C) := (1 - x_A) \cdot \gamma_C$ $a_D(P) := \dfrac{P}{10^5 \cdot Pa}$

$Ka := \exp\left(-\dfrac{G_{rxn}}{R \cdot T}\right)$ $Ka = 2.633$

Part (a):

$x_A := 0.5$ (initial guess)

Given $Ka = \dfrac{a_D(0.5 \cdot 10^5 \cdot Pa) \cdot a_C(x_A, 1)}{a_B \cdot a_A(x_A, 1)}$ $x_A := Find(x_A)$

$x_C := 1 - x_A$

$x_A = 0.16$ $x_C = 0.84$

Part (b):

Recognizing that the partial molar Gibb's excess is in the form of the one constant Margules expression yields:

$\gamma_A = \exp\left(0.3 \cdot x_C^2\right)$ $\gamma_C = \exp\left(0.3 \cdot x_A^2\right)$

Given
$$Ka = \frac{a_D \left(0.5 \cdot 10^5 \cdot Pa\right) \cdot a_C \left(x_A, \exp\left(0.3 \cdot x_A^2\right)\right)}{a_B \cdot a_A \left[x_A, \exp\left[0.3 \cdot \left(1 - x_A\right)^2\right]\right]}$$
$x_A := Find\left(x_A\right)$

$x_C := 1 - x_A$

$x_A = 0.132$ $x_C = 0.868$

Part (c):

Mass Balance Table:

Species	In	Out
A	1	1-X
B	2	2-X
C	0	X
D	0	X

Assuming that D is an ideal gas:

$$P = (n \cdot R \cdot T)/V \qquad P(X) := \frac{X \cdot R \cdot T}{V}$$

$X := 0.5$ (initial guess)

Given
$$Ka = \frac{a_D \left(\dfrac{X \cdot R \cdot T \cdot mole}{V}\right) \cdot a_C(X, 1)}{a_B \cdot a_A (1 - X, 1)}$$
$X := Find(X)$

$X = 0.425$

$N_A := 1 - X$ $N_B := 2 - X$ $N_C := X$ $N_D := X$

$x_A := 1 - X$ $x_C := X$ $P_D := \dfrac{X \cdot R \cdot T \cdot mole}{V}$

$N_A = 0.575$ $N_B = 1.575$ $N_C = 0.425$ $N_D = 0.425$

$x_A = 0.575$ $x_C = 0.425$ $P_D = 2.633 \cdot 10^5 \cdot Pa$

9.39   (also available as a Mathcad worksheet).

9.39

Without dissociation:

$$Amount\_Adsorbed\_Without = K1 \cdot a_{H2}$$

Assuming the activity of molecular hydrogen gas is equal to the pressure of hydrogen g

$$Amount\_Adsorbed\_Without = K1 \cdot P_{H2}$$

With dissociation:

$$Amount\_Adsorbed\_With = K1 \cdot a_{H2} + \frac{1}{2} \cdot K3 \cdot a_H$$

Using the equilibrium constant for the reaction H2 = 2H, the activity of atomic hydrogen solved for in terms of the activity of molecular hydrogen:

Given $$K2 = \frac{a_H^2}{a_{H2}}$$ $$Find(a_H) \rightarrow$$

Using the positive root for the activity of hydrogen yields:

$$Amount\_Adsorbed\_With = K1 \cdot a_{H2} + \frac{1}{2} \cdot K3 \cdot \sqrt{K2} \cdot \sqrt{a_{H2}}$$

Assuming the activity of molecular hydrogen gas is equal to the pressure of hydrogen g

$$Amount\_Adsorbed\_With = K1 \cdot P_{H2} + \frac{1}{2} \cdot K3 \cdot \sqrt{K2} \cdot \sqrt{P_{H2}}$$

If the amount adsorbed varies linearly with the partial pressure of molecular hydrogen then no dissociation is occurring. If the amount adsorbed varies as the square root of the partial pressure, then dissociation is occurring.

9.40   (also available as a Mathcad worksheet).

9.40

Since this is a combustion reaction, the reaction can be assumed to go to completio

Rxn:

$$C4H10 + \frac{13}{2} \cdot O2 + \frac{0.79}{0.21} \cdot \frac{13}{2} \cdot N2 = 4 \cdot CO2 + 5 \cdot H2O + \frac{0.79}{0.21} \cdot \frac{13}{2} \cdot N2$$
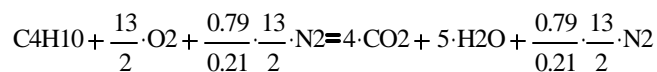
Given:

$$\Delta Gf_{C4H10} := -16600 \cdot \frac{joule}{mole}$$

(The values for the Gibbs free energy of formation are given at one bar. The difference in Gibbs free energy between one bar and one atmosphere will be ignored because it is insignificant in this calculation.)

$$\Delta Gf_{O2} := 0 \cdot \frac{joule}{mole} \qquad \Delta Gf_{CO2} := -394400 \cdot \frac{joule}{mole} \qquad T := 298.15 \cdot K$$

$$\Delta Gf_{N2} := 0 \cdot \frac{joule}{mole} \qquad \Delta Gf_{H2O} := -237100 \cdot \frac{joule}{mole} \qquad R := 8.31451 \cdot \frac{joule}{K \cdot mole}$$

$$MW_{C4H10} := 4 \cdot 12.001 \cdot \frac{gm}{mole} + 10 \cdot 1.0079 \cdot \frac{gm}{mole}$$

$$N_I := 1 + \frac{13}{2} + \frac{0.71}{0.21} \cdot \frac{13}{2} \qquad\qquad N_F := 4 + 5 + \frac{0.71}{0.21} \cdot \frac{13}{2} \qquad\qquad \text{(Total number of moles)}$$

$$G_I := \Delta Gf_{C4H10} + \frac{13}{2} \cdot \Delta Gf_{O2} + \frac{0.79}{0.21} \cdot \frac{13}{2} \cdot \Delta Gf_{N2} + R \cdot T \cdot \left(\ln\left(\frac{1}{N_I}\right) + \frac{13}{2} \cdot \ln\left(\frac{\frac{13}{2}}{N_I}\right) + \frac{0.79}{0.21} \cdot \frac{13}{2} \cdot \ln\left(\frac{\frac{0.79}{0.21} \cdot \frac{13}{2}}{N_I}\right) \right)$$

$$G_F := 4 \cdot \Delta Gf_{CO2} + 5 \cdot \Delta Gf_{H2O} + \frac{0.79}{0.21} \cdot \frac{13}{2} \cdot \Delta Gf_{N2} + R \cdot T \cdot \left(4 \cdot \ln\left(\frac{4}{N_F}\right) + 5 \cdot \ln\left(\frac{5}{N_F}\right) + \frac{0.79}{0.21} \cdot \frac{13}{2} \cdot \ln\left(\frac{\frac{0.79}{0.21} \cdot \frac{13}{2}}{N_F}\right) \right)$$

$$G_I = -6.067 \cdot 10^4 \quad \cdot mole^{-1} \cdot joule$$

$$G_F = -2.82 \cdot 10^6 \quad \cdot mole^{-1} \cdot joule \qquad\qquad N_{C4H10} := \frac{20000 \cdot gm}{MW_{C4H10}}$$

From eqn 9.8-5: $\qquad W_{molar} := \left(G_F - G_I\right) - R \cdot T \cdot \left(N_F - N_I\right)$

$$W := N_{C4H10} \cdot W_{molar} \qquad W = -9.515 \cdot 10^8 \quad \cdot joule$$

9.41 (also available as a Mathcad worksheet).

9.41

Process #1:   N2(gas) = N2(metal)

$$Ka_1 = \frac{aN2_{metal}}{aN2_{gas}} = \frac{H_{N2} \cdot xN2_{metal}}{P_{N2}}$$

$$xN2_{metal} = \frac{Ka_1 \cdot P_{N2}}{H_{N2}}$$

$$wt\%\,nitrogen = A \cdot P_{N2} \qquad\text{where}\qquad A = \frac{2 \cdot Ka_1}{H_{N2}}$$

Process #2:   N2(gas) = 2*N(metal)

$$Ka_2 = \frac{aN_{metal}^2}{aN2_{gas}} = \frac{\left(H_N \cdot xN_{metal}\right)^2}{P_{N2}}$$

$$xN_{metal} = \frac{\sqrt{Ka_2} \cdot \sqrt{P_{N2}}}{H_N}$$

$$wt\%\,nitrogen = B \cdot \sqrt{P_{N2}} \qquad\text{where}\qquad B = \frac{\sqrt{Ka_2}}{H_N}$$

The empirical expression given in the problem is supported by process #2.

9.42   (also available as a Mathcad worksheet).

9.42
(All Units are SI)

Because this is a combustion reaction, the reaction can be assumed to go to completion. This assumption was verified using CHEMEQ where Ka at all temperatures under 4000 K was found to be greater than 10^10.
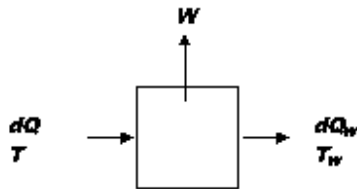
Rxn: CH4 + 2*O2 = CO2 + 2*H2O $R := 8.31451$

$\Delta Hf_{H2O} := -241800$ $\Delta Hf_{CO2} := -393500$ $\Delta Hf_{O2} := 0$ $\Delta Hf_{N2} := 0$ $\Delta Hf_{CH4} := -74500$

$\Delta Gf_{H2O} := -228600$ $\Delta Gf_{CO2} := -394400$ $\Delta Gf_{O2} := 0$ $\Delta Gf_{N2} := 0$ $\Delta Gf_{CH4} := -50500$

Heat capacity:

$$Cp_{CH4}(T) := 19.875 + 5.021 \cdot 10^{-2} \cdot T + 1.268 \cdot 10^{-5} \cdot T^2 - 11.004 \cdot 10^{-9} \cdot T^3$$

$$Cp_{O2}(T) := 28.167 + 0.630 \cdot 10^{-2} \cdot T - 0.075 \cdot 10^{-5} \cdot T^2$$

$$Cp_{N2}(T) := 27.318 + 0.623 \cdot 10^{-2} \cdot T - 0.095 \cdot 10^{-5} \cdot T^2$$

$$Cp_{H2O}(T) := 29.163 + 1.449 \cdot 10^{-2} \cdot T - 0.202 \cdot 10^{-5} \cdot T^2$$

$$Cp_{CO2}(T) := 75.464 - 1.872 \cdot 10^{-4} \cdot T - \frac{661.42}{\sqrt{T}}$$

Defining z as the methane to air ratio:

Mass Balance Table:

Species	In	Out
CH4	9.524*z	(9.524*z)-X
O2	2	2-2*X
N2	7.524	7.524
CO2	0	X
H2O	0	2*X
Total	9.524*(z+1)	9.524*(z+1)

$$\Delta Hrxn_{25} := \Delta Hf_{CO2} + 2 \cdot \Delta Hf_{H2O} - \Delta Hf_{CH4} - 2 \cdot \Delta Hf_{O2} \qquad \Delta Hrxn_{25} = -8.026 \cdot 10^5$$

If z<0.105, then methane is the limiting reactant and X=9.524*z
If z>0.105, then oxygen is the limiting reactant and X=1

$$X(z) := if(z < 0.105, 9.524 \cdot z, 1)$$

$$Cp_{out1}(z, T) := (9.524 \cdot z - X(z)) \cdot Cp_{CH4}(T) + (2 - 2 \cdot X(z)) \cdot Cp_{O2}(T)$$

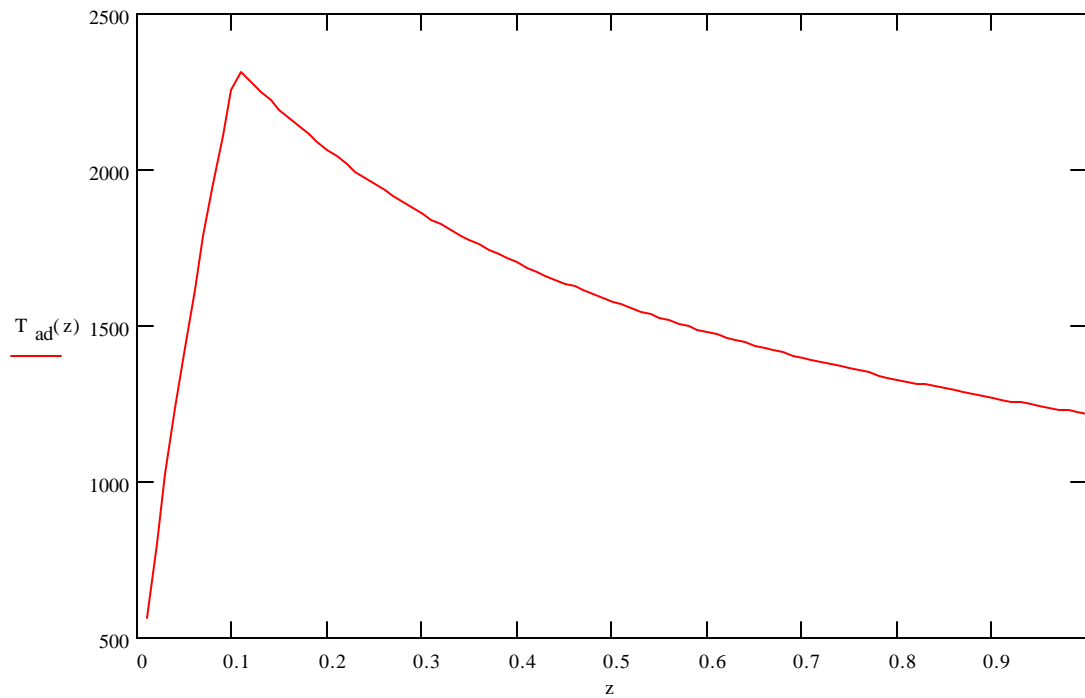$$Cp_{out2}(z, T) := 7.524 \cdot Cp_{N2}(T) + X(z) \cdot Cp_{CO2}(T) + 2 \cdot X(z) \cdot Cp_{H2O}(T)$$

$$Cp_{out}(z, T) := Cp_{out1}(z, T) + Cp_{out2}(z, T)$$

Using equation 9.7-10b:

$$Tout := 2500 \qquad \text{(initial guess)}$$

$$T_{ad}(z) := root\left(\int_{298.15}^{Tout} Cp_{out}(z, T) \, dT + \Delta Hrxn_{25} \cdot X(z), Tout \right)$$

$$z := 0.01, 0.02 .. \ 1$$

The solution is approximate because the range for the heat capacity of methane used is only valid between 273 K and 1500 K.

9.43   (also available as a Mathcad worksheet).

9.43:

From eqn 3.3-4:

$$-W = Q_1 \cdot \left(\frac{T_1 - T_2}{T_1} \right) \qquad \text{(for a Carnot cycle)}$$

$$-dW = dQ_1 \cdot \left(\frac{T_1 - T_2}{T_1} \right)$$

$$-W = \int_{T_1}^{T_2} \frac{T_1 - T_2}{T_1} dQ_1$$

$$dQ_1 = Cp_{out} \cdot dT_1$$

$$W_{Carnot}(z) := -\int_{298.15}^{T_{ad}(z)} \frac{T_1 - 298.15}{T_1} \cdot Cp_{out}(z, T_1) dT_1$$

$$\text{Wobtained}_{\text{Carnot}}(z) := \frac{-W_{\text{Carnot}}(z)}{9.524}$$ (Dividing by 9.524 gives the work per mole of air)

The work obtained by the Carnot cycle is plotted versus z at the end of Problem 9.44

9.44   (also available as a Mathcad worksheet).

9.44

$\text{Nout}_{N2} := 7.524$ $\text{Nout}_{CH4}(z) := 9.524 \cdot z - X(z)$ (from the mass balance table)

$\text{Nout}_{CO2}(z) := X(z)$ $\text{Nout}_{H2O}(z) := 2 \cdot X(z)$ $\text{Nout}_{O2}(z) := 2 - 2 \cdot X(z)$ $N(z) := 9.524 \cdot (z + 1)$

$\text{Nin}_{CH4}(z) := 9.524 \cdot z$ $\text{Nin}_{O2} := 2$ $\text{Nin}_{N2} := 7.524$

$T := 298.15$

Partial Molar Gibb's Free Energy:

$$\text{Gout}_{N2}(z) := \Delta\,\text{Gf}_{N2} + R \cdot T \cdot \ln\left(\frac{\text{Nout}_{N2}}{N(z)}\right)$$

$$\text{Gout}_{O2}(z) := \Delta\,\text{Gf}_{O2} + R \cdot T \cdot \ln\left(\frac{\text{Nout}_{O2}(z)}{N(z)}\right)$$

$$\text{Gout}_{H2O}(z) := \Delta\,\text{Gf}_{H2O} + R \cdot T \cdot \ln\left(\frac{\text{Nout}_{H2O}(z)}{N(z)}\right)$$

$$\text{Gout}_{CO2}(z) := \Delta\,\text{Gf}_{CO2} + R \cdot T \cdot \ln\left(\frac{\text{Nout}_{CO2}(z)}{N(z)}\right)$$

$$\text{Gout}_{CH4}(z) := \Delta\,\text{Gf}_{CH4} + R \cdot T \cdot \ln\left(\frac{\text{Nout}_{CH4}(z)}{N(z)}\right)$$ $$\text{Gin}_{N2}(z) := \Delta\,\text{Gf}_{N2} + R \cdot T \cdot \ln\left(\frac{\text{Nin}_{N2}}{N(z)}\right)$$

$$\text{Gin}_{CH4}(z) := \Delta\,\text{Gf}_{CH4} + R \cdot T \cdot \ln\left(\frac{\text{Nin}_{CH4}(z)}{N(z)}\right)$$ $$\text{Gin}_{O2}(z) := \Delta\,\text{Gf}_{O2} + R \cdot T \cdot \ln\left(\frac{\text{Nin}_{O2}}{N(z)}\right)$$

From eqn 9.7-16b:

$\text{Out1}(z) := \text{Nout}_{N2} \cdot \text{Gout}_{N2}(z) + \text{Nout}_{O2}(z) \cdot \text{Gout}_{O2}(z) + \text{Nout}_{CH4}(z) \cdot \text{Gout}_{CH4}(z)$

$Out2(z) := Nout_{H2O}(z) \cdot Gout_{H2O}(z) + Nout_{CO2}(z) \cdot Gout_{CO2}(z)$

$In(z) := Nin_{N2} \cdot Gin_{N2}(z) + Nin_{O2} \cdot Gin_{O2}(z) + Nin_{CH4}(z) \cdot Gin_{CH4}(z)$

$W_{FuelCell}(z) := Out1(z) + Out2(z) - In(z)$

$Wobtained_{FuelCell}(z) := \dfrac{-W_{FuelCell}(z)}{9.524}$

The work obtained has units of joules per mole of air.
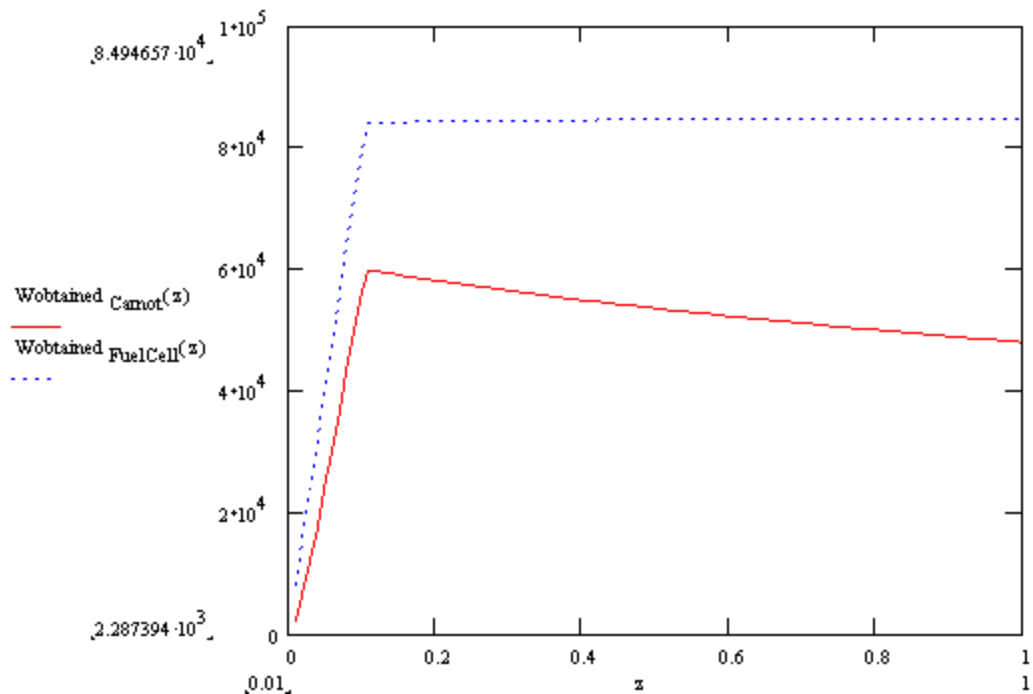
9.45   (also available as a Mathcad worksheet).

9.45

Given:

$\Delta G_{AgCl} := -108700 \cdot \dfrac{joule}{mole}$ $\Delta G_{Ag} := 77110 \cdot \dfrac{joule}{mole}$ $\Delta G_{Cl} := -131170 \cdot \dfrac{joule}{mole}$

$\Delta G_{TlCl} := -186020 \cdot \dfrac{joule}{mole}$ $\Delta G_{Tl} := -32450 \cdot \dfrac{joule}{mole}$

$R := 8.31451 \cdot \dfrac{joule}{K \cdot mole}$ $T := 298.15 \cdot K$

Part (a):

$$\Delta \text{Grxn}_{\text{AgCl}} := \Delta G_{\text{Ag}} + \Delta G_{\text{Cl}} - \Delta G_{\text{AgCl}} \qquad\qquad \Delta \text{Grxn}_{\text{AgCl}} = 5.464 \cdot 10^{4} \cdot \text{mole}^{-1} \cdot \text{joule}$$

$$K_{\text{AgCl}} := \exp\left(-\frac{\Delta \text{Grxn}_{\text{AgCl}}}{R \cdot T}\right) \qquad\qquad K_{\text{AgCl}} = 2.676 \cdot 10^{-10}$$

The solubility product given in illustration 9.3-2 is 1.607E-10. This experimental value is of the same order of magnitude as the theoretical value calculated above.

Part (b):

$$\Delta \text{Grxn}_{\text{TlCl}} := \Delta G_{\text{Tl}} + \Delta G_{\text{Cl}} - \Delta G_{\text{TlCl}} \qquad\qquad \Delta \text{Grxn}_{\text{TlCl}} = \quad \cdot \text{joule}$$

$$K_{\text{TlCl}} := \exp\left(-\frac{\Delta \text{Grxn}_{\text{TlCl}}}{R \cdot T}\right) \qquad\qquad K_{\text{TlCl}} =$$

The solubility product given in illustration 9.3-2 is 1.116E-2. This experimental value is two orders of magnitude greater than the theoretical value calculated above.
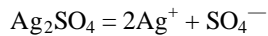
9.46   a) From Table 9.1-4, we have that

$$\Delta \underline{G}^{o}_{f,\text{Ag}^{+}} = 77.11 \frac{\text{kJ}}{\text{mol}} \quad \text{and} \quad \Delta \underline{G}^{o}_{f,\text{SO}_4^{--}} = -741.991 \frac{\text{kJ}}{\text{mol}}$$

Also, from Perry's Handbook,

$$\Delta \underline{G}^{o}_{f,\text{Ag}_2\text{SO}_4} = 614.21 \frac{\text{kJ}}{\text{mol}}$$

Now consider the reaction
$$\text{Ag}_2\text{SO}_4 = 2\text{Ag}^{+} + \text{SO}_4^{--}$$
The chemical equilibrium relation for this reaction is

$$K_a = \exp\left(-\frac{(2 \times 77110 - 741991 - (-641210))}{8.314 \times 298.15}\right) = \exp\left(-\frac{53439}{8.314 \times 298.15}\right)$$

$$= \exp(-21.5580) = 4.3388 \times 10^{-10} = \frac{a^2_{\text{Ag}^+} a_{\text{SO}_4^-}}{a_{\text{AgSO}_4}} = K^o_s$$

Now from eqn. (9.2-7), assuming the simple Debye-Hückel equation

$$\ln K_s = \ln K_s^o + (\boldsymbol{n}_+ + \boldsymbol{n}_-)|z_+ z_-| \boldsymbol{a} \sqrt{\frac{1}{2} \sum z_i^2 M_i}$$

$$= \ln K_s^o + (2+1)|1 \times 2| \boldsymbol{a} \sqrt{\frac{1}{2} \left(M_{Ag^+} + 4 M_{SO_4^{--}} \right)}$$

$$= \ln K_s^o + 3 \times 2 \boldsymbol{a} \sqrt{\frac{1}{2} \left(M_{Ag^+} + 4 M_{SO_4^{--}} \right)}$$

But $M_{SO_4^{--}} = \dfrac{1}{2} M_{Ag^+}$ so that

$$\ln K_s = \ln K_s^o + 6 \boldsymbol{a} \sqrt{\frac{3}{2} M_{Ag^+}} = \ln \frac{\left(M_{Ag^+} \right)^2 M_{SO_4^{--}}}{(1\ \text{molal})^3} = \ln \left(M_{Ag^+} \right)^3$$
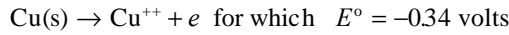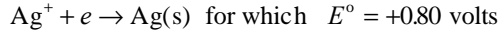
This has the solution

$$M_{Ag^+} = 8.224 \times 10^{-4} \frac{\text{mol}}{\text{liter}} \quad \text{and} \quad M_{SO_4^{--}} = 4.112 \times 10^{-4} \frac{\text{mol}}{\text{liter}}$$

Therefore,

$$K_s = \left(8.224 \times 10^{-4} \frac{\text{mol}}{\text{liter}} \right)^2 \times 4.112 \times 10^{-4} \frac{\text{mol}}{\text{liter}} = 2.781 \times 10^{-10} \left(\frac{\text{mol}}{\text{liter}} \right)^3$$

b)   Note that there is a error in the problem statement of the first printing of the text. The solution should be 0.5 M $CuSO_4$ and saturated with $AgSO_4$. The The half-cell reactions are

$Ag^+ + e \rightarrow Ag(s)$ for which $E^o = +0.80$ volts

$Cu(s) \rightarrow Cu^{++} + e$ for which $E^o = -0.34$ volts

Therefore for the reaction

$2Ag^+ + Cu(s) \rightarrow 2Ag(s) + Cu^{++}$ $E^o = +0.80 - 0.34 = 0.46$ volts

Next we have from eqn. (9.9-7) that

$$E = E^o - \frac{RT}{2F} \ln \frac{\left(a_{Cu^{++}} \right)}{\left(a_{Ag^+} \right)^2} = E^o - \frac{RT}{F} \ln \frac{\left(a_{Cu^{++}} \right)^{0.5}}{\left(a_{Ag^+} \right)} = E^o - \frac{RT}{F} \ln \frac{\left(M_{Cu^{++}} (\boldsymbol{g}_\pm)_{Cu^{++}} \right)^{0.5}}{\left(M_{Ag^+} (\boldsymbol{g}_\pm)_{Ag^+} \right)}$$

$$= 0.46 - 0.0257 \left(\ln \frac{\left(M_{Cu^{++}} \right)^{0.5}}{\left(M_{Ag^+} \right)} + \ln \frac{(\boldsymbol{g}_\pm)_{Cu^{++}}^{0.5}}{(\boldsymbol{g}_\pm)_{Cu^{++}}} \right)$$

$$= 0.46 - 0.0257 \left(\ln \frac{(0.5)^{0.5}}{\left(M_{Ag^+} \right)} + \ln \frac{(\boldsymbol{g}_\pm)_{Cu^{++}}^{0.5}}{(\boldsymbol{g}_\pm)_{Cu^{++}}} \right)$$

To proceed further, we have to compute the solubility of $AgSO_4$ in the 0.5M $CuSO_4$ solution. For this and all the calculations that follow, we will use the fact that since the $CuSO_4$ concentration is so much higher than that of $AgSO_4$, we will neglect the contribution of $AgSO_4$ to the total solution ionic strength. Also, because of the high ionic strength of the solution, we will use Eqn. (7.11-18) to compute the mean ionic activity coefficient, as follows:

$$\ln \boldsymbol{g}_{\pm} = -\frac{1.178|z_+ z_-|\sqrt{I}}{1+\sqrt{I}} + 0.3I$$

where $I = \dfrac{1}{2}\left(2^2 \times 0.5 + 2^2 \times 0.5\right) = \dfrac{1}{2}(2+2) = 2$

Therefore,

$$\ln(\boldsymbol{g}_{\pm})_{Ag_2SO_4} = -\frac{1.178|1\times 2|\sqrt{2}}{1+\sqrt{2}} + 0.3\times 2 = -0.7801$$

$$\ln(\boldsymbol{g}_{\pm})_{Ag_2SO_4} = -\frac{1.178|2\times 2|\sqrt{2}}{1+\sqrt{2}} + 0.3\times 2 = -2.1602$$

So now we have

$$\ln K_s = \ln K_s^o + (\boldsymbol{n}_+ + \boldsymbol{n}_-)(-0.7801)$$

$$= \ln K_s^o + (2+1)(-0.7801)$$

$$= -21.5580 - 2.3403 = -23.8983$$

so

$$K_s = 4.1793\times 10^{-11} = \frac{\left(M_{Ag^+}\right)^2 M_{SO_4^-}}{(1 \text{ molal})^3} = \frac{\left(M_{Ag^+}\right)^2 0.5}{(1 \text{ molal})^3}$$

and

$$M_{Ag^+} = \sqrt{\frac{4.1793\times 10^{-11}}{0.5}} = 9.1425\times 10^{-6} \text{ molal}$$

$$E = 0.46 - 0.0257\left(\ln\frac{(0.5)^{0.5}}{\left(9.1425\times 10^{-6}\right)} + 0.5\times(-2.1602) - 1\times(-0.7801)\right)$$

$$= 0.46 - 0.0257(11.256 - 1.0801 + 0.7801) = 0.46 - 0.2816 = 0.178 \text{ volt}$$

Since this is positive, it is the potential that is produced by the cell (rather than must be applied) for metallic silver to form.

9.47   (also available as a Mathcad worksheet).

9.47

Given (Ka and Hrxn were calculated on CHEMEQ): $R := 8.31451 \cdot \dfrac{\text{joule}}{\text{K}\cdot\text{mole}}$

Ka := 345.0   Hrxn := - 103940 $\cdot \dfrac{\text{joule}}{\text{mole}}$ $P := 10^5 \cdot \text{Pa}$ $T := 600 \cdot \text{K}$ Ni := 2·mole

Mass Balance Table:

Species	In	Out	y
C6H6	1	1-X	(1-X)/(2-X)
C2H4	1	1-X	(1-X)/(2-X)
C6H5C2H5	0	X	X/(2-X)

$$aC6H6(X) := \frac{1-X}{2-X} \qquad aC2H4(X) := \frac{1-X}{2-X} \qquad aC6H5C2H5(X) := \frac{X}{2-X}$$

$$KaX(X) := \frac{aC6H5C2H5(X)}{aC6H6(X) \cdot aC2H4(X)}$$

$X := 0.9$ (initial guess)

Given $KaX(X) = Ka$ $X := Find(X)$

$X = 0.946$ $XX := X \cdot mole$

Assuming the contents of the reactor behave as an ideal gas:

$$Vi := \frac{Ni \cdot R \cdot T}{P} \qquad Nf := (2-X) \cdot mole \qquad Vf := \frac{Nf \cdot R \cdot T}{P} \qquad Nf = 1.054 \cdot mole$$

An energy balance on the reactor yields:

$$Q := XX \cdot Hrxn + \int_{Vi}^{Vf} P \, dV$$

$Q = -1.031 \cdot 10^5$ $\cdot$joule   (Heat must be removed because Q is negative)

9.48   (also available as a Mathcad worksheet).

9.48

Part (a):
Using equation 9.1-20b:

$$\ln(Ka) = -\frac{\Delta Grxn}{R \cdot T}$$

$$\frac{d}{dT} \left\{ -\frac{57.33}{R \cdot T} + \frac{0.17677}{R} \right\} = \frac{\Delta Hrxn}{R \cdot T^2}$$

$$\frac{57.33}{R \cdot T^2} = \frac{\Delta Hrxn}{R \cdot T^2}$$

$$\Delta Hrxn = 57.33 \cdot \frac{kJ}{mole}$$

Part (b):

$$\Delta G_{rxn}(T) := 57330 \cdot \frac{joule}{mole} - 176.77 \cdot \left(\frac{joule}{mole \cdot K} \right) \cdot T \qquad\qquad R := 8.31451 \cdot \frac{joule}{K \cdot mole}$$

$$Ka(T) := exp\left(-\frac{\Delta G_{rxn}(T)}{R \cdot T} \right)$$

Mass Balance Table:

Species	In	Out
N2O4	1	1-X
NO2	0	2*X
Total	1	1+X

Calculation of mole fractions and activities:

$$y_{N2O4}(X) := \frac{1 - X}{1 + X} \qquad\qquad y_{NO2}(X) := \frac{2 \cdot X}{1 + X}$$

$$a_{N2O4}(X, P) := y_{N2O4}(X) \cdot \left(\frac{P}{10^5 \cdot Pa} \right) \qquad\qquad a_{NO2}(X, P) := y_{NO2}(X) \cdot \left(\frac{P}{10^5 \cdot Pa} \right)$$

$$KaX(X, P) := \frac{a_{NO2}(X, P)^2}{a_{N2O4}(X, P)}$$

$$X := 0.7 \qquad \text{(initial guess)}$$

Given $\qquad\qquad Ka(T) = KaX(X, P) \qquad\qquad X(T, P) := Find(X)$

$$Xb_{0.1} := X\left(323.15 \cdot K, 10^4 \cdot Pa\right) \qquad Xb_1 := X\left(323.15 \cdot K, 10^5 \cdot Pa\right) \qquad Xb_{10} := X\left(323.15 \cdot K, 10^6 \cdot Pa\right)$$

$$y_{NO2}\left(Xb_{0.1}\right) = 0.91 \qquad y_{NO2}\left(Xb_1\right) = 0.605 \qquad y_{NO2}\left(Xb_{10}\right) = 0.261$$

$$y_{N2O4}\left(Xb_{0.1}\right) = 0.09 \qquad y_{N2O4}\left(Xb_1\right) = 0.395 \qquad y_{N2O4}\left(Xb_{10}\right) = 0.739$$

Part (c):

$$Xc_{0.1} := X\left(473.15 \cdot K, 10^4 \cdot Pa\right) \qquad Xc_1 := X\left(473.15 \cdot K, 10^5 \cdot Pa\right) \qquad Xc_{10} := X\left(473.15 \cdot K, 10^6 \cdot Pa\right)$$

$$y_{NO2}\left(Xc_{0.1}\right) = 1 \qquad y_{NO2}\left(Xc_1\right) = 0.999 \qquad y_{NO2}\left(Xc_{10}\right) = 0.988$$

$$y_{N2O4}\left(Xc_{0.1}\right) = 1.246 \cdot 10^{-4} \qquad y_{N2O4}\left(Xc_1\right) = 1.243 \cdot 10^{-3} \qquad y_{N2O4}\left(Xc_{10}\right) = 0.012$$

9.49   (also available as a Mathcad worksheet).

9.49

Given:

$$\Delta H_{rxn} := -58620 \cdot \frac{joule}{mole} \qquad \Delta S_{rxn} := -138.2 \cdot \frac{joule}{K \cdot mole} \qquad R := 8.31451 \cdot \frac{joule}{K \cdot mole}$$

$$Ta := 298.15 \cdot K \qquad Tb := 373.15 \cdot K \qquad P1 := 10^4 \cdot Pa \qquad P2 := 10^5 \cdot Pa \qquad P3 := 10^6 \cdot Pa$$

Mass Balance Table:

Species	In	Out	y
M	2	2-2*X	(2-2*X)/(2-X)
D	0	X	X/(2-X)
Total		2-X	

Activities, Equilibrium Constant, and Equilibrium Expression:

$$a_M(X,P) := \frac{2 - 2 \cdot X}{2 - X} \cdot \left(\frac{P}{10^5 \cdot Pa} \right) \qquad\qquad a_D(X,P) := \frac{X}{2 - X} \cdot \left(\frac{P}{10^5 \cdot Pa} \right)$$

$$\Delta G_{rxn}(T) := \Delta H_{rxn} - T \cdot \Delta S_{rxn} \qquad\qquad Ka(T) := \exp\left(\frac{-\Delta G_{rxn}(T)}{R \cdot T} \right)$$

$$KaX(X,P) := \frac{a_D(X,P)}{a_M(X,P)^2}$$

$X := 0.999$ (initial guess for solver)

Given $KaX(X,P) = Ka(T)$ $X \le 1$ $DegreeOfDimerization(T,P) := Find(X)$

Part (a):

$DegreeOfDimerization(Ta, P1) = 0.953$

$DegreeOfDimerization(Ta, P2) = 0.985$

$DegreeOfDimerization(Ta, P3) = 0.995$

Part (b):

DegreeOfDimerization(Tb, P1) = 0.547

DegreeOfDimerization(Tb, P2) = 0.842

DegreeOfDimerization(Tb, P3) = 0.949

Part (c):

Nomenclature
N = initial number of moles before dimerization
Nm = number of moles of monomer after dimerization = N-2X
Nd = number of moles of dimer = X
Total # of moles = N-X
yM=(N-2X)/(N-X)
yD=X/(N-X)
P = (Nm + Nd)*R*T/V

$$P = (Nm + Nd) \cdot \frac{(R \cdot T)}{V} = \frac{(Nm + Nd)}{N} \cdot \frac{(N \cdot R \cdot T)}{V} = \frac{(N - X)}{N} \cdot \frac{(N \cdot R \cdot T)}{V}$$

$$Ka = \frac{yd}{ym^2 \cdot \left(\dfrac{P}{1\ bar}\right)} = \frac{(X \cdot (N - X))}{(N - 2\ X)^2 \cdot \left(\dfrac{P}{1\ bar}\right)} \qquad \text{which has the solution}$$

$$X = \frac{N}{2} - \frac{N}{2} \cdot \sqrt{1 - \frac{\left(4 \cdot Ka \cdot \dfrac{P}{1\ bar}\right)}{\left[4 \cdot Ka \cdot \left(\dfrac{P}{1\ bar}\right) + 1\right]}} \qquad \text{or} \qquad \frac{X}{N} = \frac{1}{2} \cdot \left[1 - \sqrt{\frac{1}{\left[4 \cdot Ka \cdot \left(\dfrac{P}{1\ bar}\right) + 1\right]}}\right]$$

and
$$\frac{(N - X)}{N} = 1 - \frac{X}{N} = 0.5 + 0.5 \cdot \sqrt{\frac{1}{\left[4 \cdot Ka \cdot \left(\dfrac{P}{1\ bar}\right) + 1\right]}} = 0.5 \cdot \left[1 + \sqrt{\frac{1}{\left[4 \cdot Ka \cdot \left(\dfrac{P}{1\ bar}\right) + 1\right]}}\right]$$

$$P = \left[0.5 \cdot \left[1 + \sqrt{\frac{1}{\left[4 \cdot Ka \cdot \left(\dfrac{P}{1\ bar}\right) + 1\right]}}\right]\right] \cdot \frac{(N \cdot R \cdot T)}{V} \qquad \text{where} \qquad Ka = \exp\left[\frac{-(\Delta\ Hrxn - T\Delta\ Srxn)}{R \cdot T}\right]$$

Note that the EOS goes to the ideal gas limit as Ka goes to zero, and 1/2 the ideal gas limit when Ka goes to infinity (all dimer). Also, the equation of state will have an other than linear dependence on temperature due to the temperature dependence of Ka.

9.50   (also available as a Mathcad worksheet).

9.50

Given (All Units are SI):

$T1 := 267$ $T2 := 255$ $P1_{CH4} := 2 \cdot 10^6$ $P2_{CH4} := 1.5 \cdot 10^6$ $R := 8.31451$

Activities:

$a_{hydrate} := 1$ $a_{H2O} := 1$ $a_{CH4}(P_{CH4}) := \dfrac{P_{CH4}}{10^5}$

Part (a):

$Ka(P_{CH4}) := \dfrac{a_{hydrate}}{a_{H2O}^{5.75} \cdot a_{CH4}(P_{CH4})}$ $\Delta G_{rxn}(T, P_{CH4}) := - R \cdot T \cdot \ln(Ka(P_{CH4}))$

$\Delta G_{rxn}(T1, P1_{CH4}) = 6.65 \cdot 10^3$

$\Delta G_{rxn}(T2, P2_{CH4}) = 5.742 \cdot 10^3$

Part (b):

$\Delta H_{rxn} := 10^3$ $\Delta S_{rxn} := 10$ (initial guesses)

Given $\Delta G_{rxn}(T1, P1_{CH4}) = \Delta H_{rxn} - T1 \cdot \Delta S_{rxn}$ $\Delta G_{rxn}(T2, P2_{CH4}) = \Delta H_{rxn} - T2 \cdot \Delta S_{rxn}$

$ans := Find(\Delta H_{rxn}, \Delta S_{rxn})$ $\Delta H_{rxn} := ans_0$ $\Delta S_{rxn} := ans_1$

$\Delta H_{rxn} = -1.357 \cdot 10^4$ $\Delta S_{rxn} = -75.737$

Part (c):

$Ka_{273} := Ka(P1_{CH4}) \cdot \exp\left[-\dfrac{\Delta H_{rxn}}{R} \cdot \left(\dfrac{1}{273} - \dfrac{1}{T1} \right) \right]$ $Ka_{273} = 0.044$
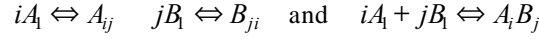
$P273_{CH4} := 10^6$ (initial guess)

Given $Ka(P273_{CH4}) = Ka_{273}$ $P273_{CH4} := Find(P273_{CH4})$

$P273_{CH4} = 2.288 \cdot 10^6$

9.51 The reactions are

$$iA_1 \Leftrightarrow A_{ij} \quad jB_1 \Leftrightarrow B_{ji} \quad \text{and} \quad iA_1 + jB_1 \Leftrightarrow A_i B_j$$

The overall mass balance on species A

$$N_A = \frac{\text{initial number of}}{\text{moles of } A_1} = \sum_i iN_{A_i} + \sum_i \sum_j iN_{A_i B_j} = \sum_i \left(iN_{A_i} + i \sum_j N_{A_i B_j} \right)$$

Overall mass balance on species B

$$N_B = \frac{\text{initial number of}}{\text{moles of } B_1} = \sum_j jN_{Bj} + \sum_j \sum_i jN_{A_i B_j} = \sum_j j \left(N_{B_j} + \sum_i N_{A_i B_j} \right)$$

At equilibrium

$$\overline{G}_{A_i} - i\overline{G}_{A_1} = 0; \quad \overline{G}_{B_i} - i\overline{G}_{B_1} = 0; \quad \overline{G}_{A_i B_j} - \left(i\overline{G}_{A_1} + j\overline{G}_{B_1} \right) = 0;$$

and

$$G_{\text{total}} = \sum_i N_{A_i} \overline{G}_{A_i} + \sum_j N_{B_j} \overline{G}_{B_j} + \sum_i \sum_j N_{A_i B_j} \overline{G}_{A_i B_j}$$

At equilibrium $dG_{\text{total}} = 0$ with respect to each extent of reaction.

$$dG_{\text{total}} = \sum \overline{G}_{A_i} dN_{A_i} + \sum \overline{G}_{B_i} dN_{B_i} + \sum \sum \overline{G}_{A_i B_j} dN_{A_i B_j}$$

$$\left[+ \sum N_{A_i} d\overline{G}_{A_i} + \sum N_{B_i} d\overline{G}_{B_i} + \sum \sum N_{A_i B_j} d\overline{G}_{A_i B_j} = 0 \right]$$

0 by the Gibbs-
Duhem equation

Also, using the equilibrium equations

$$dG_{\text{total}} = 0 = \sum i\overline{G}_{A1} dN_{Ai} + \sum i\overline{G}_{B1} dN_{Bi} + \sum \sum \left(i\overline{G}_{A1} + j\overline{G}_{B1} \right) dN_{A_i B_j}$$

$$= 0 = \overline{G}_{A1} \sum idN_{Ai} + \overline{G}_{B1} \sum idN_{Bi} + \sum_i i\overline{G}_{A1} \sum dN_{A_i B_j} + \sum_j j\overline{G}_{B1} \sum dN_{A_i B_j}$$

$$= \overline{G}_{A1} \left[\sum_i \left(idN_{Ai} + i \sum_j dN_{A_i B_j} \right) \right] + \overline{G}_{B1} \left[\sum_j \left(jdN_j + j \sum dN_{A_i B_j} \right) \right]$$

$$= \overline{G}_{A1} dN_A + \overline{G}_{B1} dN_B$$

$$\left(\frac{\partial G_{\text{total}}}{\partial N_A} \right)_{N_B T, P} \equiv \overline{G}_A = \overline{G}_{A_i}. \quad \text{Also} \quad \left(\frac{\partial G_{\text{total}}}{\partial N_B} \right)_{N_A, T, P} \equiv \overline{G}_B = \overline{G}_{B_i}$$

Therefore $\overline{G}_{A1} = \overline{G}_A$ and $\overline{G}_{B1} = \overline{G}_B$ $\qquad\qquad(1)$

Also, we have that, by definition

$$\left(\frac{\P \overline{G}_i}{\P P}\right)_T = RT\left(\frac{\P \ln \bar{f}_i}{\P P}\right)_T \qquad\qquad(2)$$

Thus, integrating between any two states, we have

$$\overline{G}_i(T,P_2) - \overline{G}_i(T,P_1) = RT\ln\frac{\bar{f}_i(T,P_2)}{\bar{f}_i(T,P_1)} \qquad\qquad(3)$$

Now using Eqn. (3) with Eqns. (1), and recognizing that Eqns. (1) must be satisfied at *all* T and P implies that
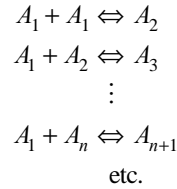
$$\bar{f}_A(T,P) = \bar{f}_{A1}(T,P) \text{ and } \bar{f}_B(T,P) = \bar{f}_{B1}(T,P)$$

Alternatively we could integrate Eqn. (2) between $P = 0$ and the pressure P and note that Eqn. (1) must be satisfied at all T and P. This implies that

$$\frac{\bar{f}_{A1}(P)}{\bar{f}_{A1}(P=0)} = \frac{\bar{f}_A(P)}{\bar{f}_A(P=0)}$$

but as $P \to 0$ only A_1 will be present (LeChatelier's principle) $\Rightarrow \bar{f}_A(P=0) = \bar{f}_{A1}(P=0)$ so that $\bar{f}_{A1}(P) = \bar{f}_A(P)$.

9.52

$$A_1 + A_1 \Leftrightarrow A_2$$
$$A_1 + A_2 \Leftrightarrow A_3$$
$$\vdots$$
$$A_1 + A_n \Leftrightarrow A_{n+1}$$
$$\text{etc.}$$

$$N_0 = \frac{\text{Total moles}}{\text{of } A_1 \text{ initially}} = N_1 + 2N_2 + 3N_3 + \cdots + nA_n + \cdots = \sum iN_i$$

$$= N_T \sum i \frac{N_i}{N_T} = N_T \sum ix_i \text{ where } N_T = \text{ total number of moles in system}$$

$$\Rightarrow \frac{N_0}{N_T} = \sum ix_i$$

Now $b = \sum x_i b_i = \sum ix_i b_1 = b_1 \sum ix_i$ and

$$a = \sum\sum x_i x_j \sqrt{a_{ii}a_{jj}} = \sum\sum ix_i jx_j a_1 = a_1\left(\sum ix_i\right)^2$$

which implies that

(a) $a = a_1\left(\dfrac{N_0}{N_T}\right)^2$ and $b = b_1\left(\dfrac{N_0}{N_T}\right)$

Also

$$K_{j+1} = K = \frac{a_{j+1}}{a_j a_1} = \frac{\boldsymbol{f}_{j+1}x_{j+1}(P/1\text{ bar})}{\boldsymbol{f}_j\boldsymbol{f}_1x_jx_1(P/1\text{ bar})^2} = \frac{\boldsymbol{f}_{j+1}x_{j+1}(1\text{ bar})}{\boldsymbol{f}_j\boldsymbol{f}_1x_jx_1 P}$$

Then

$$\frac{\boldsymbol{f}_j\boldsymbol{f}_1P}{\boldsymbol{f}_{j+1}} = \frac{x_{j+1}}{x_jx_1K} \quad\text{or}\quad \frac{\boldsymbol{f}_{j+1}}{\boldsymbol{f}_j\boldsymbol{f}_1P} = \frac{x_jx_1K}{x_{j+1}}$$

For the moment we will assume that

$$\frac{\boldsymbol{f}_j\boldsymbol{f}_1P}{\boldsymbol{f}_{j+1}} = \frac{x_{j+1}}{x_jx_1K} = \boldsymbol{a}$$

is independent of the index j and then show that this is indeed the case. Then

$$x_1^2\boldsymbol{a}K = x_2$$
$$x_1x_2\boldsymbol{a}K = x_3 = (x_1\boldsymbol{a}K)x_2 = (x_1\boldsymbol{a}K)x_1^2\boldsymbol{a}K = x_1^3(\boldsymbol{a}K)^2$$

Similarly

$$x_4 = x_1^4(\boldsymbol{a}K)^3$$
$$\vdots$$
$$x_j = (\boldsymbol{a}K)^{j-1}x_1^j$$
$$\vdots$$
$$\text{etc.}$$

Then $N_T = N_0\sum i x_i = N_0\sum i(K\boldsymbol{a})^{i-1}x_1^i$.

Also $\sum x_j = 1 = \sum(K\boldsymbol{a})^{j-1}x_1^j = 1$

Now from the properties of geometric sums

$$\sum_{i=0}^{\infty} \boldsymbol{q}^i = \frac{1}{1-\boldsymbol{q}}$$

we have

$$\sum_{j=1}^{\infty}(K\boldsymbol{a})^{j-1}x_1^j = x_1\sum_{j=1}^{\infty}(K\boldsymbol{a}x_1)^{j-1} = x_1\sum_{j=0}^{\infty}(K\boldsymbol{a}x_1)^j = \frac{x_1}{1-K\boldsymbol{a}x_1} = 1 \qquad (*)$$

so that

$$x_1 = 1 - K\boldsymbol{a}x_1 \ \text{ or } \ x_1(1 + K\boldsymbol{a}) = 1; \ K\boldsymbol{a} = \frac{1}{x_1} - 1$$

Also

$$\sum_{i=0}^{\infty} i\boldsymbol{q}^{i-1} = \frac{d}{d\boldsymbol{q}}\left(\sum_{i=0}^{\infty}\boldsymbol{q}^{i}\right) = \frac{d}{d\boldsymbol{q}}\left(\frac{1}{1-\boldsymbol{q}}\right) = \frac{1}{(1-\boldsymbol{q})^2} = \sum_{i=1}^{\infty} i\boldsymbol{q}^{i-1}$$

so that

$$\sum_{i=1}^{\infty} i(K\boldsymbol{a})^{i-1}x_1^{i} = x_1\sum_{i=1}^{\infty} i(K\boldsymbol{a}x_1)^{i-1} = x_1\sum_{i=0}^{\infty} i(K\boldsymbol{a}x_1)^{i-1}$$

$$= \frac{x_1}{(1 - K\boldsymbol{a}x_1)^2} = \frac{N_T}{N_0} = \frac{1}{x_1}\left(\frac{x_1}{1 - K\boldsymbol{a}x_1}\right)^2 = \frac{1}{x_1}1^2$$

from Eqn. (*) above

$$\Rightarrow \frac{N_T}{N_0} = \frac{1}{x_1} \ \text{ and } \ b = b_1\left(\frac{N_0}{N_T}\right) = x_1 b_1; \ a = a_1\left(\frac{N_0}{N_T}\right)^2 = x_1^2 a_1$$

For the van der Waals equation of state we have

$$P = \frac{RT}{\underline{V} - b} - \frac{a}{\underline{V}^2} = \frac{NRT}{V - Nb} - \frac{N^2 a}{V}$$

and

$$\ln \boldsymbol{f}_i = \frac{B_i}{Z - B} - \ln(Z - B) - \frac{2\sum x_j a_{ij}}{RT\underline{V}}$$

which here becomes

$$\ln \boldsymbol{f}_i = \frac{iB_1}{Z - B} - \ln(Z - B) - \frac{2\sum x_j ij a_1}{RT\underline{V}} = \frac{iB_1}{Z - B} - \ln(Z - B) - \frac{2ia_i}{RT\underline{V}}\sum jx_j$$

$$\ln \boldsymbol{f}_i = \frac{iB_i}{Z - B} - \ln(Z - B) - \frac{2ia_1}{RT\underline{V}}\frac{N_0}{N_T}$$

so that

$$\ln\frac{\boldsymbol{f}_j\boldsymbol{f}_1}{\boldsymbol{f}_{j+1}} = \ln\boldsymbol{f}_j + \ln\boldsymbol{f}_1 - \ln\boldsymbol{f}_{j+1}$$

$$= (j+1-(j+1))\frac{B_1}{z-B} + (-1-1+1)\ln(Z-B)$$

$$-\frac{2a_1}{RT\underline{V}}\frac{N_0}{N_T}(j+1-(j+1))$$

$$= -\ln(Z-B)$$

$$\frac{\boldsymbol{f}_j\boldsymbol{f}_1}{\boldsymbol{f}_{j+1}} = \frac{1}{Z-B} = \frac{RT/P}{\underline{V}-b}$$

or

(b)
$$\frac{P\boldsymbol{f}_j\boldsymbol{f}_1}{\boldsymbol{f}_{j+1}} = \frac{RT}{\underline{V}-b} = \frac{RT}{\underline{V}-b_1(N_0/N_T)} = \frac{N_T RT}{N_T\underline{V}-N_0 b_1} = \boldsymbol{a}$$

which is independent of the index j as was assumed. Now that we know that $\boldsymbol{a}$ is independent of the index j. We can use

$$x_1(1+\boldsymbol{a}K) = 1 \text{ and } \boldsymbol{a} = \frac{N_T RT}{N_T\underline{V}-N_0 b_1} = \frac{RT}{\underline{V}-(N_0/N_T)b} = \frac{RT}{\underline{V}-x_1 b}$$

$$x_1\left(1+\frac{RTK}{\underline{V}-x_1 b_1}\right) = 1 \Rightarrow x_1(\underline{V}-x_1 b_1 + RTK) = \underline{V}-x_1 b_1$$

$$-x_1^2 b_1 + x_1(\underline{V}+RTK+b_1) - \underline{V} = 0$$

$$b_1 x_1^2 - x_1(\underline{V}+RTK+b_1) + \underline{V} = 0$$

(c)
$$x_1 = \frac{(\underline{V}+RTK+b_1) \pm \sqrt{(\underline{V}+RTK+b_1)^2 - 4b_1\underline{V}}}{2b_1} \qquad (**)$$

Also

$$P = \frac{RT}{\underline{V}-b} - \frac{a}{\underline{V}^2} = \frac{RT}{\underline{V}-x_1 b} - \frac{x_1^2 a_1}{\underline{V}^2} \qquad (***)$$

Equations (**) and (***) are the set which forms the equation of state for the associating van der Waals fluid. Notice that to solve for $\underline{V}$ we need x_1 which depends on $\underline{V}$; therefore, the equation is no longer cubic.

Note that if the fluid is non-associating, then $K = 0$ in this limit

$$x_1 = \frac{(\underline{V}+b_1) \pm \sqrt{(\underline{V}^2 - 4b_1\underline{V} + b_1^2)}}{2b_1} = \frac{(\underline{V}+b_1) - (\underline{V}-b_1)}{2b_1} = 1$$

so that

$$P = \frac{RT}{\underline{V}-b_1} - \frac{a_1}{\underline{V}^2}$$

which is the usual van der Waals equation.

9.53 The description of HF containing systems is described in the article "Collection of Phase Equilibrium Data for Separation Technology" by William Schotte in *Ind. Eng. Chem. Process Des. Dev.* (1980), *19*, 432–439. By a careful examination of the density and other data, he proposed that HF associates in the vapor phase according to the reactions

$$2HF \Leftrightarrow (HF)_2$$
$$6HF \Leftrightarrow (HF)_6$$
$$8HF \Leftrightarrow (HF)_8$$
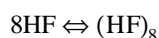
and, over the temperature range of 195 to 240 K, the equilibrium constants are

$$K_2 = \frac{\bar{f}_2}{\bar{f}_1^2} = \exp\left[\frac{6429.4}{T} - 24.1456\right]$$

$$K_6 = \frac{\bar{f}_6}{\bar{f}_1^6} = \exp\left[\frac{21100.9}{T} - 69.7292\right]$$

$$K_8 = \frac{\bar{f}_8}{\bar{f}_1^8} = \exp\left[\frac{25224.5}{T} - 83.4689\right]$$

where K_n has units of $(atm)^{n-1}$, and f_i is the fugacity of species i. Next, Schotte used a (questionable) argument by Tamir and Wisniak [*Chem. Eng. Sci* (1978), *33*, 651] that the fugacity coefficients $\boldsymbol{f}_i = \bar{f}_i / x_i P$ of the monomers, dimers, hexamers and octamers are all aproximately equal, and can be calculated from the fugacity of pure HF. This alleviated the need to specify the molecular parameters for the association complexes. Using this model, Schotte obtained very good agreement for the association factor (density) of pure HF and an HF-Freon mixture using a simple equation of state such as Peng-Robinson (which must be solved iteratively since chemical equilibrium is superimposed on the phase equilibrium calculation).

An alternative, instead of using the Tamir-Wisniak assumption of equality of fugacity coefficients is to use the model in Problem 9.52

$$a_j = j^2 a_1 \text{ and } b_j = jb_1$$

and then treat HF as a chemical reaction system with HF, $(HF)_2$, $(HF)_6$ and $(HF)_8$. Similarly, HF + non-associating component would be treated as a five component system: non-associating component + HF, $(HF)_2$, $(HF)_6$ and $(HF)_8$. In each of these cases the compositions of the HF components change as the equilibrium changed. The problem with this proposal is that the *a* parameters for the association complexes become unrealistically large. For example, $a_8 = 64 \times a_1$. Consequently, no completely theoretically-correct model for the HF associating system exists, though the models now in use are probably satisfactory for engineering calculations.