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From Crystal to Solution

Mir Publishers

Moscow

G. A. Krestov, V. A. Kobenin


ИЗДАТЕЛЬСТВО · МИР ·

Г. А. Крестов,
В. А. Кобенин

ОТ КРИСТАЛЛА К РАСТВОРУ

ИЗДАТЕЛЬСТВО
«ХИМИЯ»
МОСКВА

From Crystal to Solution

G. A. Krestov, V. A. Kobenin

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Contents

Glossary

Auto-diffusion—spontaneous and continuous motion of particles of gas, liquid, or solid matter caused by heat.

Chemotronics—branch of science which arose at the junction of electrochemistry and electronics. It deals with the general principles of electrochemical converters of information.
Colloidal particles—dispersed phase particles in colloidal solutions, sizing 10^{-8} to 10^{-6} nm.

Diamagnetic substances—substances which are expelled from a magnetic field.
Dielectric constant — a quantity indicating the number of times the electrostatic interaction of particles in a certain medium decreases (as compared with a vacuum).
Dispersion—fine reduction of size of solid or liquid substances in a surrounding medium.

Ferromagnetism—magnetization of crystalline substances in complete absence of an external magnetic field due to strong interactions amongst atoms, molecules, or ions, having their own magnetic moment.

Half-life—the time required for the reaction of half of the initial amount of a substance.

Heterogeneous system—a physico-chemical system consisting of two or more phases.

Homogeneous system—a physico-chemical system consisting of only one phase.

Hydrophilic and hydrophobic—terms describing the affinity of substances or surfaces of bodies for water. Hydrophilic substances may be well wetted by water, while hydrophobic substances repel it.

Ideal solution—a homogeneous system which is formed without energy or volume changes. The role of this concept in the theory of solutions is in many respects similar to the role of an ideal gas in the study of the gaseous state.

Ionic bond—electrostatic interaction of oppositely charged ions.

Ionic sublimation—ion transfer from the crystal to the gaseous state omitting the liquid phase.

Level splitting—division of energy level into two or more sublevels under the action of external fields.

Liquid crystals—substances in the liquid state having properties of a liquid (fluidity) and some properties of solid crystals (anisotropy of properties).

Molar fraction of a component—is the number of molecules of a given substance divided by the total number of molecules of all other components in solution.

Nucleus shielding—decreasing the action of the positive nucleus charge on a given electron by placing other electrons between them.

Osmotic pressure—pressure which must be applied to a solution to bring it to equilibrium with the pure solvent separated from the solution by a membrane permeable only to the solvent.

Paramagnetism—magnetization of substances in an external magnetic field. Paramagnetic substances are pulled into a magnetic field.

Plasma—partly or completely ionized gas in which the densities of positive and negative charges are practically the same.

Polytherm—a curve describing the dependence of properties on temperature.

Radiolysis—chemical decomposition of substances by the action of ionizing radiation.

Recombination—aggregation of atoms or radicals in the gaseous state and solution.

Relaxation time—time required for the return to the initial state of a system (electrolyte solution) excited externally.

Resistance thermometer—a thermometer whose action depends on the property of metals to change their electric resistance under the action of temperature variations.

Solvolysis (hydrolysis)—reaction of the solute with the solvent (water).

Supramolecular structure of solution—stable order of the interacting molecules of the solvent caused by the van der Waals forces and the hydrogen bonding.

Thermistor—a semi-conductor instrument whose resistance varies with temperature.

Thermocouple battery—a set of in-series connected thermosensitive elements (thermocouples) in the form of unlike metal conductors soldered to one another.

Translation motion—motion in which all particles move in one direction.

van der Waals forces—the physical attraction of particles to one another which arise from the interaction of their dipoles (permanent dipoles, induced dipoles, and dipoles arising from the motion of electrons).

Editor's Preface

Crystal and solution. The two words often go together. Crystals of salts dissolve in water, and saturated solutions of mineral salts precipitate crystals ...

Crystals have long been a paragon of perfection of form. With them, matter attains its maximum order and regularity, whether at the level of the minutest particles such as atoms or ions, or as visible regular polyhedra with their symmetrically arranged plane surfaces. As a crystal passes into solution it seems to lose all its properties, and first of all its most important characteristic, the symmetry of its structure.

But the transfer to solution does not mean complete loss of structure. Despite the visible absence of orderly forms solution has a very complicated and perfect structure. True, it is not the structure of a crystal, but in many cases the solution seems to keep a "memory" of the symmetry that the solute had in its solid state. This property is, primarily, inherent in solvents themselves, and this is especially so in the most important solvent, water. Fascinated as we are with the perfect beauty of a snow flake, we must remember that when it melts on the palm to turn into water, its inner structure is not fully destroyed but only becomes invisible to the eye. The structure persists in the mutual arrangement of molecules, in the intricate ice-like structure of liquid water ...

As substances dissolve in water, they occupy their own "apartments" in this invisible but orderly "molecular building" partly destroying its separate sections and partly introducing their own new order around the ions and molecules.

So it is not for nothing that crystal and solution are put together in the title of this book. They are related and the modern scientist believes that the study of the close connections between them will give him the clue to understanding the nature of solution, which is perhaps the most important state of matter.

P. B. Dobrotin

Chapter One

A Look at Past, Present, and Future

SOLUTIONS IN THE AGE OF SCIENCE AND TECHNOLOGY

Man has been dealing with solutions since time immemorial. Life itself would never have developed on Earth without solutions. Without them it would be difficult to devise or organize any industrial enterprise. Among them, aqueous solutions are particularly important for both man and nature. Water is the most readily available solvent and its properties are unique. But with the vigorous development of industry it has become necessary to limit the use of water as a solvent. Obtaining desalinated water, purifying contaminated water, and recovery of industrial effluents have become vital problems in many countries. Water is no longer the only solvent and medium for many processes, and non-aqueous and mixed solvents having specific properties are now used more and more often. Non-aqueous solvents are used in the manufacture, use, and analysis of new substances, to accelerate or retard chemical processes, or to produce a desired effect on the course of many reactions. Non-aqueous solvents are widely used as heat-carriers and coolants, etc. The successful use of non-aqueous solvents promotes the solution of the environmental protection problem with the creation of an ecologically "clean" technology with closed industrial cycles, and the solution of many other problems of vital importance. The development of scientific principles for the selection of solvents is very important for the optimal organization of many processes and for the creation of entirely new processes for the manufacture of various substances and materials.

In this book we shall mainly discuss liquid solutions since many chemical processes are most readily accomplished in liquid media.

WHAT IS SOLUTION?

By solution we understand a single-phase, or a homogeneous system of variable composition formed by at least two independent components. A homogeneous system is characterized by the absence of an interphase between the component parts of the solution, and by uniform composition and properties throughout its entire volume.

The components of a solution are the individual chemical substances which can be isolated from the system and which can exist in the isolated state. For example, an aqueous solution of potassium chloride consists of water and potassium chloride. The solution components are the solute and the solvent. The solute is the component of the solution whose state of aggregation in normal conditions differs from that of the solution. The other components of the solution are known as solvents. In the case of liquid solutions, solutes are substances which under normal conditions are solid or gaseous, while the solvents are liquids.

The composition of a solution, in contrast to the composition of definite chemical compounds, can vary continually within wide limits. In this respect solutions are similar to mechanical mixtures, differing from them by their homogeneity and the change of many properties on mixing. The properties of a solution depend on the interactions between the particles of the solute, on the interaction between the particles of the solvent, and on the interaction between the particles of the solute and the solvent.

SOLUTIONS OF THE FUTURE

Many theories have been suggested to explain the properties of solutions. However, there is no general theory of solution which can explain the observed phenomena or predict new phenomena from a unified point of view. But the scientists need a general theory of solution since they cannot solve many urgent problems without such a theory. The role of the theory of solution is especially important for our future. To illustrate this importance we shall just mention the role of the theory of the liquid state in the development of stable and reliable control and information systems. A new branch of science and technology, chemotronics, will play a very important part in this. The development of chemotronics has led to the creation of liquid electrochemical converters, in which ions in solution (instead of electrons) perform the role of current carriers. At the present time these apparata are inferior to those utilizing solids or gases with respect to the rate of information processing, but the future of liquid converters looks promising. A liquid base has at least two important advantages: a multitude of various processes can occur simultaneously within a small volume of liquid, and liquids are able to retain and stabilize very complicate systems without limiting their mobility or interactive possibilities. Neither solids nor gases can possess these two properties simultaneously, whereas liquids allow the creation of complex and multifunctional control systems. Note that prototypes of such systems are the living cell and the human brain.

Chapter Two

Structure of Liquid

The most significant results of the theory of the liquid state have been obtained on the basis of our understanding of liquids as disordered solids which retain the short-range order (order in the vicinity of each particle), while the long-range order, which is characteristic of the solid state, is destroyed by heat motion.

This idea was suggested in the '20's by Ya.I. Frenkel,* the Soviet scientist from Leningrad. The hypothesis was later supported roentgenographically, radio-optically, spectroscopically, thermodynamically, etc. As a result we are now able to discuss the structure of liquids, and the structure of solutions.

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* Frenkel, Yakov Ilyich, (1894-1952), a Soviet physicist, corresponding member of the USSR Academy of Sciences. Famous for his work in quantum theory of metals. He was the founder of the theory of ferromagnetism. The author of fundamental works on the theory of the liquid state, atmospheric electricity, physics of the atmosphere, and terrestrial magnetism, biophysics and astrophysics.

One of the direct methods of obtaining information on the structure of solvents and solutions is roentgenography. It is based on the determination of the intensity of diffusion of X-rays and the calculation of the so-called radial distribution function which in turn enables one to find internuclear distances, angles, etc.

RADIAL DISTRIBUTION FUNCTION

The radial distribution function, normally designated as $g(r)$, shows how particles are grouped round an arbitrarily selected particle. In other words, it shows at what distance from the given particle other particles are compacted (the function maximum) or least concentrated. The physical sense of the function $g(r)$ is that it gives the relative probability of finding molecules at a distance r from the fixed molecule. (Fig. 1). The straight line depicting the function $g(r)$ for a gas indicates the random distribution of gas molecules relative to one another, while the peaks on the graph indicate the fixed position of the molecules in a solid body. The function of interatomic distances is continuous for liquids, with extrema in the form of fading oscillations about unity. An observed molecule can be at any distance from the fixed molecule but there exists a greater probability of meeting it at certain distances, which depend on the intermolecular interaction. They are characterized by the maxima on the curve of the function $g(r)$.

POSSIBILITIES OFFERED BY EXPERIMENTAL METHODS

X-ray structural analysis has shown that the arrangement of particles in a liquid (especially near the solidification point) is similar to the regular arrangement

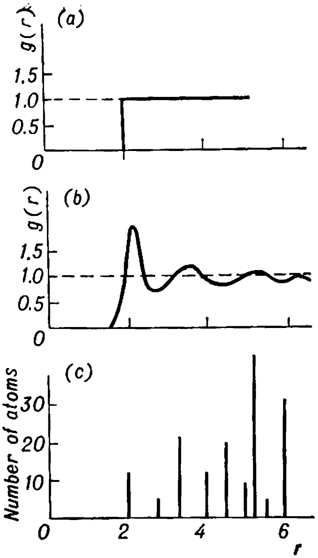

Fig. 1. Radial functions $g(r)$ of interatomic distances r: *a* — for rarefied gas; *b* — for liquids with compact arrangement of monatomic molecules; c — for solid crystal.

of particles characteristic of a solid substance. Liquid is characterized by the short-range order in the relative location of molecules at small distances, but the long-range order, inherent in solids, is absent. The roentgenographic method, which is successfully used to analyse the structure of monatomic liquids, encounters certain difficulties in deciphering the molecular structure of solutions, the structure of polyatomic solvents, the coordination of ions in the region of short- and long-range solvation. Radiophysical methods offer new possibilities for studying the structure of polyatomic solvents. High-frequency measurements of the dielectric constant and dielectric loss supply information on the structure of polyatomic solvents. Optical, ultrasonic and thermodynamic methods can also be used to obtain valuable information on the structure of solvents and solutions. Magnetic resonance and nuclear spin echo methods seem to offer many advantages in measuring the absolute value of relaxation time and in studying auto-diffusion in water and other liquids. But none of these methods alone can supply sufficiently complete information on the structure of solvents and solutions. The problem can only be solved by the intelligent combination of various methods of investigation. Strange as it may seem, despite the wide use of the structural concepts of solution, the structure of solvents and solution was not determined until recently.

CHARACTERISTICS OF STRUCTURE OF SOLUTIONS

It is customary to differentiate between molecular and supramolecular structures in solution. The former is associated with the interaction of ions with the nearest molecules of the solvent and shows itself in the molecular structure of the solvate (a case of strong interaction between ion and solvent). The supramolecular structure is due to the interaction between the molecules of the solvent; it concerns their arrangement relative to one another. These structures are intimately connected with each other and make up the complete structure of the solution which is characterized by the short-range order (more stable molecular structures), whereas the long-range order is destroyed by heat motion (less stable supramolecular structures).

The solution structure could be said to be fluctuating or intermittent because of the incessant exchange between the solvent molecules both in the regions of short-range and long-range solvation and between these regions. The structures are in dynamic equilibrium in the solution. Structures of one type are destroyed to form structures of the other type, but under certain conditions the structure of the solution remains constant within a long period of time.

DEFINITION OF STRUCTURE

Thus, the structure of a solution is a certain orderliness of the arrangement of the interacting particles of solute and solvent molecules (relatively stable in space and time) with respect to an arbitrarily chosen particle, which corresponds to their most probable distribution.

The structure of pure and mixed solvents is defined similarly. It is the orderliness of the arrangement, relatively stable in space and time, of the interacting solvent molecules with respect to an arbitrarily chosen molecule, which corresponds to their most probable distribution.

LIQUID WATER

The theory of the structure of water has made an appreciable advance in recent years. Entirely new models of the structure of water have been created which have greatly helped us in our understanding of aqueous solutions. The way in which molecules of water arrange themselves with respect to one another (the short-range order) has been established and the role played by the electron state of water and hydrogen bonding has been determined.

MODELS FOR THE STRUCTURE OF WATER

Several models for the structure of pure water are known. These models range from the simplest associates and an ice-like model to gel-like masses which are characteristic of polypeptides and polynucleotides (an endless random branching gel with hydrogen bonds being quickly formed and destroyed). The selection of a model of liquid water depends on the particular properties under study. Each model illustrates certain properties of water structure and cannot be regarded as the only correct model.

The model developed by O.Ya. Samoilov* is confirmed by much experimental data. According to this model, the short-range order in the arrangement of molecules, which is inherent in water, is an ice-like tetrahedral structure distorted by heat motion whose cavities are partly filled with water molecules. The energy of water molecules inside the cavities of this ice-like framework is different from the energy of water molecules at its vertices. Water is characterized by the tetrahedral structure of its molecules. Three neighbours of each molecule in liquid water are located in one layer and are farther from this molecule (0.294 nm) than the fourth molecule in the middle layer (0.276 nm). Each water molecule in the ice-like structure forms one mirror-symmetrical (strong) and three centre-symmetrical (less strong) bonds. The former is the bond between the water molecules of a given layer with the neighbouring layers, and the latter are the intermolecular bonds of water molecules inside one layer (Fig. 2). One bond out of four is therefore mirror-

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* Samoilov, Oleg Yakovlevich (b. 1921), a prominent Soviet investigator in the field of theory of solution. He invented the ice-like model of the structure of water and is one of the founders of the kinetic theory of hydration of ions.

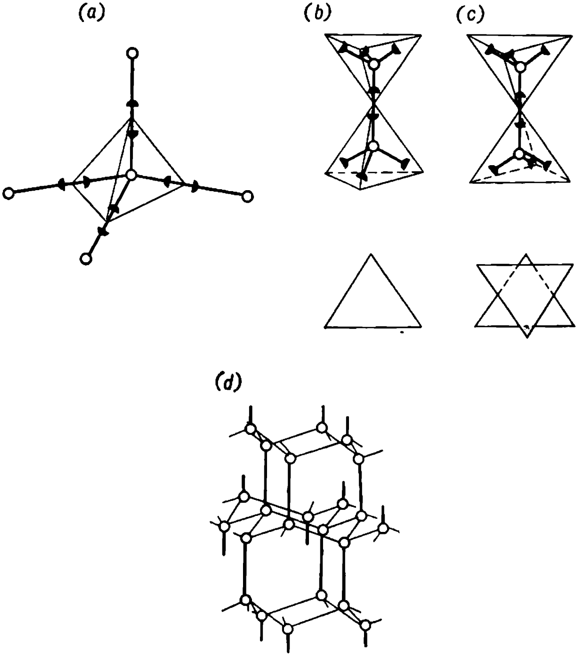


Fig. 2. Elements of liquid water structure:

a — elementary water tetrahedron (hollow circles indicate oxygen atoms and black half-circles indicate probable position of protons on the hydrogen bond); *b* — mirror symmetrical position of tetrahedrons; *c* — centre-symmetrical arrangement of tetrahedrons; *d* — arrangement of oxygen centres in the structure of common ice.

symmetrical, and the other three centre-symmetrical. The idea of the tetrahedral surrounding of the water molecule has led to the conclusion that its structure is very open and delicate and has cavities whose dimensions are equal to or exceed the size of the water molecule.

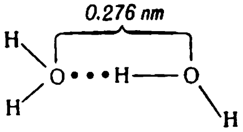


Fig. 3. Hydrogen bond between water molecules.

INTERMOLECULAR ACTION

Liquid water is characterized by strong intermolecular forces arising from hydrogen bonding that forms the space lattice. The hydrogen bonding is due to the ability of the hydrogen atom, connected with the electronegative element, to form an additional bond with the electronegative atom of another molecule (Fig. 3). The hydrogen bond is relatively strong and is measured by several kilojoules per mole. Its strength is somewhere between the van der Waals forces and the energy of a typical ion bonding. The energy of the chemical bond H—O in a water molecule is 456 kJ/mole, while the energy of the hydrogen bond H · · · O is 21 kJ/mole.

NON-AQUEOUS AND MIXED SOLVENTS

LIQUIDS ARE DIFFERENT . . .

The situation when modelling structures of other liquids is worse. Only details of the structures of the molecules themselves are known sufficiently well. Therefore in discussing the structure of liquids the investigators content themselves as a rule with establishing whether or not liquids are characterized by association. The models we have are too general. This is so even for the liquids most studied, e.g. alcohols. Most of the research connected either directly or indirectly with the structure of solutions and pure solvents has shown that compared with water, non-aqueous solvents are characterized by a closer packed structure. So it can be said that at the present time we can only outline general trends in the development of the theory of liquid state of non-aqueous solvents and special cases in which this problem has been solved. Much tedious work should be done in this field.

According to their physical nature, liquids are classified as normal liquids, liquid crystals with a strongly expressed anisotropy (the dependence of properties on the direction) and quantum liquids, e.g. liquid ^{4}He, ^{3}He, and their mixtures having specific quantum properties at very low temperatures. Normal pure liquids have only one liquid phase, i.e. there exists only one type of each normal liquid. ^{4}He can exist in two liquid phases, namely in the normal and superfluid states, whereas liquid crystals can exist in the normal liquid phase and in one or even two anisotropic phases.

CLASSIFICATION OF SOLVENTS

The classification of non-aqueous solvents is very important. As a rule, solvents are grouped according to the classes of chemical compounds, viz., alcohols, ketones, carboxylic acids, ethers, etc. But this approach fails to show what the solvents belonging to different classes have in common and how they differ. Many attempts have been made to work out a classification based on physical or chemical properties of non-aqueous solvents. It is obvious that such a classification cannot be universal since only particular qualitative or quantitative characteristics are considered. Nevertheless this classification is useful in many cases.

Using the value ε, it is possible to distinguish between solvents with high (>50), medium (12-50) and low (<12) dielectric constants. Electrolytes in solvents with high values of ε behave like strong electrolytes and in solvents with medium and low values of ε, like weak ones. As the value of ε increases, solvents become more polar as a rule. Solvents with low dielectric constants are non-polar liquids.

The chemical classification of solvents is based mainly on their acid-base properties. In this respect they are divided into aprotic and protolytic solvents. The former group comprises solvents that cannot enter into acid-base interaction connected with the proton transfer (hydrocarbons, halogen derivatives, etc). The latter group includes solvents that are capable of proton transfer and act like proton donors or acceptors with respect to the solute. Depending on whether the solvent acts like a donor or an acceptor of protons, solvents are subdivided into protogenic (acid), protophilic (basic), and amphiprotic solvents (exhibiting both protogenic and protophilic properties).

Solvents can also be classified according to their ability to form complexes, hydrogen bonds, and other properties of more special character.

INORGANIC SOLVENTS

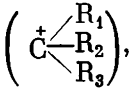
The most widely used and best studied inorganic solvents are sulphuric acid and ammonia. Sulphuric acid is a good solvent for electrolytes since it is characterized by a high dielectric constant and marked polarity of its molecules which are capable of forming strong hydrogen bonds. When dissolved in sulphuric acid, electrolytes can act like acids:

$$HA + H_2SO_4 = H_3SO_4^+ + A^-$$

or like bases:

$$B + H_2SO_4 = BH^+ + HSO_4^-$$

Since sulphuric acid is characterized by high acidity, most electrolytes behave like bases in the acid. Sulphuric acid has proved to be a valuable solvent for weak bases: ketones and nitro compounds. Moreover, sulphuric acid can be used to prepare stable solutions of reactive particles such as the carbonium ion



$\left(\overset{+}{C}\begin{matrix}R_1\\R_2\\R_3\end{matrix}\right)$, and the nitronium ion ($O=\overset{+}{N}=O$), etc. These ions are unstable in solvents with stronger basic properties.

ORGANIC SOLVENTS

Monohydric alcohols are the most well studied organic solvents. Owing to the structure of their molecules, saturated monohydric alcohols cannot form three-dimensional network of hydrogen bonds. They are susceptible to chain-like association. In addition to linear associations, monohydric alcohols can form cyclic associates. The association degree decreases markedly with the increasing molecular mass of alcohols, with the transition of normal alcohols to isomeric ones, with increasing temperature, addition of certain substances, etc. The distinctive characteristic of monohydric alcohols is their denser packing compared with water.

The structure of polyhydric alcohols (ethylene glycol, glycerol, diethylene glycol, etc.) is less well-known. Their molecules have two or more hydroxyl groups and so polyhydric alcohols form three-dimensional grating of hydrogen bonds. The density of hydrogen bonds in ethylene glycol is 1.5-2 times higher

TABLE 1. Dielectric Constant ε of Solvents at 298.15°K

Solvent	ε	Solvent	ε
Hexane	1.88	Benzonitrile	25.2
Heptane	1.93	Diethylene glycol	29.4
Octane	1.94	Methyl alcohol	32.63
Cyclohexane	2.02	Nitrobenzene	34.82
Carbon tetrachloride	2.28	Acetonitrile	36.02
Benzene	2.3	N,N-dimethyl formamide	36.71
Carbon disulphide	2.63	Ethylene glycol	37.67
Acetic acid	6.19	Glycerol	42.5
Aniline	6.99	Dimethyl sulphoxide	46.6
Pyridine	12.3	Formic acid	56.1
Benzyl alcohol	13.1	Propylene carbonate	65.1
Amyl alcohol	13.2	Heavy water	78.25
Ammonia	16.9	Water	78.35
Isobutyl alcohol	17.24	Sulphuric acid	101
Butyl alcohol	17.7	Hydrocyanic acid	106.8
Isopropyl alcohol	18.3	Formamide	109.5
Propyl alcohol	20.1	N-Methylformamide	182.4
Acetone	20.70		
Ethyl alcohol	24.30		

than in monohydric alcohols. Polyhydric alcohols have hardly any comparatively small associations or separate molecules. The heat motion of the molecules destroys or distorts the hydrogen bonds to weaken the local intermolecular forces, but the similarity to a moving three-dimensional grating of molecules connected by hydrogen bonding remains. Information on the structure of the other liquid non-aqueous solvents is either insufficient, or controversial, and so we shall not discuss it in this book.

The structure of mixed solvents depends on the mutual effects that the components produce on one another. This influence is irrefutably confirmed firstly by the divergence of the actual properties of solutions from the average values of the properties of their constituent parts, and secondly by the presence of extrema on the composition-property curves. Aqueous solutions of monohydric alcohols are the best understood of all mixed solvents with respect to their structure. According to modern views three structural regions are distinguished in them, namely, water, mixed alcohol-water region, and alcohol. The concentration boundaries of these regions are shifted in this or that direction depending on the nature of the alcohol, temperature, and some other factors. X-ray structural analysis has shown that the tetrahedral structure of pure water is retained to concentrations of monohydric alcohols of 0.2-0.3 molar parts. In this region of concentrations the alcohol molecules enter the cavities of the ice-like structure of water to limit the translation motion of water molecules and to stabilize its structure. The stabilization is accompanied by the decreasing factor of auto-diffusion, and by the appearance of extrema on the curves illustrating the dependence of the heat effects of mixing and dissolving on the composition. This phenomenon is also observed when mixing other liquids. It has also been discovered that the structure of one liquid is destroyed upon the addition of another liquid.

In the literature two mechanisms have been considered for stabilization of the structure of water by molecules of non-electrolytes: interstitial and interstitial-substitutional. According to the former mechanism (hydrophobic) the molecules of non-electrolyte are fully accommodated in the cavities of the water lattice. By the other mechanism (hydrophilic), part of the dissolved molecule substitutes for water at the points of the ice-like lattice, whereas the remaining part fills the cavities. Smaller molecules, e.g. of methyl alcohol, enter the cavities to slightly deform the lattice, while larger molecules bring about a strong deformation or rearrangement into a dodecahedral structure.

In the interpretation of experimental results, such notions as the stabilizing of a solvent structure, and its destruction are used. First, they were understood in the narrow sense and were used only for aqueous solutions, but later their meaning was considerably widened. At present, the stabilization of the structure of a solvent by adding another solvent is understood as the weakening of solvation of its particles with increasing concentration of the second component. And vice versa, by the collapse of the structure is understood the intensification of the particle solvation. In the general case, the stabilization (destruction) of the solvent structure should be understood as decreasing (increasing) mobility of the solvent molecule and the associated effects produced by adding non-electrolyte or by varying temperature, pressure, etc.

Chapter Three

Electrolytes in Solution

In the first half of the past century several phenomena were discovered which are associated with the passage of an electric current through a salt solution. The most important discoveries in this field were made by Michael Faraday*. He made a thorough study of electrolysis and classified substances into electrolytes whose solutions conduct electricity and non-electrolytes whose solutions do not conduct electric current. It was discovered that salts, acids, bases are electrolytes and most organic substances are non-electrolytes. Faraday introduced into science the terms electrode (cathode and anode), ion (cation and anion), electrolysis, etc.

Aqueous solutions of electrolytes have a number of properties that distinguish them from solutions of non-

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* Faraday, Michael (1791-1867), the English physicist, the founder of the theory of electromagnetic field. He discovered electric and magneto-electric induction, paramagnetism and diamagnetism, and the magnetic rotation of the plane of polarized light. The laws of electrolysis were established by Faraday in 1833-1834.

electrolytes. They have a higher osmotic pressure, higher boiling points and lower freezing points, they conduct electric current, etc. These specific properties can be explained only if we suppose that the molecules of electrolyte fully or partly separate into their constituent parts, ions. As reacting particles, ions take part in dissolution, solvation, ionic sublimation, in electrochemical, oxidation-reduction processes, etc. In other words, along with atoms, molecules and radicals, ions are fundamental structural units of substances.

IONS AS SPECIAL PARTICLES

The specific property of ions is the charge which determines their behaviour in the gaseous and solid states, and in solution. Ions are the basis of plasma, electrolyte solutions, many crystals, etc.

CLASSIFICATION OF IONS

Ions can be classified according to various attributes. By the sign and magnitude of the charge on the ion, they may be classified as singly charged ions, e.g. Na^+, F^-, and as multiply charged ions, e.g. Ca^{2+}, S^{2-}, Al^{3+}, or as cations (positively charged ions) and anions (negatively charged ions). By the number of atoms and the character of bond between them, ions can be classified as monatomic (K^+, Cl^-) and polyatomic (NO_3^-, SO_4^{2-}), simple ions (Ni^{2+}, Cu^{2+}) and complex ions, such as $[Co(NH_3)_6]^{3+}$, $[Ag(CN)_2]^-$*. Ions can also differ in mass and size. Ions are often subdivided according to the element position in the

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* Information on complex compounds can be found in the book by Yu. A. Makashev and V. M. Zamyatkina, *Compounds in Brackets*, Khimiya, Leningrad, 1976 (in Russian).

Periodic Table (e.g. ions of the elements of groups I-VIII, ions of the elements of periods I-VI, ions of the transition elements, etc.). According to their electron structure, ions may be divided into four groups (*s*-, *sp*-, *sd*-, and *sf*- or *sdf*-ions).

GENERAL CHARACTERISTICS OF IONS

The most interesting among *s*- and *sp*-ions are those having s^2 and s^2p^6 electron configurations in their outer shells (Li^+, Cs^+, Mg^{2+}, Se^{2-}, Br^-, I^-, etc.). The electron configurations of these ions are described by the electron formulae of the noble gases, He, Ne, Ar, Kr, while their distinguishing feature is their stability in various states of aggregation.

The *sd*-ions of the transition elements (Ti^{2+}, Cr^{3+}, Fe^{3+}, Zr^{4+}, Hf^{4+}, and others) are rather unusual. Ions having the charge 2+ and higher have no electrons at the *s*-subshell and therefore they are converted into *d*-ions. These peculiarities of the electron structure account for the special properties of the transition elements. They are characterized by many states of oxidation, their solutions are often brightly coloured, they often form complex compounds, etc. A special place is also occupied by the *sf* (*sdf*)-ions of rare earth elements and actinoid elements (Eu^{2+}, Gd^{3+}, Pu^{4+}, and others), in which the electrons are absent in the *s*- and *d*-subshells. Such ions convert into *f*-ions and show much similarity in their chemical behaviour since deep electron subshells are being filled in this case.

The rule of increased stability of unfilled, half-filled, and completely filled *d*- and *f*-subshells (electron configurations d^0, d^5 and d^{10}; f^0, f^7 and f^{14}) holds for the transition element ions. The characteristics of the electron distribution of these ions and the differences in their oxidation numbers well explain this rule. It should be noted that to understand the special properties of ions of the transition elements it is very important to consider the small difference between the energies of the $(n-2)f$- and $(n-1)d$-orbitals, the strengthening of the bond of the f- and d-electrons with the nucleus compared with the s-electrons during ionization, the penetrating character of f- and d-orbitals, etc.

Other more particular properties that determine ions behaviour in various processes can be used in their classification. The general character of ions is based on the combination of many properties such as charge, size, mass, electron structure, and so on. It should be noted that the properties of ions strongly depend on the medium in which they are present and the conditions. All these characteristics will be discussed in more detail below.

STOICHIOMETRIC MIXTURE OF IONS

In the gaseous state and in solution, in normal conditions, ions exist as inseparable mixtures of oppositely charged particles in which the ratio between the numbers of cations and anions is expressed by strictly discrete magnitudes. Such mixtures are known as stoichiometric. A stoichiometric mixture of cations and anions in the gas state and solution is such a mixture in which the ratio of the number of their gram-ions is equal to the ratio of the ion charge values with their signs reversed, i.e.

$$\frac{a}{b} = \frac{[z_A]}{[z_k]}$$

where a and b are the stoichiometric coefficients of cation and anion in the formula of salt $M_a X_b$. For example, $Na^+ + Cl^-$, $2K^+ + SO_4^{2-}$, $2Al^{3+} + 3SO_4^{2+}$,

$Ti^{4+} + 4Cl^-$, etc. Since most of the properties have been established not for individual ions in solution but for their stoichiometric mixtures, it is necessary to use this concept. We shall use the concept of stoichiometric mixture in the discussion of the thermodynamic characteristics of solvation, activity coefficients, etc.

IONS IN SOLUTION

When many compounds dissolve, solvated ions are formed or the electrolytic dissociation process occurs.

WHERE DO IONS APPEAR FROM IN SOLUTION?

An important role in the process of electrolytic dissociation is played by the solvent. It consists in the decomposition of the electrolyte, solvation of the formed ions, and formation of conditions for separation of oppositely charged ions. The process of electrolytic dissociation runs easier when the solvent molecules are more polar. The formation of solvated ions during dissolution of covalent compounds is connected with the so-called heterolytic cleavage of bonds. The electron pair responsible for the covalent bond remains at one atom or a group of atoms, i.e. the process is as follows:

$$A \,|\, : B \rightarrow A^+ + B^- \quad \text{or} \quad A : |\, B \rightarrow A^- + B^+$$

Strongly ionizing solvents are water, alcohols, and liquid ammonia.

STRONG AND WEAK ELECTROLYTES

Electrolyte solutions are classified as weak and strong, according to their ability to dissociate into ions. Weak electrolyte solutions consist of molecules that partly fall into ions by the action of the solvent. Strong electrolytes consist of ions. In solution they quickly form solvated ions which fact accounts for the special properties of such solutions. It should be remembered that the classification of electrolytes into weak and strong is only conventional. It depends on the concentration of the electrolyte, the nature of the solvent, and on some other factors. For example, all electrolytes behave like strong electrolytes in very dilute solutions. Sodium iodide in water behaves like a strong electrolyte, while in acetone or acetic acid like a weak one.

MODELLING SOLVATED ION

The state of a solvated ion in solution can be represented as follows

$$\left\{\left[\mathrm{M}^0 \overset{\mathrm{I}}{\underset{\mathrm{I}}{\vdots}} \mathrm{R}_n^{z_1}\right]\overset{\mathrm{II}}{\underset{\mathrm{II}}{\vdots}} \mathrm{R}_{p+t}^{z_2}\right\}^{z}\overset{\mathrm{III}}{\underset{\mathrm{III}}{\vdots}}, \qquad z = z_1 + z_2$$

where M and R are the ion and the molecule of the solvent; n and $(p + t)$ are the number of molecules of the solvent in the short- and long-range environment.

Separation of the whole mass of the solvent molecules in the long-range environment into two parts p and t is essential when the molecules in the short-range environment R_n form the complex ion $[\mathrm{MR}_n]$ which can be considered as a complex particle; I — I, II — II, and III — III are the interphases characterizing the division of the system "solution" into sub-systems: ion proper (I), solvent molecules in the short-range (II) and long-range (III) environment.

This scheme shows vividly the dependence of the state of ion in solution on various factors, such as concentration of electrolyte, nature of solvent, ion, etc. This accounts for certain indefiniteness in characteristics of ions even by the interphase I — I. Let us consider this indefiniteness using the radii and charges of ions in solution as an example. According to some authors, the numerical values of radii of monoatomic ions are close to crystallochemical, obtained by a certain method of dividing interion distances in crystals, and according to other authors they differ from them. Various 'effective' radii are usually used. The constancy or variation of the radius of ion, as it transfers from the crystal state into solution, depends on the charge which is attributed to the ion. If we assume that the charge on the ion in a crystal and in solution is the same as in the gaseous state, then it would be more correct to assume that the radius of an ion in solution is equal to the crystallochemical radius. On the other hand, if we assume that the charge on the ion in crystal and in solution is equal to a certain effective charge, which is different from the charge on the ion in the gaseous state, then the radius of the ion in solution and in crystal can differ significantly. However, it is very difficult to account for all these changes.

It is even more difficult to characterize the ions by the other interphases between the ions and the solvent. The study of the coordination of ions by the solvent molecules is important here. The analysis of data on the effect of the nature of the solvent on the state of monatomic ions in solution has shown that their translatory motion is limited compared with gas, this limitation being greater in aqueous solutions compared with non-aqueous solutions. At higher temperatures (60-70°C) this difference practically disappears.

ELECTROLYTIC DISSOCIATION

WEAK ELECTROLYTES

The theory of electrolytic dissociation relates to solutions of weak electrolytes. In discussion of the properties of weak electrolyte solutions, one should pay special attention to two points. The first point is that the physical properties of weak electrolyte solutions (osmotic pressure, relative lowering of the saturated vapour pressure over the solution, elevation of the boiling point and lowering of the freezing point) approximately obey the ideal solution laws, i.e. they depend only on the number of particles in solution. The explanation of this can be found in the low concentration of ions in a weak electrolyte solution, so the electrostatic interactions between the ions are insignificant especially in dilute solutions. Moreover, if the solution is dilute and is close in its properties to the ideal solution, we can apply the law of mass action to the process of electrolytic dissociation since the dissociation of a weak electrolyte is a reversible process and a dynamic equilibrium is established in the solution' between the ions and the undissociated molecules. This is the second of the points mentioned above concerning weak electrolyte solutions.

QUANTITATIVE CHARACTERISTICS

The process of electrolytic dissociation can be characterized quantitatively by the following: the degree of dissociation α (the ratio of the number of dissociated molecules to the total number of dissolved molecules), isotonic coefficient (van't Hoff coefficient)* i (the ratio

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* van't Hoff, Jacobus Heinricus (1852-1911), an outstanding Dutch chemist, one of the founders of modern physical chemistry and stereochemistry. He was the first to win the Nobel Prize for chemistry.

of the total number of ions and undissociated molecules of the electrolyte to the number of dissolved molecules), the dissociation constant K_d and others.

The degree of electrolytic dissociation depends on the nature of the electrolyte and its concentration, on the nature of the solvent, and temperature. The dissociation degree of weak electrolytes quickly diminishes with increasing concentration of solution. The equivalent conductivity λ of these solutions changes in a similar fashion. Electrolytic dissociation is more easily accomplished in media with higher dielectric constants, since the interaction between the ions weakens in them. But it should be understood that a high dielectric constant only facilitates dissociation, and it is not an 'active force' responsible for the dissociation process. As we have already mentioned this role is played by the interactions between the molecules of the solute and the polar molecules of the solvent which have an electrostatic or donor-acceptor character.

The quantitative characteristics in question, i.e. the degree of dissociation α and the isotonic coefficient i are not convenient for a comparative assessment of the ability of electrolytes to dissociate into ions. The point is that both characteristics depend on the concentration of the electrolyte in solution. Therefore, in order to compare the ability of two or more electrolytes to dissociate into ions, it is necessary to study solutions of equal concentration. It is desirable to have a characteristic that could be used to assess the ability of an electrolyte to dissociate without taking into consideration its concentration in solution. This characteristic is the dissociation constant K_d of a given electrolyte which is determined from the law of mass action. For the process $KA \rightleftharpoons K^+ + A^-$

$$K_d = \frac{[K^+]\cdot[A^-]}{[KA]}$$

where $[K^+]$ and $[A^-]$ are the ion concentrations in solution, in moles per litre, and [KA] is the concentration of undissociated molecules (also in moles per litre).

Each electrolyte is characterized by its own dissociation constant whose magnitude does not depend on the concentration of solution, but depends on temperature. The higher the value of K_d, the stronger the electrolyte. Substituting concentrations of the reacting substances expressed in terms of the degree of dissociation into the equation for K_d, it is easy to obtain a relationship between the dissociation constant K_d and the degree of dissociation α:

$$K_d = \frac{c\alpha^2}{1-\alpha}$$

where c is the concentration of the solute (in moles per litre).

This expression, known as the dilution law, can be used to calculate K_d for weak electrolytes, provided α and c are known, and also to calculate α for any c provided K_d is known. If the degree of dissociation is small, a simplified expression for the dilution law is often used, $\alpha = \sqrt{\frac{K_d}{c}}$, from which its formulation becomes quite evident: the degree of dissociation increases with increasing dilution (lowering concentration).

SPECIFIC PROPERTIES OF STRONG ELECTROLYTE SOLUTIONS

Arrhenius* in his days was of the opinion that strong electrolytes differ from weak electrolytes only in their higher degree of dissociation, and that solutions of strong electrolytes also contain undissociated molecules. In this connection, the degree of dissociation of strong electrolytes was determined by the same methods as for weak electrolytes, namely, by measuring electric conductivity, changes in osmotic pressure, elevation of the boiling point and lowering of the freezing point, etc. However, data obtained by various methods for strong electrolytes had considerable divergences while for weak electrolytes discrepancies were not observed in the data.

As we have already mentioned, strong electrolytes are fully dissociated into ions in solution. In this case it is impossible to disregard the interaction between the ions. The interionic electrostatic forces depend largely on the charge of the ions, the concentration of the electrolyte, the dielectric constant of the medium, and on some other factors. The interionic effects weaken with decreasing charge on the ions and lowering concentration of the electrolyte. The increase in the dielectric constant produces the same effect. It should be noted that the intensification of the electrostatic action between the ions in solution due to an increase in the concentration of the electrolyte produces an apparent lowering of the

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* Arrhenius, Svante August (1859-1927), the Swedish physico-chemist. One of the founders of the physico-chemical theory of solutions. Suggested the theory of electrolytic dissociation, established the dependence of the reaction rate constant on temperature. He is the author of some investigations concerning application of the physico-chemical laws to biological processes. A Nobel Prize winner (1903).

degree of electrolytic dissociation of a strong electrolyte. Several properties of strong electrolyte solutions confirm this. For example, optical methods fail to detect the existence in solution of the molecular form of a strong electrolyte. If undissociated molecules existed in a strong electrolyte solution, they would be detected in the absorption spectra of the solution. Dark bands indicating the molecular absorption of light would then appear in the spectra. But even the absorption spectra of very concentrated solutions of typically strong electrolytes have no such bands. This experimental fact indicates complete dissociation of the electrolyte. This conclusion can also be reached by measuring the heat effects of neutralization reactions for strong electrolyte solutions. They prove to be independent of the nature of the substances involved since solutions of strong electrolytes are completely dissociated, i.e. $\alpha = 1$, and we can measure the heat effect of the process

$$H^+ + OH^- = H_2O$$

On the other hand, the degree of electrolytic dissociation calculated from data on the electric conductivity of strong electrolyte solutions at their limit concentration λ and at infinite dilution λ_∞, i.e. from the ratio $\alpha = \frac{\lambda}{\lambda_\infty}$, turns out to be less than unity. It is known as the apparent degree of dissociation, α_{app}. The term emphasizes the fact that α_{app} is not at all characteristic of the actual degree of dissociation (it is always unity for strong electrolytes).

Ions in solution are not so free and independent of one another as it seemed to Arrhenius. The conductivity of strong electrolyte solutions at a given concentration seems to correspond to a smaller number of ions than one would expect in a completely dissociated solution.

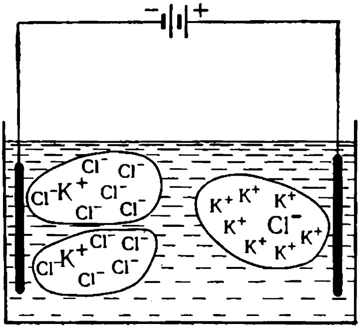

Fig. 4. Effect of ionic atmosphere on ion mobility in an electric field.

But this apparent reduction in the number of ions cannot be explained by their aggregation into molecules but can be accounted for the decreasing velocity of their motion due to electrostatic interaction. Each ion in a strong electrolyte solution seems to be surrounded by an "atmosphere" of ions of the opposite charge which impedes the movement of a given ion toward the electrode as the conductivity of the solution is being measured (see Fig. 4).

Another specific property of strong electrolyte solutions is that the law of mass action does not apply to the process of dissociation, at least in the form it is applied to weak electrolyte solutions. If we attempt to apply this law, for example to the dissociation of KCl, and calculate K_d (from α which could be determined experimentally from the conductivity for various concentrations) using the dilution law, then the "constants" of dissociation for concentrations 1.0, 0.1 and 0.01 N turn out to be 2.34, 0.54 and 0.15, respectively. The contradiction is quite clear: the invariable, known as the "constant" of dissociation, becomes a variable changing with the concentration of the solution. And yet we *can* apply the law of mass action to strong electrolyte solutions. True, we must replace concentration by another quantitative characteristic, called the "activity".

ELECTROLYTE ACTIVITY AND IONIZATION OF MEDIUM

The properties of a strong electrolyte solution at limit concentrations will be affected by the electrostatic interaction between the ions.

ELECTROLYTE ACTIVITY

Let us imagine that the interionic attraction suddenly disappeared. If despite this we want to preserve the former properties in this new solution, we must change its concentration. This new "concentration" is called the effective concentration or the activity a of the electrolyte in solution. In other words, the activity of an ion in solution is that effective conventional concentration of the ion at which it takes part in chemical reactions:

$$a = fc$$

where f is the activity coefficient and c is the concentration.

Once we know what the activity is, we can use it to make the law of mass action applicable to solutions of strong electrolytes. The dissociation constant for a solution of KCl can be expressed as

$$K_d = \frac{a_{K^+} a_{Cl^-}}{a_{KCl}}$$

The activity coefficient of an electrolyte can be considered a measure of non-ideality of a system. The coefficient is closely connected with other factors, such as interionic action, ionic association, and ionic repulsion, most of which can be considered from the standpoint of electrostatic interaction. The magnitude of the coefficient can be determined experimentally. This is usually done by measuring the e.m.f., the electric conductivity, etc.

IONICITY OF MEDIUM

Another quantitative characteristic of strong electrolyte solutions is the ionicity I of medium. A less suitable name for this phenomenon is "ionic strength".

The ionicity of the medium in the general form takes into account the interaction between all ions present in solution. It makes it possible to draw correct conclusions about the activity of any particular ion. The extent to which the properties of an electrolyte solution deviate from those of an ideal solution depends on the intensity of the electric field resulting from the appearance of positively and negatively charged ions. The ionicity of a medium is a measure of the electrostatic interaction between all ions in solution. If ions of another electrolyte are also present in an electrolyte solution the intensity of the total electric field will be the sum of the field intensities of both electrolytes. Theory shows that the contribution of each kind of ion to the intensity of the electric field is proportional to the concentration of the ion and to the square of the charge, the proportionality factor being 1/2. Thus, the ionicity of the medium can be described by the following expression:

$$I = \frac{1}{2} z_1^2 c_1 + \frac{1}{2} z_2^2 c_2 + \ldots + \frac{1}{2} z_n^2 c_n = \frac{1}{2} \sum_{i=1}^{N} z_i^2 c_i$$

where c_1, c_2 . . . are the concentrations of different ions, and
z_1, z_2 . . . are the corresponding charges on these ions.

RELATIONSHIPS BETWEEN ACTIVITY COEFFICIENT AND IONICITY OF MEDIUM

There exists a relationship between the molar coefficient of electrolyte activity and the ionicity of the medium of the solution. This relationship can be formulated thus: the more dilute the solution, i.e. the less the ionicity of the medium, the higher the value of f, i.e. the closer the activity to the analytical concentration. For one and the same dilution (i.e. for given I) the activity coefficient increases with decreasing charge on the ion. The dependence of the variation of f on the ionicity of the medium is stronger for ions bearing greater charges than for ions carrying smaller charges. The mathematical relationship between the activity coefficient and the ionicity of the medium, which can be derived from the Debye-Hückel theory, is given in Chapter 6. The main disadvantage of the relationship is the limited possibilities for its application to medium and high concentrations of the electrolyte. Hence for practical purposes a series of empirical equations are used. These equations describe the mutual relationship between the activity coefficient and the ionicity of medium for these concentrations.

ASSOCIATION OF IONS IN SOLUTIONS

If an electrolyte solution contains a sufficient quantity of ions, then there will develop appreciable interionic attraction which will result in their association.

WHAT CAUSES ASSOCIATION OF IONS IN SOLUTION

The first attempt to discover the cause of ionic association in solution was made by the Soviet chemist V.K. Semenchenko* early in the 20's. He explained the association by the Coulomb interaction between oppositely charged ions. The energy of electrostatic attraction of such ions must exceed their heat (kinetic) energy, so a new particle is formed by them in solution, the so-called ionic pair, which is sufficiently stable to survive for long periods of time without being destroyed by molecules of the solvent. An ionic pair is not an undissociated molecule since its action is characterized by purely electrical forces.

The formation of an ionic pair from ions can be shown schematically as this

$$M^{b+} + X^{a-} \rightarrow [M^{b+}X^{a-}]^{b-a}$$

where the ionic pair is on the right-hand side. For example,

$$Ba^{2+} + Cl^{-} \rightleftarrows [Ba^{2+}Cl^{-}]^{+}$$

$$Ag^{+} + NO_3^{-} \rightleftarrows [Ag^{+}NO_3^{-}]^{0}$$

The association processes obey the law of mass action and other thermodynamic equations. The existence of ionic pairs has been verified experimentally by measuring electrical conductivity, e.m.f., optical properties, etc. It should be remembered that solvated ions undergo association. The formation of ionic pairs can be accompanied by complete or partial desolvation of ions, as well as by invariability of the solvate shells. If desolvation is complete, the ionic

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* Semenchenko, Vladimir Ksenofontovich (b. 1894), a Soviet scientist working in the field of the theory of solution. He formulated the general principle of solubility, developed the theory of ionic association, the molecular theory of superficial phenomena, etc.

pairs are called contact pairs, and in the other cases non-contact pairs (here ions are connected via the solvent molecules). Ionic pairs are characterized by high dipole moments.

In the discussion of ionic association, the question arises: when can two neighbouring ions of opposite charge be called an ionic pair? It is obvious that the life of an ionic pair must be relatively long for its role as a whole particle, a kinetic unit, to be appreciable. In his investigations of ionic association, V. Semenchenko equated the energy of electrostatic interaction between ions with the root mean square of the kinetic energy of ions, which is equal to 3/2 kT per ion (here k is the Boltzmann constant, equal to 1.38×10^{-23} J/deg). In this case the boundary condition for the generation of ionic pairs is the equality of these values. Further development of the theory of ionic association by N. Byerrum is based on the use of the most probable kinetic energy of the 2KT ions and Boltzmann's law in the consideration of ion distribution in solution.

EFFECT OF MEDIUM

One should not expect ionic pairs to be formed in great quantities in solvents with high dielectric constants (for example, water), even for high concentrations of ions. The formation of ionic pairs is more probable in solvents having low dielectric constants (which is the case for majority of non-aqueous solvents). Measurements of the electric conductivity of non-aqueous solutions of electrolytes conclusively demonstrate this is so. Moreover, triplets of the type (+ — +) or (— + —), for example,

$$Ag^+ + [Ag^+NO_3^-]^0 \rightleftarrows [Ag^+NO_3^-Ag^+]^+$$

$$NO_3^- + [Ag^+NO_3^-]^0 \rightleftarrows [NO_3^-Ag^+NO_3^-]^-$$

may be formed in such solvents. Larger ionic associations, reaching the size of a colloidal particle, are formed in solvents having very low dielectric constants. In addition to these particles, associations of the quadrupole type (± ∓ or − + + −) and others can be formed in strongly concentrated electrolyte solutions. Ion association in solution produces an important effect on the thermodynamic and kinetic properties of solutions.

Chapter Four

Solvation of Ions

The scientific principles of the theory of chemical interaction between the components of a solution were established by D.I. Mendeleyev*. He saw that the main shortcoming in the theory of electrolytic dissociation was the disregarding of the chemical interaction between particles of the solute and the solvent molecules. Kablukov's** idea of ion hydration in aqueous solutions and solvation in the general case accounts for this interaction. For a long period of time, ion solvation was explained by the electrostatic interaction of ions with the dipoles of the solvent molecules. But it is now clear that the electrostatic theory

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* Mendeleyev, Dmitrii Ivanovich (1834-1907), the great Russian scientist who discovered the Periodic Law of chemical elements. Mendeleyev's theory of solution became a foundation of the modern theory of solution. Mendeleyev established the concept of the critical boiling point. His investigations in the field of gases, metrology, etc. are also of great importance.

** Kablukov, Ivan Alekseyevich (1857-1942), an outstanding Soviet physico-chemist; worked in the field of electrochemistry of non-aqueous solutions, one of the founders of the physico-chemical theory of solutions.

of solvation has several significant defects. The interaction between atomic and molecular systems can be explained and calculated on the basis of quantum mechanical concepts. The phenomena observed in solutions depend on the intricate electronic structure of the ion and molecule of the solvent. At the same time, the electrostatic theory fails to explain the redistribution of electrons between the ions and the solvent molecules, which becomes quite obvious with spectral, X-ray structural, and other methods of investigating electrolyte solutions. However, for the sake of simplicity, we shall limit ourselves to the electrostatic approach to this problem, since it is the first natural step towards understanding of the causes of ion solvation.

Solvation of ions is involved in all the physical and chemical processes that occur in solutions. Suffice it to say that it determines the equilibrium and the rate of dissolution of solid and liquid substances, and of the various chemical transformations in solutions, etc. On the one hand, solvation changes the nature of the reacting particles (solvate complexes are formed, the ion charge is redistributed, polarization takes place and reacting centres are aggregated), and on the other hand, it leads to the formation of a medium in which chemical and physical processes occur. The manifestations of solvation and structure are unique among the phenomena of chemical kinetics. Here solvation of the starting substances, of the transition complex, and of the reaction products determines not only the rate of the process and other kinetic parameters of the reaction, but also their mechanism. It should be noted that the solvation interaction of the solvent with the transition complex has to be taken into consideration and analyzed in the development of a theory for the reactivity of molecules and the ion.

Before we go on to the discussion of the mechanism and thermodynamic characteristics of the ion solvation process, it is necessary to define in more detail the phenomenon in question.

DEFINITION OF SOLVATION AND ITS TYPES

WHAT IS SOLVATION?

The main disadvantage in the existing approaches to the phenomenon of solvation is the attempt to limit it to the interaction between the ion and the solvent only. But solvation is characterized by all types of interaction in solution: ion-solvent, solvent-solvent, ion-ion. Solvation is characterized by the dialectic integrity of all these interactions, the ion-ion interaction included. The latter is described tentatively as the interaction of point charges or charges of particles having a definite size. Here we must bear in mind the partial transfer of the ion charges onto molecules of the solvent. The role of the various types of interaction varies within wide limits depending on the concentration of the electrolyte, temperature, admixtures of non-electrolytes, and other factors.

An important element of ionic solvation is the coordination of the solvent molecules round the ion with the formation in the nearest surroundings of chemical bonds of the ionic or ionic-covalent type. In the solvation of ions of the type tetraalkylammonium $[N(CH_3)_4]^+$, these bonds are practically purely ionic for all known solvents. Ions of cobalt, platinum group metals, and some other ions form strong covalent bonds with many solvents, for example liquid ammonia. The concepts of solvation and complex formation are inseparable in this case. And if we remember that the short-range interaction of ion and solvent is accompanied by electron transfer from the orbital of the donor (reducer) onto the orbital of the acceptor (oxidant), it becomes quite obvious that the phenomenon of solvation can be considered as an oxidation-reduction process.

The ion-solvent interaction is accompanied by a substantial change in the structure of the solvent molecule (and also of the ion), especially if the molecules (or ions) contain sufficiently polar bonds, X—H. Under the influence of ions, the polarity increases to the cleavage of the proton. This process is nothing but the acid-base interaction, whose final stage is solvolysis (hydrolysis). The actual solvation process can be accompanied by ionic association since in solution we deal with a stoichiometric mixture of the interacting oppositely charged ions. Ionic association is the initial stage in the formation of the solid phase.

Ionic solvation illustrates the fact that the phenomenon of solvation (so far we speak only of short-range solvation) is a complex process embracing all known types of chemical interaction. At the same time, limiting cases of such interactions where chemical bonds are broken (solvolysis, association, and dissociation) are not included into the concept of solvation.

Thus, solvation is understood as the sum total of energy and structural changes occurring in a system in the process of the transition of gas molecules, ions, radicals, or atoms into the liquid phase, with the formation of a solution having a definite composition, excluding changes associated with the breakdown of the chemical bonds in the molecules of the solvent and solute. This definition assumes that only those bonds can be broken in the process of solvation that were involved in the construction of supramolecular structures of the solution. The combination of changes occurring during solvation of ions shows itself in the change of state of ions in solution, in their mobility, in the formation of definite aggregates of the ions and molecules of solvent, and in the change of the properties and structure of the solvent.

ION SURROUNDINGS

The changes associated with the ion-solvent and solvent-solvent interactions, occurring during solvation of ions, are usually divided into two groups: primary or short-range and secondary or long-range. The former group characterizes the interaction of the ion with molecules of the solvent that come in contact with the ion (the solvent molecules in the immediate vicinity of the ion), whereas the latter is the interaction of the ion with the other molecules of the solvent, beyond the near surroundings of the ion. Other terms are sometimes also used to describe these types of solvation: chemical and physical, first and second type, hydrophobic and hydrophilic, etc. Specific and non-specific solvations are also distinguished. Specific solvation of ions depends on the donor-acceptor interactions and the hydrogen bonding. Non-specific solvation is due to weak van der Waals forces.

TWO VIEWS OF ONE PHENOMENON

There are two general interpretations of the solvation phenomenon. One goes by the name of thermodynamic solvation (hydration). It is based mainly on the interaction ion-solvent and suggests that during solvation ions strongly bind a certain definite number of molecules of the solvent. This number is called solvation number.(hydration number for aqueous solutions). Solvation numbers are inconvenient for quantitative characteristics since they strongly depend on the method of determination. For example, according to various authors, the hydration numbers for the ion Li^+ vary from 158 to 4, for the ion Ca^{2+} from 16 to 6 and for the ion Al^{3+} from 39 to 6, etc. The number of solvent molecules that immediately surround the ion has a more definite sense. It is known as the coordination number. It is one of the most important quantitative characteristics of the solvation process. It is expressed in whole numbers and depends on the nature of the solvated particles, their concentration, etc. The approach to the solvation phenomenon on the basis of the prevalent role of the interaction ion-solvent is connected with the thermodynamic stability of the associate ion-solvent molecules, the measure of which is the total energy of the interaction between them. Apart from the coordination numbers, thermodynamic properties are widely used to characterize the thermodynamic solvation.

The other approach to the solvation phenomenon is known as kinetic solvation. It considers predominantly the interaction solvent-solvent and is connected with the concept of the kinetic stability of the associate ion-solvent molecules. The kinetic stability is determined by the activation energy, i.e. the surplus energy of the solvent molecules in the immediate vicinity of the ion, which is sufficient to accomplish their exchange for the solvent molecules, in the bulk or by the change of the potential barriers that separate the neighbouring equilibrium states of the solvent molecules due to the action of ions. This approach was suggested two decades ago by O.Ya. Samoilov to explain hydration of ions in aqueous solutions. The quantitative characteristics of ion hydration are values determining the frequency of exchange of water molecules in the vicinity of the ions

$$\tau_i/\tau \text{ and } \Delta E_i = E_i - E$$

where τ_i and τ are mean time of the presence of water molecules in the position nearest to the *i*th ion in the structure of solution and pure water; E_i and E are the activation energies of exchange of the water molecules nearest to the ion in solution and in pure water respectively; ΔE_i is the change in the value of the potential barrier that is overcome by the water molecule as it leaves the immediate surroundings of the *i*th ion. The quantities τ_i/τ and ΔE_i are connected by the appropriate relationship

$$\frac{\tau_i}{\tau} \cong e^{\frac{\Delta E_i}{KT}}$$

The expression is approximate mainly because the frequency of oscillations of the water molecules as of a whole is assumed to be the same as for pure water. This assumption is justified at least for small values of ΔE.

Samoilov has developed the method to assess ΔE_i for particular ions on the basis of experimental data on the dependence of ion mobility in solution on temperature and the coefficients of auto-diffusion of water, which characterize spontaneous and incessant heat motion of water molecules. It was found that two cases could be distinguished:

1. $\Delta E_i > 0$ and $\tau_i/\tau > 1$ (Mg^{2+}, Li^+, Na^+)
2. $\Delta E_i < 0$ and $\tau_i/\tau < 1$ (K^+, Cs^+, Cl^-)

In the former case the exchange of water molecules in the immediate surroundings of the solute ions occurs less often than usual, i.e. a certain effective binding of the nearest water molecules to the ions takes place. This is known as positive hydration.

In the second case, the exchange of water molecules nearest to the ion occurs more frequently than usual,

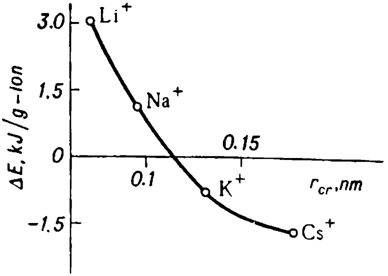

Fig. 5. Dependence of energy of auto-diffusion o water on crystal-chemical radii of ions.

i.e. the water molecules nearest to the ion are more mobile than in pure water. This is negative hydration.

Terms of positive and negative hydration are associated with the sign of the quantity ΔE_i. The case with $\Delta E_i = 0$ and $\tau_i/\tau = 1$ corresponds to the interphase between positive and negative hydration. The numerical value of ΔE_i strongly depends on the main characteristics of the ion, viz., its radius, charge, and the structure of its electron shell. The value diminishes with increasing radius and decreasing charge on the ion. Fig. 5 shows the dependence of the quantity ΔE_i on the crystallochemical radii of ions.

The transition from positive to negative hydration occurs at $r_i = 0.11$ nm.

Both kinetic and thermodynamic concepts of hydration employ the idea of the coordination number. Meaning is, however, somewhat different: the coordination number of an ion in a dilute aqueous solution is understood as the mean number of molecules of water that immediately surround the ion. The coordination number here can be expressed by figures other than whole numbers. It is a statistical value depending on the heat motion, especially on translation motion of particles. The kinetic concept has been developed for aqueous solutions and is especially valuable in cases where ions do not strongly interact with the water molecules that immediately surround it. At the same time, it is characterized by some general features: strong attachment of the nearest water molecules to the ion can be regarded as a limiting case of decreased mobility of these molecules.

The approach to solvation from the kinetic standpoint holds also for solvation of ions in many other solvents. The main postulates of the kinetic solvation theory (the existence of negative solvation included) are now well verified by experimental methods (such as thermochemical, radiospectroscopic, etc.) and by theoretical methods.

The thermodynamic and kinetic approaches to the solvation phenomenon do not rule out but rather supplement each other. A correct understanding of ion solvation is only possible on the basis of the concepts of the kinetic and thermodynamic stability of the associate ion-solvent molecule, which describe the same complex process of solvation from different viewpoints. The thermodynamic interpretation of solvation leads to the same conclusions as does the kinetic approach.

DONOR-ACCEPTOR INTERACTION

We can now imagine the picture of the interaction between ions and molecules of the solvent in detail. The first outlines of this picture were drawn by John Bernal* and his collaborators. In his investigation of the energy needed to remove an electron from an atom,

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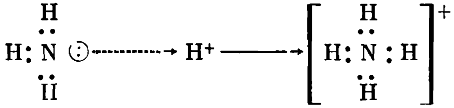
* Bernal, John Desmond (1901-1972), the English physicist and public figure, fighter for peace. Known for his numerous papers concerning the structure of substances and hydration.

i.e. ionization potential, Bernal discovered its surprising closeness to another value, the energy of hydration, but with the sign reversed. For example, for the ion Na^+ these values are 497 and 476 kJ/mole and for the ion Ca^{2+}, 1573 and 1572 kJ/mole, respectively, etc. He explained the physical nature of this similarity by that the water molecules give to the ion the electrons it lacks.

ION SURROUNDED BY SOLVENT BEHAVES LIKE AN ATOM

When the electron structure of molecules became clear in more detail, it appeared that the process of electron transfer from solvent to ion is in many respects similar to the formation of chemical bonds of the donor-acceptor type. In essence it consists in that one molecule or a donating atom gives off a pair of electrons, while another atom or, more often, an acceptor ion takes it up:



$$\mathrm{H}:\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{N}}}\,(:) \dashrightarrow \mathrm{H}^+ \longrightarrow \left[\mathrm{H}:\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{N}}}:\mathrm{H}\right]^+$$

This idea was suggested by Linus Pauling*, one of the most outstanding investigators in the field of the chemical bond. He put forward a postulate concerning the electroneutrality of a hydrated ion, according to which the charge is redistributed onto the hydrogen atoms of the water molecules surrounding the ion.

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* Pauling, Linus (b. 1901), an American scientist. His scientific interests are quite varied from quantum chemistry to molecular biology. He was awarded the Nobel Prize for chemistry in 1954.

The concept of the donor-acceptor character of the interaction between the ion and the solvent molecules has become generally accepted. During solvation of an ion, it is neutralized and its charge is shifted onto the solvent particles that surround the ion. The most important conclusion that can be drawn from this postulate is that an ion can be considered a kind of a neutral particle, a complex atom with the filled electron orbitals. The analogy appears to be so close, that an ion proper in solution can now be compared with an atom of a noble gas having the same number of electrons and the same mass. This concept has been developed by one of the authors of this book (to be discussed in more detail in the next chapter). This concept has proved fruitful and has helped us understand many aspects of the complicated transformation processes that substances undergo during dissolution.

WHERE IS THE IONIC CHARGE?

The redistribution of the ion charge mentioned above produces an effect on the solvent molecules in the long-range solvation region as well. It is quite clear that the shift of a part of the electron density from the solvent molecules nearest to the cation creates electron deficit in these molecules which will partly be compensated for by the shift of the other part of the electron density from the neighbouring solvent molecules and so on. The electron density around the anions is shifted in the reverse direction. The cause of these shifts is the same, namely, the tendency to attain a certain equilibrium corresponding to the minimum energy. All what we have said leads us to certain conclusions concerning the physical nature of the ordered and disordered action of the ion on the solvent. These phenomena can be associated with strengthening of the hydrogen bond between molecules of the solvent caused by accumulation or removal from them of part of electrons. The structure of the solvent can also be distorted by molecules having surplus energy. As a result, the charge of the ion is transferred in fractional units onto the molecules of the solvent in the short-range and long-range surroundings.

NEW APPROACH—NEW PROBLEMS

From what we have said it follows that the phenomenon of solvation can be interpreted from a new aspect. The thermodynamic and kinetic approaches have their limitations. Firstly, they do not fully reflect the complexity of the changes occurring during solvation of ions, and attention is concentrated mainly on the degree of binding of the solvent molecules by the solute ion, or on the degree of limitation of the translatory motion of the molecules in the ion field. Secondly, these approaches to the solvation phenomenon depend largely on the discontinuity and contrast between the interactions ion-solvent and solvent-solvent. In reality they are closely connected with each other and can only be separated from each other by convention. And thirdly, the concepts are related to solvation of individual ions rather than to stoichiometric mixtures of oppositely charged particles which are the object of our investigation. For this reason, a number of changes in the properties of the solvent in the presence of a stoichiometric mixture of ions (as compared with the individual ions) are not accounted for (e.g. compensation of the charge by the solvent molecules in the long-range solvation region).

All this indicates the need to further develop our concept of ion solvation.

CONNECTION WITH STRUCTURE

The factors determining the structure of a solution are the coordination of the solvent molecules in the vicinity of the dissolved particle, and the interactions of all types. The same factors govern the solvation of particles in solutions. The structure of a solution and solvation of particles in it are closely interrelated. This is reflected in the definition of solvation given above where it was supposed that the bonds responsible for the supramolecular structures in solution were broken.

During solvation of monatomic uncharged particles weakly interacting with the solvent molecules, the destruction of the old and the formation of new supramolecular structures is responsible for the formation of cavities in the solvent structure, into which these particles penetrate.

During solvation of polyatomic uncharged particles, the solvent structure is even more changed at the expense of rotational degrees of freedom of the dissolved particles. When charged particles are solvated, new structures of the bound solvent are formed in addition.

Thus, solvation involves changes in both the structure of the solvent and the structure of the reactants themselves. In fact, the changes in the properties of particles during formation of solution depend on their structural changes, and hence the structure determines the energy of the system, steric factors, process rate, and equilibria.

The interconnections between the solvation and structure are so varied that it will be difficult even to enumerate them all. We shall therefore consider only some aspects of these interconnections.

EFFECT OF SOLVENT STRUCTURE

The effect of the solvent structure shows itself markedly in the thermodynamic characteristics of the particles solvation process. This is shown by much experimental data concerning the dependence of various thermodynamic parameters on the composition of the solvent, its temperature, pressure, etc. Moreover, these effects can now be assessed quantitatively. An analysis of this data indicates that the thermodynamic characteristics connected with the structural changes in the solvent during solvolysis are considerable in magnitude, have different signs, and often determine the course of the process. The interconnections between the structure and the solvating power of the solvent are clearly shown here. There are probably only a few exceptions to this rule: the more developed the structure of the solvent, the stronger it solvates polar molecules. This becomes especially clear in the light of the proposed idea of auto-solvation. Auto-solvation is the formation of solvate shells round solvent molecules as they interact with similar molecules. The more polar the solvent, the stronger the auto-solvation. Strongly structured solvents, for which auto-solvation is characteristic (water, sulphuric acid, formamide, monohydric alcohols, etc.) readily solvate and dissolve polar compounds.

CHARACTERISTICS OF ORGANIC SOLVENTS

In the analysis of the relationships between the structure of a solvent and solubility in this solvent of various compounds, in particular those with complicated structures, one should remember that most organic solvents are polyfunctional, they contain both polar and non-polar groups. For example, monohydric alcohols contain a polar functional hydroxyl group and a non-polar group, alkyl radical. While the former is susceptible to structurization and strong specific solvation of polar molecules (or their separate fragments), the latter is unable to be appreciably structured. Only non-polar molecules or their fragments can be strongly solvated (universal solvation). It is not surprizing therefore that lower alcohols dissolve substances with both polar and non-polar molecules. This gives grounds to consider polyfunctional solvents as a mixture of polar and non-polar solvents with an extremely strong bond between the two components. Mixtures of two monofunctional solvents, modelling bi- and polyfunctional solvents, can be made up.

EFFECT OF SOLVATION AND SOLVATE STRUCTURE ON PROPERTIES OF SUBSTANCES

The so-called solvation effects are based on the changes in the physico-chemical properties of particles in the process of their transfer from the gas phase into the solvent, or from one solvent into another, one differing from the former in polarity and solvating power. The solvation effects connected with the structurization of the reacting system have been known for a long time. But they were not always given the attention they deserved in the study of reactions in solution. Let us discuss, for example, the solvation effect of electron excitation. It is known in the literature as the solvatochromic or solvatofluorochromic effect. It consists in the shifts of different magnitude in the bands of the electron absorption and emission spectra of molecules during their solvation in the ground and excited states. The solvatochromic effect can be used to judge the degree of the solvation effect of the solvent, the solvating power of the solvent, and the nature of solvation, not only of a molecule as a whole but also of its separate parts. A more general case is the solvato-optic effect that the solvent produces on various optical properties of a substance.

A solvatokinetic effect can be observed in chemical reactions in solutions. It is manifested in the changes in the activation parameters and rates of gas-phase reactions as they occur in solutions, or in the reactions in solutions when the solvent is changed. The kinetic compensation effect can also be mentioned in this context. It is characterized by a lowering in the activation energy of reactions occurring in solutions compared with the gas-phase reactions.

The effect of the solvent is especially noticeable in the thermodynamics of chemical reactions. The thermodynamic characteristics of solvation of a stoichiometric mixture of ions determined for many systems serve as a quantitative measure of this effect. The solvation effects in this case show themselves in that they compensate the energy of decomposition of the crystal lattice and often exceed this energy.

QUANTITATIVE CHARACTERISTICS

The complexity of the solvation phenomenon is quite clear from the previous sections of the book. Only full quantitative deciphering of all the processes occurring during solvation would answer the need for a general theory of solutions. At the present time classical thermodynamics imposes limitations on the problem. Strictly defined thermodynamic relationships can formally be applied to solvation only as the sum of all processes occurring during the transition of the stoichiometric mixture of gas ions into solution. Subsequent interpretations or subdivisions of the solvation phenomenon are connected with the introduction of subjective model ideas, more or less arbitrary assumptions, and simplifications. But this should not give reason for the reader or the future investigator to despair. The tremendous advances in experimental techniques, the development of new experimental methods and the improvement of old ones offer great possibilities in this field of research.

What is the current quantitative interpretation of the solvation phenomenon?

MAIN CONCEPTS

The quantitative characteristics of solvation are numerical expressions of properties which, according to the methods of investigation, can be classified as thermodynamic, kinetic, structural properties, etc. Thermodynamic properties are especially convenient for the purpose. These are usually functions of variables (temperature, pressure, volume, number of moles, heat, work), the appropriate type being determined by the laws of thermodynamics. The most important and fundamental of these functions are the functions of state that are not connected with the method by which the process is accomplished, but depend only on the initial and final states of the system. Let us consider some of these functions.

The enthalpy (H), the "energy of the expanded system". It is equal to the internal energy plus the expansion work. Under constant pressure and temperature, the changes in enthalpy (ΔH) are equal to the heat effect of the reaction*.

The entropy (S). This property characterizes the measure of bound energy ($P = -TS$) which in the

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* For heat effects see I. N. Semenov and R. V. Bogdanov *Energy and Chemical Process*, Khimiya, Leningrad, 1973 (in Russian).

isothermic process cannot be converted into work. It is defined as the logarithm of the thermodynamic probability and indicates the direction of a spontaneous process in an isolated system. Entropy is a measure of disorder in a system.

The Gibbs* free energy, (G), (free energy) or isobaric-isothermic potential. It is related to the former values as this:

$$G = H + P = H - TS$$

The variation of this potential during the process (ΔG) characterizes the maximum useful work and indicates the direction of the process and the state of equilibrium. By analyzing the above equation, one can deduce that in a given process simultaneous variation of the free energy of a system and the degree of its disorder is possible. A spontaneous process proceeds in that direction in which the overall motive force of the process will decrease, while $\Delta G < 0$. The overall motive force is composed of two components, one of them being the tendency to pass into a state having least energy (i.e. the enthalpy of the system decreases), while the other is the tendency to pass into the most probable state with the degree of disorder the greatest possible in these conditions (maximum entropy). If the degree of disorder does not change in the process ($\Delta S = 0$), the direction of the process will be determined by the changing enthalpy. On the other hand, if no energy changes occur in

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* Gibbs, Josiah Willard (1839-1903), the great American physicist, one of the founders of chemical thermodynamics and statistical mechanics. Gibbs worked out the theory of thermodynamic potentials, the phase rule—the main law of heterogeneous equilibrium. His writings deal also with problems of the electromagnetic and mechanical theory of light, vector analysis, etc.

the process ($\Delta H = 0$), the process will proceed spontaneously in the direction of increasing entropy.

Of the other properties we mention the temperature coefficients of enthalpy (heat capacity C_p) and of bound energy e_p*. If we understand solvation as a sum of processes connected with the formation of an infinite dilute solution of electrolyte from a stoichiometric mixture of gas ions and pure solvent, then the following equation will be true

$$\Delta H_{\text{soln}} = \Delta H_{\text{lattice}} + \Sigma\, \Delta H_{\text{solv}.i}$$

where ΔH_{soln} is the change in the enthalpy during the formation of an infinitely dilute solution out of an ionic crystal and a solvent (the first integral heat of dissolution); $\Delta H_{\text{lattice}}$ is the change in the enthalpy during mutual separation of ions in the process of breakdown of crystal lattice of a salt; $\sum \Delta H_{\text{solv}.i}$ is the change in the enthalpy during solvation of a stoichiometric mixture of positive and negative ions (heat of solvation).

The balance of the two contributors in the equation determines the sign of the heat effect of salt dissolution (exothermic or endothermic), since $\Delta H_{\text{lattice}}$ is a large endothermic value, while $\sum \Delta H_{\text{solv}.i}$ is an exothermic one close to the former in magnitude.

The thermodynamic process of solvation can be characterized by the change in the isobaric-isothermic potential $\sum \Delta G_{\text{solv}.i}$, its enthalpy component $\sum \Delta H_{\text{solv}.i}$ and the entropy component $-T \sum \Delta S_{\text{solv}.i}$ and also by their temperature coefficients, changes in the entropy $\sum \Delta S_{\text{solv}.i}$, heat capacity $\sum (\Delta C_p)_{\text{solv}.i}$ and the entro-heat capacity $\sum (\Delta e_p)_{\text{solv}.i}$.

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* By analogy with heat capacity, this value is sometimes alled 'entro-heat' capacity.

They are all interconnected by the following equations

$$\sum \Delta G_{\text{solv}.i} = \sum \Delta H_{\text{solv}.i} - T \sum \Delta S_{\text{solv}.i}$$

$$\frac{d\,\Sigma \Delta G_{\text{solv}.i}}{dT} = -\sum \Delta S_{\text{solv}.i};$$

$$\frac{d\,\Sigma\,\Delta H_{\text{solv}.i}}{dT} = \sum (\Delta C_p)_{\text{solv}.i}$$

$$\frac{d\,(-T\,\Sigma\,\Delta S_{\text{solv}.i})}{dT} = \sum (\Delta e_p)_{\text{solv}.i}$$

A BARRIER TO UNDERSTANDING SOLUTION

All thermodynamic characteristics in the above equations relate to the electrolyte as a whole. The problem becomes much more difficult if we make an attempt to describe thermodynamically the transition of an individual ion (a gram-ion of ions having the same sign) from the gas phase into solvent. All attempts to experimentally evaluate the individual changes in the energy or enthalpy during solvation of a cation or anion have foundered on an insuperable obstacle of electrical neutrality. Moreover, if we discuss the transfer of ion of a given sign from the gas to the liquid phase from a thermodynamic point of view, it is necessary to take into account the changes in the energy and enthalpy determined by electrical properties of phases and the electrical potential of the interphase, which are eliminated in stoichiometric mixtures of ions as a result of mutual compensation of cation and anion effects equal in magnitude and opposite in sign.

In this connection, when we discuss solvation of separate ions, we mean either actual or chemical energy of solvation. The actual energy of solvation of ions of type i is the change in the isobaric-isothermic potential $\Delta G^{p}_{\text{solv}.i}$ which accompanies the transfer of one gram-ion of type i ions from the standard state in vacuum to the standard state of infinite dilution. During the transfer process, the ions meet the interphase between vacuum and solution, at which energy is either liberated or absorbed, depending on the nature of the double layer.

If we characterize the field formed by the boundary layer by a surface potential φ, then the work that must be expended to take a gram-ion of ions across the interphase will be $z_i F\varphi$, where z_i is the charge on the ion, F is the Faraday number. But $\Delta G^{x}_{\text{solv}.i}$, the chemical energy of ion solvation (usually obtained by dividing the energy of solvation for stoichiometric mixtures of ions by the ionic components), does not take into account the phase transfer work. Thus, the quantities $\Delta G^{p}_{\text{solv}.\,i}$ and $\Delta G^{x}_{\text{solv}.\,i}$ are related as follows:

$$\Delta G^{p}_{\text{solv}.i} = \Delta G^{x}_{\text{solv}.i} + z_i F\varphi$$

where the ion charge z_i is taken with its appropriate sign. To find the value of φ, it is necessary to know the difference in potentials between two points in different phases. We are unable to find this difference experimentally and some investigators think that it has no physical sense. The question then arises: is the above equation valid, and also can we divide the energy change occurring during solvation of a stoichiometric mixture of ions by the ionic components? Is it not more correct to divide by the real ionic energies of solvation. Nevertheless, the concept of the chemical energy of ion solvation is widely accepted and used. Later on we shall talk more about this energy (for the sake of convenience we shall omit the exponent 'x'

in the designation of the thermodynamic functions of solvation).

What we have said shows how complicated the problem of obtaining true thermodynamic characteristics of solvation of separate ions is. To solve it by purely thermodynamic means seems impossible. But these difficulties must not discourage the investigator in his attempt to obtain thermodynamic characteristics of the solvation of individual ions since only then will it become possible to establish the actual connections between the thermodynamic characteristics of solvation and the other properties of ions and thus ensure deeper understanding of the nature of electrolyte solutions.

HOW CAN ION PROPERTIES BE ESTIMATED?

Theoretical methods of calculating thermodynamic characteristics of ion solvation are usually divided into two groups. In one group the solvent is considered as a continuous dielectric. In the other group the foundation is provided by the molecular structure of the solvent.

The first attempt to calculate the thermodynamic characteristics of hydration, based on the model of the medium as a continuous dielectric, was undertaken by M. Born* in 1920. In Born's theory an ion is considered to be a rigid sphere with the radius r, carrying charge e in a continuous dielectric medium with dielectric constant ε. The change in the isobaric-isothermic potential, according to Born, is equal to the difference between its potential energies in solution

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* Born, Max (1882-1970), the outstanding German physicist. Famous for his work in the dynamics of the crystal lattice, the theory of the structure of the atom, quantum mechanics, and the theory of relativity.

and in vacuum, i.e.

$$\Delta G_{\text{hydr}} = -\frac{N_A z^2 e^2}{2r}\left(1 - \frac{1}{\varepsilon}\right)$$

where N_A is the Avogadro number and e is the electron charge.

It should be noted that the thermodynamic characteristics of hydration found on the basis of the Born equation differ substantially from those determined experimentally because of the inherent shortcomings of the theory itself. Born's theory can be improved by specifying more precisely the radii of ions in aqueous solutions, by taking into account changes in the dielectric constant in the vicinity of the ion (by analogy with its variation under the effect of pressure), by introducing additional terms or by combined elimination of these defects, etc. In order to give up the concept of the solvent as a continuous and homogeneous medium, it is necessary to take into account individual properties of its molecules.

New methods of theoretically calculating the thermodynamic characteristics of hydration are based on structural concepts, especially the tetrahedral coordination of water. Methods based on the various thermodynamic cycles are also used here.

To summarize the discussion of theoretical calculations of the thermodynamic characteristics of ion solvation, it is necessary to note that despite the marked progress made in this field, connected with the use of structural models, thermodynamic cycles, there exists no complete theory enabling us to obtain accurate values of the thermodynamic characteristics of solvation. The reason for this can be found in the possibilities of the electrostatic approach itself. Most formulas of electrostatics hold only for distances significantly greater than the size of the interacting particles, but this condition is not fulfilled in solutions of electrolytes. Furthermore, all variants of the theoretical calculations considered make use of the dependence of the thermodynamic functions of ion solvation on certain parameters, but in the choice of their magnitudes arbitrariness is introduced. For example, for the dipole moment and polarizability, numerical values determined from experiments on pure gases and liquids are used, though it is known that these parameters have different values in the ion field, etc. So, until we develop reliable methods or more exact quantum mechanical approximations, the determination of the thermodynamic characteristics of ion solvation by separating the experimentally found overall magnitudes into ionic components will play an essential and sometimes decisive role.

Many classifications are based on the equality of certain thermodynamic properties for some pairs of ions (the ion-pair Cs^+ and I^- seems to be most suitable), on the constancy of their relationships for various solvents and temperatures, and on a direct or indirect application of Born's equation. In this connection it would be appropriate to mention research carried out by the Soviet scientists A.F. Kapustinsky*, N.A. Izmailov**, K.P. Mishchenko*** and by the authors of this book.

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* Kapustinsky, Anatolii Fedorovich (1906-1960), the Soviet physico-chemist. Known for his work in crystallochemistry, and the thermodynamics of ionic crystals and solutions.

** Izmailov, Nikolai Arkadievich (1907-1961), the Soviet physico-chemist. He studied the effect of the medium on properties of electrolytes, acidity of medium, and other problems of electrochemistry of non-aqueous solutions.

*** Mishchenko, Konstantin Pavlovich (b. 1901), the Soviet physico-chemist. Famous for his investigations in the structure and thermodynamics of electrolyte solutions in various solvents, and also many problems of the solvation theory.

The classification of thermodynamic characteristics of solvation for stoichiometric mixtures of ions into ionic components is difficult, not only because it means a search for a classification principle, but also because it is necessary to establish a correspondence between the reference points for the thermodynamic characteristics of individual ions. There are only a few papers devoted to finding this correspondence for aqueous solutions of electrolytes.

The coordination of solvent molecules around the dissolved particle is an important quantitative characteristic of solvation. It determines the structure and is closely connected with the type of interaction in solutions. The coordination of both short- and long-range solvation can be determined at the present time. The study of selective solvation is also of great interest. Among the other important characteristics of solvation the structural and non-structural components of their thermodynamic characteristics should be mentioned (they will be used in further discussion).

Chapter Five

Properties of Electrolyte Solutions

In our every-day life we deal with solutions whose concentrations vary within a very wide range, from very dilute to saturated and supersaturated solutions. Electrolyte solutions are characterized by various properties depending on the concentration; significant qualitative changes are often observed when passing from one region of concentrations to another. Dilute solutions having an infinitely small concentration of the solute acquire the properties of an ideal solution. Here the dissociation degree is unity and we deal with solutions in which ions play the role of the particles. In addition to ions, solutions of high and medium concentrations can also form molecules, associates, ion-pairs, etc., which give new properties to the solution. The situation is even more complicate with unstable supersaturated solutions. The main difficulty in describing the properties of electrolyte solutions is that it is impossible to establish the boundaries of concentration and the ranges in which the changes in properties obey one law.

As a rule, the properties of dilute solutions are divided into two groups. One comprises the properties which, for a given solvent, are independent of the nature of the solute. These are the saturated vapour pressure of the solvent over the solution, elevation of the boiling point and lowering of the freezing point of the solution (compared with the solvent), the osmotic pressure, and others. The laws that govern their changes, associated with the variation of the solute concentration, have become the foundation of the physical theory of solution. The other group comprises the properties which depend on the nature of the solute. These are the heat effects of dissolution, electrical conductivity, volumetric, optical, and other properties. The characteristics of the dissolution process are quite vivid here. We have already discussed the properties classified in each group, but in this chapter we shall concentrate on the chemical and structural properties of electrolyte solutions.

CHEMICAL PROPERTIES

The most specific characteristics of electrolyte solutions become especially marked in dilute solutions. The main particles participating in the conversions, i.e. the kinetic entity, are solvated ions, or simply ions (by convention). The dissociation degree is close to unity. The chemical properties of such solutions are determined by the chemical properties of the solute ions. The result of this is the group chemical properties of electrolyte solutions which characterize solutions containing this ion. An example of group reaction in solution is precipitation of a sparingly soluble salt with a set of reagents having the same cation or anion, neutralization reactions, and other ionic exchange reactions, for which the equation in the ionic form is the same:

$$BaCl_2 + Na_2SO_4 = 2NaCl + \downarrow BaSO_4$$

$$Ba(NO_3)_2 + K_2SO_4 = 2KNO_3 + \downarrow BaSO_4$$

etc.

$$Ba^{2+} + SO_4^{2-} = \downarrow BaSO_4$$

$$HCl + NaOH = NaCl + H_2O$$

$$2HNO_3 + Ba(OH)_2 = Ba(NO_3)_2 + 2H_2O$$

etc.

$$H^+ + OH^- = H_2O$$

Examples of group properties are the acid-base properties of solutions of compounds containing hydrogen and hydroxyl ions. These ions determine the ability to change the colour of indicators, to dissolve metals, neutralize acids and bases, etc. It is easy to see that in these processes, acids do not act by anions and bases do not act by cations, but they act by ions of hydrogen and of hydroxyl respectively, and the higher the ion concentration, the more pronounced are their acid and base properties. The colour of solutions caused by the presence of an ion is also a group property, e.g. a blue colour results from the presence of hydrated ions of Cu (II), a green colour from Ni (II) and pink from the presence of Co (II). Electrical conductivity, heat capacity, and many other properties can also be attributed to group properties. It should be remembered that strictly speaking this additivity holds only for infinitely dilute solutions.

In each particular case, the manifestation of chemical properties of electrolyte solutions depends on certain quantitative characteristics of the process. Let us consider some of them.

SOLUBILITY PRODUCT

An equilibrium of a solution of a strong electrolyte M_mX_n with its crystals is characterized by the product of activities of the ions M^{n+} and X^{m-}:

$$SP_{M_mX_n} = a^m_{M^{n+}} a^n_{X^{m-}}$$

This value is known as the solubility product. For sparingly soluble compounds, in the absence of other electrolytes in solution, the solubility product can be expressed via concentrations $c_{M^{n+}}$ and $c_{X^{m-}}$:

$$SP_{M_mX_n} = c^m_{M^{n+}} c^n_{X^{m-}}$$

An electrolyte precipitates if the product of the concentrations of ions (ion activities) is greater than the product of solubility.

The following conditions are therefore valid here:

$$a^m_{M^{n+}} a^n_{X^{m-}} > SP_{M_mX_n} \text{ — precipitate}$$

$$a^m_{M^{n+}} a^n_{X^{m-}} = SP_{M_mX_n} \text{ — no precipitate}$$

$$a^m_{M^{n+}} a^n_{X^{m-}} = SP_{M_mX_n} \text{ — saturated solution}$$

Table 2 gives solubility products for some sparingly soluble electrolytes. The solubility product depends on the nature of the salt and solvent, the temperature, and the presence of other electrolytes.

IONIC PRODUCT OF WATER

The ionic product of water K_w is the product of the activities of hydrogen and hydroxyl ions

$$K_w = a_{H^+} a_{OH^-}$$

TABLE 2. **Solubility Products of Some Electrolytes Sparingly Soluble in Water at 298.15°K**

Compound	$SP_{M_mX_n}$	Compound	$SP_{M_mX_n}$
AgCl	1.8×10^{-10}	$Fe(OH)_3$	3.2×10^{-38}
$BaSo_4$	1.1×10^{-10}	HgS	4.0×10^{-53}
$CaCO_3$	4.8×10^{-9}	PbI_2	1.1×10^{-9}
CdS	7.9×10^{-27}	$SrCrO_4$	3.6×10^{-5}
CuS	6.3×10^{-36}	$ZnCO_3$	1.5×10^{-11}

At 25°C the ionic product of water is 1.008×10^{-14}. The condition for neutrality of the medium is in this case

$$a_{H^+} = a_{OH^-} = \sqrt{K_w} = 1.004 \times 10^{-7} \text{ g-ion/litre}$$

The ionic product of water increases with temperature. The above equations show that the concentrations of hydrogen and hydroxyl ions are interdependent. An increase in the concentration of hydrogen ions decreases the concentration of hydroxyl ions, and vice versa. The single valued nature of their interconnection makes them interchangeable in characterizing acidity or alkalinity.

HYDROGEN ION CONCENTRATION (pH)

For the purpose indicated above the hydrogen index pH is used defined by the equation

$$pH = -\log a_{H^+}$$

At a temperature of 25°C, the pH of a neutral medium is 7, of an acid medium below 7 and of an alkaline medium above 7. The pH can be determined instrumentally and by using indicators, i.e. substances that change their colour within certain pH ranges. Examples of some indicators are given in Table 3. Universal indicators are widely used. These are mixtures of separate indicators, which change their colour within a wide range of pH.

TABLE 3. **pH Range of Some Indicators**

Indicator	Acid medium	pH range	Alkaline medium
Methyl orange	Red	3.0-4.4	Orange-yellow
Litmus	Red	4.0-6.4	Blue
Methyl red	Red	4.4-6.2	Yellow
Phenolphthalein	Colourless	8.2-10.0	Purple

Besides these quantitative characteristics, the instability constants of complex compounds, the dissociation constants of weak electrolytes, of hydrolysis, as well as some others are very important. But they are not directly related to the subject of this booklet and so will not be discussed here.

STRUCTURE OF SOLUTIONS

The solvated ion structure problem is very important in the description of the properties of solutions. The structure and properties of electrolyte solutions in water, in non-aqueous and mixed solvents largely depend on the interactions between the ions and the solvent molecules, i.e. solvation.

The solvation process can be described by the following equation

$$\mathrm{M}_{\mathrm{g}}^{z} + m\mathrm{R}_{\mathrm{l}} \rightarrow \mathrm{M}_{\mathrm{soln}}^{z} = \mathrm{M}_{\mathrm{solv}}^{z} + k\mathrm{R}_{\mathrm{soln}}$$

The actual form of a solvated ion $\mathrm{M}_{\mathrm{solv}}^{z}$ in solution can be represented as one of the forms which correspond to the interphases described in Chapter 3. The relation between the number of solvent molecules and the type of solvation, depending on the interphase, can be represented as this:

I—I	$k = m$	Solvation (hydration) according to Samoilov, or kinetic solvation
II—II	$k = m - n$	Division of solvation (hydration) into short-range and long-range solvation
III—III	$k = m - n - (p + t)$	Commonly accepted or thermodynamic solvation (hydration)

The study of aqueous solutions by roentgenographic, optic, thermodynamic, relaxation, and other methods shows that the ion hydration is accompanied by the destruction of the water structure. The experiments have shown that in this case, according to their action on water molecules in solution, the ions can be divided into two groups. One of them, as a rule, comprises large, single-charge monatomic and polyatomic ions (K^+, Cs^+, Br^-, I^-, ReO_4^-, etc.), for which the disordering effect of water structure prevails (negative hydration). The other group comprises multi-charge and small single-charge mon- and polyatomic ions (Al^{3+}, Mg^{2+}, Li^+, Po_4^{3-}, SO_4^{2-}, and others), for which the ordering effects of water structure prevail (positive hydration).

In the studies of X-ray scattering, I-R spectra, Raman effect (spectra of combination scattering) and some other studies, two rules have been established: firstly, ions act like temperature, and secondly, ions act like pressure. The first group ions produce the same disorder in the orderly structure of water as does the elevation of temperature, while the second group ions produce the reverse effect.

Various concepts are used to describe the structure of solution. One of them is based on the model concepts of the structure of a solvated ion in solution. The most important point in this approach is the recognition of solvate formations as the main structure component in solution. The other concept is based on the idea of the dominant role of the structure of the components of solution. According to this concept there exist several regions in which the structure of solution is determined either by the structure of the solvent (dilute solutions) or by the structure of an anhydrous or solvated salt (concentrated solutions), or else by both (the region of medium concentrations).

EFFECT OF CONCENTRATION

The theory of solution attempts to describe the laws governing the behaviour of solutions in as wide range of concentrations as possible. But there are considerable difficulties connected with the qualitative changes occurring during the transition from one concentration region to another. We think that it would be impossible to put forward a rigorous general approach to the classification of solutions by concentration regions. Only an arbitrary classification by certain special properties seems to be possible here. For example, according to the role of electrostatic interactions, solutions are classified as dilute, medium strength, and concentrated solutions. The first concentration region is defined by the applicability of the equations of the theory of dilute solutions, e.g. the Debye-Hückel* equation. The third region is characterized by the formation of ionic associates. The second region is intermediate between the former two.

Defining the boundaries of existence of structures in electrolyte solutions of various concentrations, and also in solutions with multicomponent solvents, is of some interest. The boundaries show themselves in the study of the various properties of solutions and strongly depend on the particular kind of system. As a rule, these boundaries are indistinct because the transition from one structural type to another cannot be related to obvious phase transitions, such as, for example, polymorphous conversions, melting, etc. The possible number of boundaries for electrolyte solutions is determined by the quantity and stability of molecular and supramolecular structures. Their number is greater for solutions from which crystal solvates are crystallized. There are no limitations to the existence of supramolecular structures in solution in concentration regions of electrolytes which crystallize both with and without the formation of crystal solvates. The region in which the structure remains unaffected should reasonably be established on the basis of the analysis of possible ion states in solution. The appearance of small portions of electrolyte producing a very great effect on the solvent is responsible for the formation of the solution structure around the ions, this being dependent on the structure of the solvated ion and the solvent. The former is constructed by the solvent molecules in the region of short- and long-range solvation. Adding

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* Debye, Peter Joseph Wilhelm (1884-1966), a famous Dutch physicist. Worked at universities of Germany and USA. He developed the model of a solid body, and the dipole theory of dielectrics. Jointly with Schairer he suggested a method of studying structure of substances.

electrolyte destroys the structure of the pure solvent, and of the long-range and partly short-range solvation. The structure of the pure electrolyte is destroyed at concentrations of the electrolyte corresponding to the boundary of the long-range solvation (BLRS). At concentrations of electrolytes corresponding to the BLRS, all solvent molecules 'feel' the presence of the ions and under their influence they assume more or less stable positions. The solvent structure in the regions of short-range and long-range solvation does not change. The BLRS corresponds to the interphase III—III.

Further addition of electrolyte to the solution destroys the solvent structure in the region of long-range solvation. The solvent molecules of this region are consumed in the solvation of ions of a new portion of the electrolyte. Complete disappearance of the solvent molecules in the long-range environment corresponds to the boundary of complete solvation (BCS). The BCS corresponds to the interphase II—II.

Further strengthening of the electrolyte concentration induces competition of the ions for the solvent, and the solvation of cation appears to be more advantageous from the energy viewpoint in this case. A moment is attained when all solvent molecules are coordinated around the cations. Here we face incomplete solvation of ions which corresponds to the boundary of incomplete solvation (BIS). The BIS corresponds to the interphase I—I for anions and II—II for cations.

ION COORDINATION

In the discussion of the structure of solution we must not omit the problem of ion coordination in the regions of short- and long-range solvation. The former is determined by the number of solvent molecules in the immediate surroundings and their spatial arrangement around the ion with strictly pronounced symmetry. The literature gives various coordination numbers, determined by different experimental methods and on the basis of theory. The coordination numbers 4, 6, and 8 occur most frequently. Higher coordination numbers are possible for the rare earth elements.

The coordination of ions in the region of long-range solvation has been less studied. NMR methods, derivatography, thermochemistry and other methods are being used now for the purpose. It has been established that for I — I electrolytes the number of solvent molecules in I and II regions of long-range solvation is 30 and 60 for stoichiometric ion mixtures. There are no data on the coordination of ions in the regions of short- and long-range solvation for mixed solvents. The selectivity of solvation becomes very important here.

QUANTITATIVE CHARACTERISTICS OF STRUCTURAL CHANGES IN SOLVENTS

At the present time it is possible to assess quantitatively the structural changes in solvents during ionic processes (solvation, dissolution, etc.). To that end, the entropy characteristics are used since they are the most sensitive to structural changes.

USING NOBLE GASES

One of the authors of this booklet has offered an entirely new method of studying structural changes which occur in solvent under the action of ions. The new approach is based on the model in which the ion state in solution is likened to the state of an atom of a noble gas in solution having the same number of electrons and

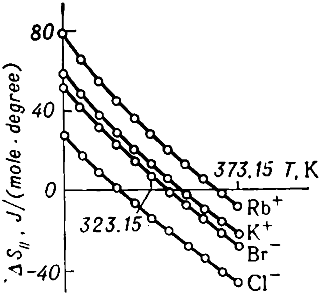

Fig. 6. Dependence of changes of liquid water entropy ΔS_{II} on temperature for some monatomic ions.

the same atomic mass. The structural contribution of the solvent into the overall values can be characterized quantitatively on the basis of the interphase I—I by the change in the entropy connected with the structural changes in the solvent (index II) during ionic processes (ΔS_{II} and $\Sigma\Delta S_{\text{II}}$), and by their non-electrostatic (ΔS_{A} and $\Sigma\Delta S_{\text{A}}$) and electrostatic ($\Delta S_{\text{c}}$ and $\Sigma\Delta S_{\text{c}}$) components. Changes in the region of short- and long-range solvation ($\Delta S_{\text{s.r}}$ and $\Delta S_{\text{l.r}}$) are distinguished. Such entropy characteristics have been determined for many ions in various individual and mixed solvents. A change of sign for the value (ΔS_{II}) for aqueous (Fig. 6) and water-alcohol solutions has been established. This established the concept of the negative solvation (hydration) of some ions. The phenomenon of negative hydration for some other monatomic, polyatomic and complex ions has been predicted.

THREE STRUCTURAL CONTRIBUTIONS

Changes in the entropy of solvent molecules (ΔS_{II}) produced by the introduction to the solvent of monatomic ions are connected with three contributions to the change of its structure: one non-electrostatic and two electrostatic contributions. Firstly, the physical transfer of an ion into solution rearranges the solvent molecules with respect to one another by the formation of cavities (at low temperatures this contribution is close to zero for water). Secondly, the interaction of a charged particle with the solvent destroys the orderly arrangement of its molecules. This effect is accompanied by increasing entropy (increased degree of disorder). And thirdly, the ion interaction with the solvent increases the order of the solvent molecules and is accompanied by decreasing entropy (increased order). An additional effect connected with the limitation of ion rotation is noted for polyatomic and complex ions. For aqueous solutions this effect shows in the stabilization of the water structure due to the additional strengthening of the hydrogen bond between its molecules.

The sign of the change in the entropy associated with the structural changes in the solvent depends on the prevalent effects of order or disorder. The dependence of these values on temperature, the solvent composition, concentration of electrolyte, and other factors has been established, and hence the dependence of ion solvation on these factors. Limit and critical parameters corresponding to the conditions of the ion transfer from the region of the positive to the region of negative solvation play a very important role here. Limiting temperatures for common and heavy water given in Table 4 serve as an illustration. It should be noted that the most important role is played by the structural changes occurring in the solvent in the region of short-range solvation. The fundamental conclusions derived from ΔS_{II} and $\Delta S_{s.r}$ are the same.

The ideas mentioned above can be applied to individual ions as well as to their stoichiometric mixtures. The values discussed have been used to derive quantitative characteristics for the effects produced by the medium on the solubility of ion crystals. The structural contributions to the thermodynamic potential of dissolution $(-T\ \Sigma\Delta S_{\text{II}},)$ $(-T\ \Sigma\Delta S_{\text{c}})$ and $(-T\Sigma\Delta S_{\text{s.r}})$ are characterized by the change of sign depending on the temperature and the nature of the salt. The negative values promote and positive values inhibit the process of dissolution. The character of the changes in these values is clear from what has been said above.

TABLE 4. **Limiting Temperature of Ions**

Ion	Ion radius, nm	Limiting temperature, °K	
		D_2O	H_2O
Na^+	0.098	285±2	282±2
K^+	0.133	333±2	351±2
Rb^+	0.149	351±2	382
Cs^+	0.165	356±2	392
Cl^-	0.181	311±2	305±2
Br^-	0.196	331±2	332±2
I^-	0.220	358±2	377

The structural components of the equilibrium constant, the solubility products, and e.m.f. have been proposed to clarify the structural changes taking place in the solvent during chemical reactions, dissolution of sparingly soluble salts, and in electrochemical processes respectively. The analysis of these values shows that the changes in the thermodynamic properties of the solvent in ionic reactions in solution is very often the motive force of the process.

COMPARISON OF AQUEOUS AND NON-AQUEOUS SOLUTIONS OF ELECTROLYTES

At the present time the thermodynamic method is mostly used in the study of electrolyte solutions, especially in the region of medium strength and high concentrations. Many other physical and physicochemical methods of investigation encounter serious difficulties in the interpretation (and quantitative treatment) of experimental data. The thermochemical measurements which directly record the heat effects of the processes in combination with the determination of the pressure of saturated vapour over the same solutions make it possible to calculate many energy aspects of a solution and its components, and also energy changes in the systems that accompany the processes of dissolution, changes in the concentration, and variations of temperature. The comparison (made in strict observation of the laws of thermodynamics) of the data with the results obtained by other methods of investigating solutions (roentgenographic, spectroscopic, electrochemical, relaxation, etc.) gives true information on the mechanism of the processes of formation of solutions and on the structural state of their components.

A CAUSE OF DIFFERENCES

How do aqueous and non-aqueous solutions differ? Let us try to find it out by considering their thermodynamic properties. The analysis of the available data on the temperature dependence of the standard changes in the enthalpy during dissolution of salts in various solvents shows that water differs significantly from other non-aqueous solvents. As an electrolyte dissolves in water, the exothermic characteristic of the process increases (or the endothermic characteristic decrea-

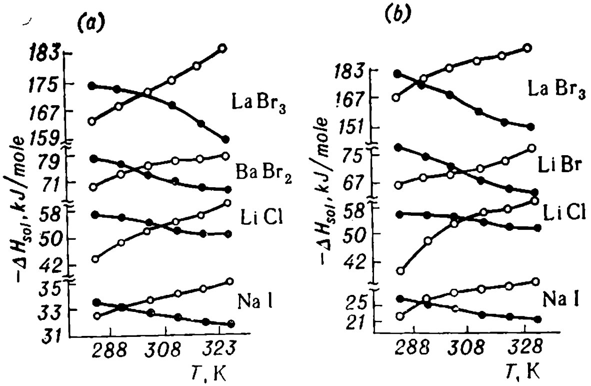

Fig. 7. Heats of salt dissolution in alcohols:
a — methyl alcohol; *b* — ethyl alcohol; ● — air-saturated solutions: ○ — air removed from solutions.

ses) with temperature. The increasing exothermicity of standard changes in enthalpy during dissolution of salt in water with temperature can easily be explained by the destruction of water structure. Therefore, as an ion gets into an aqueous solution, and as the temperature increases, it takes less energy to destroy the structure of water, while the exothermic component, characteristic of the formation of hydrates, remains approximately constant. As an electrolyte dissolves in a non-aqueous solvent, the picture is reversed: the exothermic characteristics of the dissolution process decrease with the growing temperature. Although this remains unexplained it has been proved experimentally. Our research during the past few years has shown that one of the causes of this phenomenon is the presence in the solvent of dissolved gases of the air. The removal of gases from methyl alcohol or ethyl alcohol, and carrying out the experiment in hermetic conditions has shown that the exothermic characteristics of dissolution of some salts in these alcohols (Fig. 7) increase with temperature as is the case during dissolution in water. This can be explained by the decreasing order in the solvent as the temperature rises. Thus, while the presence of dissolved gases in water does not produce a significant effect on the shape of the polytherms of the standard changes in enthalpy during dissolution of salts, the picture is different with non-aqueous solvents, such as methyl or ethyl alcohols, in which the solubility of gases is an order higher than in water, and the presence of gases reverses the polytherms. It follows that it is necessary to pay special attention to the purity of the solvents under study.

FROM THE VIEWPOINT OF STRUCTURAL CHARACTERISTICS

A thermodynamic method based on the analysis of the structural differences between pure solvents and non-electrolyte solutions has been suggested for the study of the structure of liquid solvents. The method is based on the entropy characteristics of formation of cavities in the structure of various solvents (ΔS_A). The comparison of the values ΔS_A for various solvents gives us a basis for drawing conclusions concerning their structure. Series of solvents were proposed, in which the solvents were arranged in the order of increasing compactness of the structure: $H_2O < CH_3OH, C_2H_5OH < C_6H_5Cl < CH_3COOHCH_3 < (CH_3)_2CO < CCl_4 < C_6H_6$ and other hydrocarbons.

The special nature of water as a solvent, due to its open lattice structure and the presence of cavities, explains the fact that the dissolution of non-polar gases in water at temperatures in the vicinity of 0°C is not accompanied by additional consumption of energy, nor is it associated with entropy changes for the formation of cavities in which the dissolved gases are held. Therefore the values for water differ significantly from those for other solvents. Water at a temperature close to 0°C is a'limiting' solvent and the change in the entropy, associated with the dissolution of non-polar gases, is zero. As the temperature increases the picture changes drastically: the water structure is broken down and rearranged in accordance with the changes in its nature. As the temperature increases, water gradually changes from an interstitial solvent ($\Delta S_A = 0$) to a substitutional solvent ($\Delta S_A > 0$). In other words, at each particular temperature water becomes a new, specific solvent characterized by special properties.

MIXED STRUCTURES

Extension of this method to the study of structures of mixed solvents is of interest. Fig. 8 shows the dependence of ΔS_A on the concentration of non-electrolytes in water and on the temperature. For the given systems, in which the structural characteristics are more vividly expressed at low temperatures, the addition of small amounts of non-electrolytes does not change ΔS_A. This is because the structure of water in the given regions is preserved and the number of cavities is sufficient to include the atoms of noble gases. As a non-electrolyte is further added, ΔS_A sharply increases. This is due either to the stabilization of the water structure by the addition of the non-electrolyte (in the case of water-monohydric alcohols) or to its destruction (in other systems). In both cases the open-lattice structure of water changes into a more compact structure. A mixed solvent becomes a more pronounced substitutional solvent. This process is accompanied by great entropy expenses for the cavity formation. A further strengthening of the concentration of non-

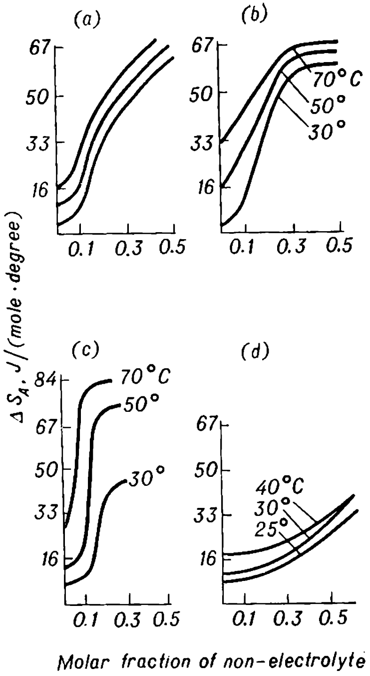

Fig. 8. Changes in the entropy during formation of cavities in solvent at various temperatures in the following systems: *a* — water-methyl alcohol; *b* — water-ethyl alcohol; *c* — water-glycerol; *d* — water-acetone. *a* — at 40, 30 and 25°C.

electrolyte indicates the tendency of the isotherm to saturation. Mixed structures, differing only slightly from one another with respect to their compactness, are formed in these concentration regions. The rise in temperature increases ΔS_A and the corresponding curves are displaced upwards along the axis of ordinates in agreement with the above mentioned effect of temperature on the solvent structure.

Chapter Six

Methods of Studying Electrolyte Solutions

As has already been said, no one separate method of investigation can give comprehensive information on solutions. One cannot but agree here with D. I. Mendeleyev who once said that "only with the study of the many properties of solutions will it become possible to arrive at a definite conclusion concerning their chemical structure".

In this chapter we shall discuss the most widely used methods. First we must mention thermodynamic, kinetic, and structural methods of investigation. The former comprise thermochemical and electrochemical methods which give the most comprehensive idea of the thermodynamics of electrolyte solutions. Experimental methods of determining chemical potentials of electrolyte solution components, and also some methods of determining solvation numbers can also be considered as belonging to this group. The second group of methods gives information on the mechanism of chemical reactions occurring in solution. The third group comprises roentgenographic, spectral, and relaxation methods, which give direct information on the structure of solvents and solutions.

THERMODYNAMIC METHODS

The determination of the thermodynamic characteristics of dissolution and solvation of substances in various solvents, and the thermodynamic characteristics of dilution and mixing, are very important in the development of a modern theory of solution.

HEAT EFFECTS OF DISSOLUTION

In order to determine changes in the enthalpy in the process of dissolution of salts, calorimetric methods are used. The changes in the enthalpy during dissolution of a mole of a substance in a definite amount of solvent are known as the integral enthalpy of dissolution. For example, the dissolution of KCl in water can be written as follows:

$$\mathrm{KCl_{solid}} + n\mathrm{H_2O_{liq}} = \mathrm{KCl_{soln\ KCl \cdot \mathit{n}H_2O}} + \Delta H_{\mathrm{dissol}}$$

Here $\Delta H_{\mathrm{dissol}}$ is the integral enthalpy of dissolution of a mole of KCl up to the point where the concentration is a mole of KCl per n molecules of water at constant pressure and temperature.

For a particular solvent-solute system out of the numerous integral enthalpies of dissolution which depend on the concentration of the solution and are therefore different two should be pointed out which are given a special meaning and special names. The integral enthalpy of dissolution corresponding to the saturated solution is called the total enthalpy of dissolution. In this case, the number of moles of water n corresponds to the concentration of the saturated solution. The integral enthalpy of dissolution corresponding to the solution of infinitely small concentration is called the first enthalpy of dissolution or the enthalpy of dissolution to infinitely dilute solution. Neither full nor the first en-

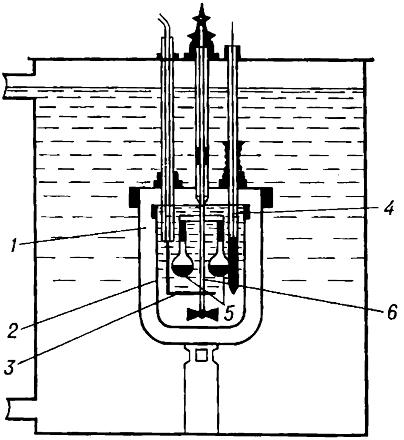

Fig. 9. Calorimeter of variable temperature:
1 — isothermic jacket; 2 — reaction vessel; 3 — heater; 4 — thermistor; 5 — solute ampoules; 6 — stirrer.

thalpy of dissolution can be measured. To determine them, the integral enthalpies of dissolution are extrapolated to the concentration of saturation or infinite dilution.

HOW CAN HEAT EFFECTS BE MEASURED?

In order to determine integral enthalpies of dissolution, experiments are carried out in a calorimeter, an instrument designed to measure amounts of liberated or absorbed heat. The design of a calorimeter depends on the character of the process in question, viz., its duration, heat effect, temperature, pressure, and also the required accuracy. The minimum amount of heat that can be measured in modern calorimeters is as small as a fraction of a calorie. Variable temperature calorimeters are widely used. They measure heat effects by the

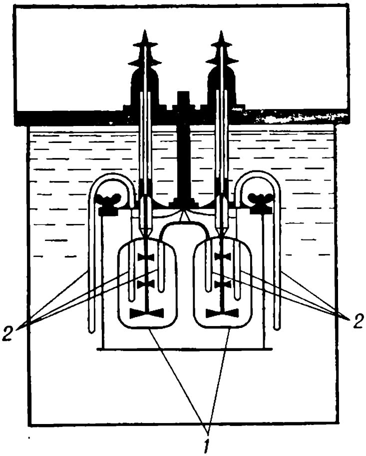

Fig. 10. Differential calorimeter:
1 — reaction vessels; 2 — thermocouples.

change in temperature. The sensing elements in such instruments are usually thermometers, resistance thermometers, thermistors, or thermocouples. Fig. 9 shows a diagram of a variable temperature calorimeter with an isothermic jacket and a thermistor as the sensing element. This calorimeter is designed to measure integral changes in the enthalpy during the dissolution of crystalline salts in liquid solvents at various temperatures. Preference in this case is given to instruments with a hermetically sealed calorimetric vessel, although they are more difficult to manufacture and the determination procedure is more complicated. The hermetic seal prevents evaporation of the solvent into the environment. To control the heat exchange with the environment the vessel is protected from direct contact with heat conducting parts and from air currents, by a heat insulating jacket. Depending on the method by which the temperature is maintained, the jackets are classified as isothermic, the temperature of which is maintained constant during the entire experiment, and adiabatic shells, whose temperature is maintained equal to that of the calorimetric system in the entire course of the experiment.

Differential calorimetric systems are more suitable for investigating lengthy processes with low heat effects. A differential calorimeter (Fig. 10) consists of two identical vessels (as identical as possible with respect to the material, mass, configuration, and size of all parts). The vessels are insulated from each other with a layer of air and surrounded with an isothermic or an adiabatic jacket. If an exothermic process takes place in one vessel, the other one is electrically heated by adjusting the electric current so as to ensure equal temperatures in both. If the process is endothermic, electric heating is applied to the vessel where the process occurs.

Twin-type differential calorimeters are usually used to measure the changes in enthalpy during dissolution and mixing of solutions, since the heats of these processes are in the majority of cases very small and highly sensitive calorimeters are therefore needed. Moreover, during dilution and mixing of solutions, the pressure of saturated vapour over the liquid can vary. The result of this phenomenon are processes of evaporation or condensation which cause large errors. In order to avoid these difficulties, calorimeters are used in which the gas phase over the mixed liquids is absent.

HEAT CAPACITY OF SOLUTION

The changes in the enthalpy of dissolution measured in various temperature conditions make it possible to calculate heat and entropy characteristics of solutions and also changes in the isobaric-isothermic potential (see formulas in Ch. 4). The heat capacity of a solution can be determined by direct calorimetric measurements as well.

For many calculations of binary systems the necessity arises of determining the heat capacity of the dissolved electrolyte, the apparent molar heat. For an aqueous solution this value is found from the following equation:

$$\Phi_s = \frac{C_s - 55.506\, C^{\circ}_{s1}}{m}$$

where C_s is the experimentally determined heat capacity of a solution containing 1 kg of water; m is the number of moles of the solute; 55.506 is the number of moles of water in its 1 kg, C°_{s1} is the molal heat of pure water.

Since in the calculation of Φ_s we assume that the heat capacity of water in solution is the same as the heat capacity of pure water, all the differences between the thermic properties of an aqueous solution and those of water in apparent heat capacity are taken as being due to the solute.

HOW IS HEAT CAPACITY OF SOLUTION MEASURED?

The twin-type Gucker adiabatic calorimeter is used to reliably measure the heat capacity of solutions. The instrument has two identical vessels which are similarly arranged in a trough which serves as an adiabatic shell. A differential thermometer unit is located between the two vessels to measure accurately the difference of temperatures of the vessels. Two experiments are carried out in this instrument to determine the heat capacity of a solution. In the first experiment both vessels contain equal portions of the solvent. In the second experiment a solution of an unknown heat capacity is placed into one vessel instead of the solvent. The vessels are heated by passing direct current through electric heaters provided with variable resistors. In both experiments the heating is done under adiabatic conditions and the ratio of the resistors and hence powers of the heaters is selected such that the difference in temperatures of the two calorimetric units is zero. Using this technique we can assume that the heat exchange in the first and the second experiment is the same, and its effect on the result of measurements is completely ruled out, which is very important for the determination. Using this instrument we determine not the absolute but the relative heat capacity of a solution (relative to the heat capacity of the solvent). This technique is very convenient for calculating the apparent heat capacity, since it obviates the need for an experimental determination of the value $C^\circ_{s_1}$ and rules out errors that could otherwise be due to this determination.

PASSING OVER TO SOLVATION CHARACTERISTICS

The thermodynamic characteristics of electrolyte dissolution and also the thermodynamic characteristics of the ionic sublimation of crystals M_mX_n (solid)$\rightarrow$ M^{n+} (gas) $+$ X^{m-} (gas) help solve one of the main problems, namely, determine the energy changes occurring during the interaction between the ion and the solvent molecules, i.e. calculate the thermodynamic characteristics of solvation. Lattice energy required for the calculations can be found from experimental data on the basis of the Born-Haber cycle* or calculat-

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* Those who want to obtain more information on the Born-Haber thermodynamic cycle can read the book by I. N. Semenov and R. V. Bogdanov *Energy and Chemical Process* published by 'Khimiya' (Leningrad) in 1973 (in Russian).

ed with the aid of the electrostatic model. Lattice energy has been well studied nowadays and determined to sufficient accuracy for many substances.

CHEMICAL POTENTIAL

In addition to the changes in thermodynamic characteristics of a system, its composition changes in the course of chemical processes as well. To characterize the equilibrium in such systems, the notion of a chemical potential μ is used. The chemical potential is a function of the component it characterizes, the temperature of the solution, and activity (concentration) of the component in solution. This dependence is expressed by the following equation

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

where μ_i° is the standard value of the chemical potential when $T = 298.15°K$, and the activity of the component a_i in solution is equal to unity; and R is the gas constant.

The thermodynamics of solutions, and the methods for determining chemical potentials of solutions in particular, are based on the equation for binary systems, which can be written as follows:

$$n_1\Delta\mu_1 + n_2\Delta\mu_2 = 0$$

From this it becomes possible to determine chemical potentials (activities) of the solute from the chemical potentials (activities) of the solvent, and vice versa. In this connection the methods for determining chemical potentials are usually divided into two groups which are based on measuring the solvent activity and the solute activity.

THE SUBJECT OF THE INVESTIGATION — THE SOLVENT

The activity of the solvent can be determined by measuring the pressure of solvent vapour over the solution by any of the following three methods. The static method is based on direct manometric measurement of the pressure of the saturated vapour of the solvent over the solution. The dynamic method, as applied to aqueous solutions, consists in the passage of a dry inert gas in turn through water, through the first water absorber, the aqueous solution, and a second water absorber. The amount of water absorbed in the first absorber is proportional to the water vapour pressure over pure water, while the amount of water absorbed in the second absorber is proportional to the water vapour pressure over the solution. The third method, the comparative one, is known as the isopiestic method, in accordance with the name of the solutions having the same vapour pressure. If we place vessels containing two solutions of a non-volatile substance, one of which is a standard electrolyte solution, into a closed space, we shall observe a flow of the solvent from one solution to the other until the concentration of both solutions changes so as to equalize the vapour pressure. The dependence of the vapour pressure on concentration must be known for the standard electrolyte solution to sufficient accuracy.

Another method of determining the activity of the solvent is based on measuring the lowering of the freezing point (cryoscopy) and elevation of the boiling point (ebullioscopy) of solutions.

THE SUBJECT OF THE INVESTIGATION — THE SOLUTE

The method of measuring the electromotive force in a galvanic cell circuit is the most widely used of the methods based on the measurement of the activity of

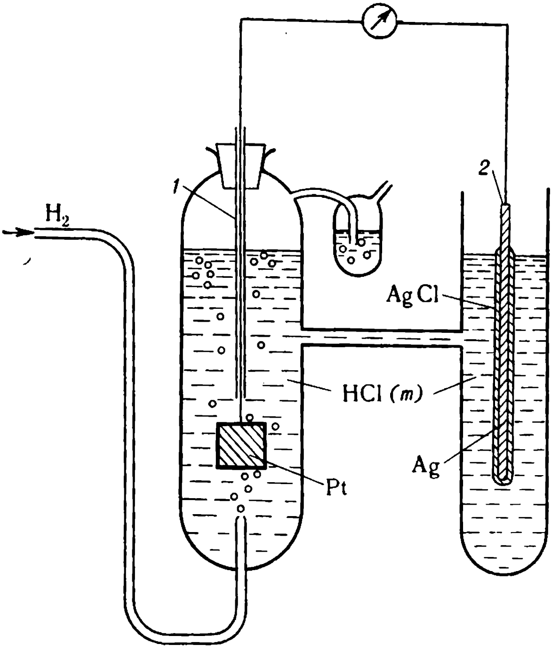

Fig. 11. Galvanic cell: $(Pt)_{H_2} \mid HCl_{(m)} \mid AgCl,\ Ag$:
1 — hydrogen electrode; 2 — silver chloride electrode.

the solute. If we assemble a galvanic cell of the type $(Pt)_{H_2} \mid HCl_{(m)} \mid AgCl,\ Ag$ comprising hydrogen and silver chloride electrodes dipped in hydrochloric acid solution having the concentration m (Fig. 11), the following reactions will occur at the electrodes:

$$AgCl + e^- \rightarrow Ag + Cl^-_{(m)}$$

$$1/2\ H_2 \rightarrow H^+_{(m)} + e^-$$

The overall reaction in a galvanic cell is as this

$$AgCl + 1/2\ H_2 = H^+_{(m)} + Cl^-_{(m)} + Ag$$

The electromotive force of such a galvanic cell is determined experimentally and is described by the Nernst* equation

$$E = E^\circ - \frac{RT}{F} \ln a_{\mathrm{H^+}} a_{\mathrm{Cl^-}} = E^\circ - \frac{2RT}{F} \ln f_{\pm} m_{\mathrm{HCl}}$$

where E° is the standard e.m.f. of a cell, the acid activity being unity; F is the Faraday number; $f_{\pm}$ is the mean ionic activity coefficient.

Now to find the activity coefficient of the solute it is sufficient to determine E°. The method based on the Debye-Hückel theory is usually used for this. According to this method, the experimental data are extrapolated to the region of infinite dilution. But a simple graphic extrapolation method had been used before the Debye-Hückel theory was developed. If we plot $E' = E + 2\frac{2.303\ RT}{F} \log m$ against a certain function of concentration, e.g. $\sqrt{m}$, the limit value of E' (with $m \to 0$) will be equal to E°.

The method of measuring the e.m.f. of a galvanic cell is also used to determine the thermodynamic characteristics of solvation of a stoichiometric mixture of ions, since the e.m.f. is directly connected with the values of free chemical energies (changes in the isobaric-isothermic potential) of ion solvation. The temperature dependence of the e.m.f. makes it possible to determine the changes occurring in the entropy and enthalpy during solvation of a stoichiometric mixture of ions.

In addition to the method of determining the activity of the solute by measuring the e.m.f., there are

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* Nernst, Walter (1864-1941), a German scientist. His work in the field of low temperatures is especially important. He enunciated the 'third law' of thermodynamics. He worked also in electrochemistry.

some other methods, but they are not widely used because of their limited applicability or experimental complications. We shall therefore only name them: measurement of the vapour pressure of the solute, measurement of solubility, distribution of the solute between two solvents, sedimentation during ultracentrifuging, etc.

KINETIC METHODS OF INVESTIGATION

During recent years much information concerning reactions formerly called 'spontaneous' has been accumulated. Examples of such reactions are electron and proton transfer, formation of the hydrogen bond, complex formation, and many others. The study of the kinetics of these reactions has significantly widened our knowledge of solutions and processes occurring in them.

Researchers usually observe a great number of elementary stages in reactions giving unstable intermediate compounds which, in the main, determine the kinetics and mechanism of the reaction. As a rule these unstable compounds can only be studied by the kinetic method. A knowledge of the mechanism enables optimal conditions to be selected and rational principles of carrying out the reaction to be developed. Much experimental material on the kinetics and mechanism of the reactions involving complex compounds in solution has been collected. But despite the considerable advances made in the chemistry of coordination compounds, the effect of the nature of the solvent on the complexation process still remains one of the least understood problems. At the same time, it is interesting to study the formation of complexes in pure or mixed solvents which do not take a direct part in chemical conversions. The main difficulty which researchers encounter in their experiments is the high rate of the complex formation processes. Traditional methods fail to measure accurately the rates of reactions having half-life periods $\tau_{1/2}$ less than ten seconds.

JET METHODS

These are the only methods that can give direct information on kinetics of processes whose half-life periods last from 10^{-3} to 30 seconds. Moreover, the apparatus used in these methods are very simple.

Solutions of the reactants are delivered into a special mixer (Fig. 12*a*) and then, in the form of a single homogeneous jet, having a constant velocity, they are delivered into a tube for observation. The course of the reaction is followed by a change in the concentration of the reactants as they move along the tube (the concentration is measured by a suitable physico-chemical method). The velocity at which the reactants pass through the tube must be constant. Then the distance from the mixer to the point where the change in the concentration is recorded is proportional to the time elapsing from the beginning of the reaction to the moment of observation.

The method described is known as the constant or continuous jet method. Similar kinetic data can be obtained by abruptly stopping the jet and determining the changes in the concentration of the reactants using a suitable sensing element and a quick-response device at any point of the observation tube (Fig. 12*b*). This method is known as the stopped jet method. In most modern instruments, the kinetic curve is recorded by an oscillograph, whose scanning is initiated either by a special photoelectric device or electromechanically.

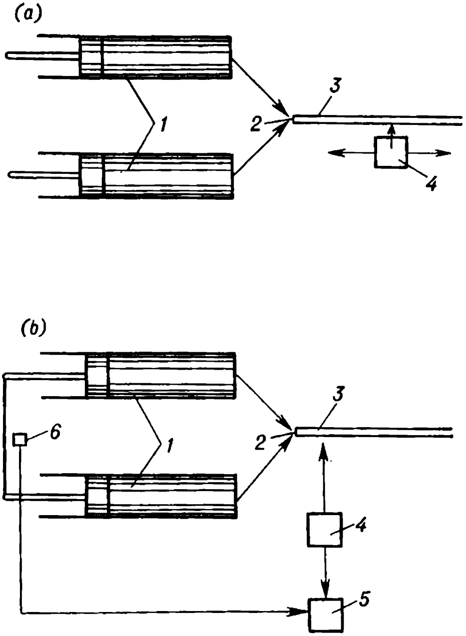

Fig. 12. Schematic diagram of apparatus for studying fast reactions by the method of (a) continuous, and (b) stopped jet: *1* — reactant syringes; *2* — mixer; *3* — observation tube; *4* — concentration pick-up; *5* — quick-response recorder; *6* — piston limiting stop.

RELAXATION METHODS

In order to study chemical processes in solution lasting less than 10^{-4} seconds use is made of various relaxation methods (abrupt change of conditions) or various magnetic resonance methods (NMR, NPR, Echo-spin, etc). These methods can be used to study only fast processes and are not suitable for studying reactions far from being in equilibrium and having a complicated mechanism (e.g. reactions with several successive or parallel stages). Relaxation methods are based on upsetting an equilibrated system by changing any of its physical parameters. As the action on the system is discontinued, a new or the initial equilibrium is gradually established in the system. The relaxation process, which continues from 10^{-7} to 1 second, is measured. Depending on the physical parameter, which is changed to upset the equilibrium in the system, we have the method of abruptly changing the temperature, the method of abruptly changing the pressure, and the method of abruptly changing the electric field intensity. Inertialess methods (spectrophotometric or electric conductance method) are used to record the changes in the concentration of the reactants produced by the relaxation.

Fast chemical reactions in solutions can be studied not only by pulse methods, but also by the method of periodic action. Methods employing absorption of ultrasound and the NMR method are most widely used now. Ultrasound can be used to study chemical reactions whose duration is approximately equal to the period of a sound wave. The NMR method is applicable to the study of the kinetics of reactions occurring at various rates. The essence of the NMR method is that the energy levels of an atomic nucleus, having a magnetic moment, are split in a uniform magnetic field, making it possible to absorb or emit quanta of energy as the nucleus jumps from one split level to another. The amount of the splitting depends on the extent to which the nucleus is shielded, which is determined by the character of the chemical compound formed. Reactions proceeding at a usual rate can be studied by changing the intensity of the absorption band in time, while information on the kinetics of reactions with half-lives between 1/2 to 10^{-9} seconds can be obtained by measuring changes in the configuration of the absorption bands, in their width in particular.

STRUCTURAL METHODS OF INVESTIGATION

Obtaining information on the structure of solvents and solutions is especially important in studying them. In Chapter 2 we said that one of the most direct methods of investigations is the roentgenographic method. P. Debye and his collaborators were the first to apply roentgenography to such investigations in 1916. X-ray studies of benzene have shown that the appearance of diffraction maxima is connected not only with the orderly arrangement of atoms in the molecule, but also with the presence of intermolecular diffusion. This could take place only if the mutual arrangement of the molecules in the liquid was not chaotic.

The X-ray method remained the main source of information on the molecular structure of liquid for a long time. It gives reliable information on the distribution of atoms in monatomic liquids, but in the case of polyatomic liquids the question concerning the orientation order arises, and the roentgenographic method based on modern experimental techniques and theory fails to lead us to any simple conclusions. Usually it can only be used to determine the interatomic distance in a liquid. It is even more difficult to interpret the molecular structure of solutions and the coordination of ions in the short-range and long-range solvation regions.

New radiophysical methods based on high-frequency measurements of the dielectric constant and dielectric losses offer new possibilities in the study of the structure of solutions. They helped obtain quantitative information on the character of the heat motion of particles in some solutions. The disadvantages of these methods are their applicability only to polar liquids and the ambiguity of the results.

Information on the structure of solutions, and also a picture of the heat motion in them can be obtained by optical methods (Rayleigh scattering, Raman spectra, absorption spectra in the U-V, visible, and I-R regions, and others). Advances made in this field have given information on the formation of intermolecular hydrogen bonds, on the hydrability of ions, on their coordination, association, etc. Optical methods are among the most reliable, although their interpretation is often fraught with ambiguity.

The ultrasound method offers good prospects as well. But there is no good theory yet that relates the velocity of sound propagation in liquids to the structure of their molecules.

The magnetic resonance method is one of the new methods for studying the structure of solvents and solutions. Depending on the particular magnetic moment responsible for the resonance, the method is called either electron paramagnetic resonance (EPR) or nuclear magnetic resonance (NMR). The magnetic resonance method is sensitive to the minutest changes in the state of the electron shells of atoms in a molecule. It can trace even weak intermolecular effects and therefore it is becoming more popular in the study of solvation in solutions of electrolytes and of structure of solutions. Chemical shifts in the spectra of the magnetic resonance of nuclei, the time of relaxation, and the related values can be determined experimentally using this technique. The proton magnetic resonance technique has been developed especially well. It is used primarily to study the state of water in aqueous solutions. Many papers have been recently published reporting research on the structure of non-aqueous and mixed solvents and their electrolyte solutions by this method.

The spin-echo method is now successfully used to study the structure of solvents. The method differs from the usual method of observing NMR signals in that the radio-frequency electromagnetic field does not continuously act on the specimen, but in pulses. This method can successfully be used to measure the absolute value of the relaxation time and to study auto-diffusion in water and other liquids

EXPERIMENTAL DETERMINATION OF SOLVATION NUMBERS

There are several methods by which the number of solvent molecules bound with ions can be determined. As a rule, the methods used for determining the solvation numbers can only determine either the sum of the solvation numbers for ions that form the electrolyte, or their difference.

. . . BY THE TRANSPORT NUMBER

One of the ways by which solvation can be studied (determination of the number of molecules that make a stable kinetic particle, ion, in solution) is by determining the transference, or transport number, which characterizes the amount of electricity transported by the ions of a particular type.

A special instrument is used to determine the transport number from the changing concentration of solution. It has three compartments, namely, cathode, anode and an intermediate compartment. The amount of electricity that passes through the instrument is measured by a coulometer, whereas the change in the composition of each compartment is determined analyti-

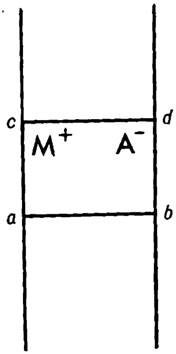

Fig. 13. Moving interphase method diagram.

cally. An inert non-electrolyte, for example, a hydrocarbon, is added to the electrolyte solution under study, and the change of its concentration in the cathode and anode compartments is measured. The difference in the transport numbers is used to calculate the difference between the quantity of water molecules that move together with the cation and the quantity of molecules that move together with the anion. By carrying out a series of measurements with various electrolytes one can find out the hydration number for each ion provided it is known for one of the ions. Hydration number determined in this way for univalent cations can be arranged in the following sequence

$$Li^+ > Na^+ > K^+ > Cs^+ > H^+$$

Another method of determining the transport number is the moving interphase method. Suppose solutions of two electrolytes, having the anion *A* in common, form a distinct interphase *ab* (Fig. 13). Let the cations move upward and the anions downward by the electric field. In a lapse of time the interphase will shift to another position *cd*. In this case all cations M^+ contained in V litres of the solution between the planes *ab* and *cd* must pass through the plane *cd*. Assume that at a given moment of time, Q coulombs of electricity has passed through the solution. Then t, the transport number of cation M^+, can be calculated from the following equation:

$$t = \frac{VcF}{zQ}$$

where c is the concentration of the cation M^+, in moles per litre.

The method of determining the transport number by the electromotive force compares circuits with and without the ion transfer. It has been found that the electromotive force E_t of a galvanic cell with transfer is connected with the e.m.f. E of a cell without transfer (the concentrations being the same) by the following equation:

$$E_t = aE + bE^2 + cE^3$$

The transport number can then be found as this:

$$t = dE_t/dE$$

We should also mention the method of determining the transport number by centrifuging a galvanic cell. In this, the e.m.f. of a cell is due to the difference of centrifugal potentials of two electrodes.

Among other methods of estimation the number of solvent molecules, that form the solvate shell, are those based on determining the size of the solvated ion.

. . . BY THE RATE OF DIFFUSION

A direct method of determining the size of a kinetic particle consists in measuring the velocity of its movement v under the action of a certain given force

F acting to overcome the viscous force of the solvent. In this case, the following classical expression holds for macroscopic spherical particles:

$$v = F/(6\pi\eta r)$$

where η is the viscosity of the medium and r is the radius of the sphere.

This formula holds for colloidal particles, but is inapplicable to the movement of smaller molecules and ions. Therefore when dealing with ions in solution the investigators have to look for methods of finding appropriate corrections. The method of determining solvate numbers on the basis of diffusion can probably be used to assess the number of strongly bonded particles of the solvent and to establish a lower limit of the solvate number.

. . . BY COMPRESSIBILITY OF SOLUTION

This method suggests that the solvent molecules inside the solvate shell are compressed to the maximum by an electrostatic field of the ion, and with the increase in pressure the remaining solvent molecules are only compressed.

. . . BY DERIVATOGRAMS

The ion coordination in the regions of short-range and long-range solvation can be studied derivatographically. As a solution is heated and evaporated, the degree of binding of the removed solvent molecules can be determined by the rate at which the mass of the solution decreases. It has been established that the dependence of the loss of the solution mass on time is expressed by straight lines (Fig. 14). The points

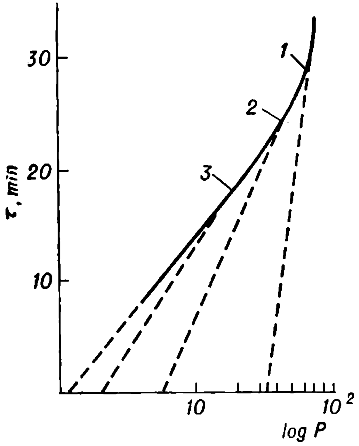

Fig. 14. Changes in mass of LiCl solution in methyl alcohol during removal of the solvent. The intersection points characterize the following:

1 — region of short-range solvation of cation; 2 — region of cation and anion solvation; 3 — region of long-range solvation.

of intersection of the straight lines with the curve correspond to the changes in the rate at which the solution mass decreases with time. Each straight line in Fig. 14 corresponds to the region of solutions characterized by the same degree of binding of the removed solvent molecules.

The analysis of derivatograms of salt solutions in water and non-aqueous solvents shows that this method can successfully determine the number of solvent molecules in the region of short-range solvation (hydration) of cations. The coordination numbers of cations in water, in methyl and ethyl alcohols are the same, and they are close to the numbers which are characteristic of them in saturated solutions: 4 for Li^+, 6 for Na^+, K^+, and Rb^+, 8 for Cs^+, 6 for Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, and 8 for M^{3+} (rare earth element ion), Cl^-, Br^-, I^-, and NO_3^-.

Discrete regions of the solvent characterized by a definite number of molecules are also found in the region of long-range solvation (hydration). But the transfer from the short-range to long-range solvation (hydration) of ions is not always distinct since the bond of the cation with the solvent molecules in the region of long-range solvation can be more pronounced than the bond of the anion with the solvent molecules in the region of short-range solvation.

. . . THERMOCHEMICALLY

The thermochemical method offers good prospects for the study of ion coordination in the region of short-range solvation. The essence of the method is the calculation of ΔH_{soln} of salts at various concentrations of electrolyte and finding, on this basis, of $\Delta(\Delta H_{soln})$ which characterize the process of removal of a certain number of solvent molecules (calculating with reference to one mole of a salt). The increase in $\Delta(\Delta H_{soln})$ with the concentration of electrolyte is jumpwise and indicates the presence of discrete regions in solution which differ in the degree of binding of the solvent molecules with the ion.

The application of this method to aqueous solutions of electrolytes of the type I—I has shown that the number of water molecules in the I and II regions of long-range hydration for stoichiometric mixtures of ions is 30 and 60. These results agree well with derivatographic data.

Very useful information on the actual kinetic entities in solution can be obtained by studying the electricity transport through electrolyte solutions by measuring their electrical conductivity. Experimental studies of electrical conductivity are very simple. This is especially important in the study of solutions in non-aqueous and mixed solvents, and also very dilute electrolyte solutions. Electrical conductivity is determined by measuring the resistance between two electrodes of certain configuration and size in a cell filled with solution. It is quite natural that the resistance depends on the geometry of the cell, the size of the electrodes, and the interelectrode distance. Therefore, the cell is first calibrated against a standard solution with the known specific resistance (KCl solution is usually used for the purpose).

Electrical conductivity can be measured with alternating and direct currents, and also at radio frequencies. The requirements for measurements are as follows: accurate maintenance of given temperature, depolarization of electrodes, and high accuracy of the measuring circuits. Errors due to polarization of electrodes when measuring electrical conductivity with alternating current are usually minimized by using sound frequencies, and also by coating the electrodes with a thick layer of platinum black. Although this method ensures maximum accuracy and is popular with the investigators, it becomes very difficult in practical high frequency measurements because of the capacitance and inductance effects. Measurements with direct current are free from these disadvantages. The method is based on the comparison of the voltage drop between two points in the solution and the voltage drop across series-connected standard resistor. But the method has a disadvantage of its own, namely, ideal reversible electrodes should be used to measure the voltage drops in solution. In cases where high accuracy is not required (analytical and industrial control), use is made of radio-frequency method, whose advantage is the absence of electrode contact with the solution. This completely eliminates the source of polarization error.

Chapter Seven

Theories of Electrolyte Solutions

The Debye-Hückel theory of solution and its further refinements by many other investigators occupy an important place in the development of the theory of solution. But the Debye-Hückel theory accounts for only the long-range Coulomb forces and describes the properties of solvents only by their dielectric constants, and the properties of ions only by their charges. The development of special theories, similar to that of Debye-Hückel, is simplified because in certain regions of solution concentration (the theory holds only for very dilute solutions), only one type of interaction predominates. This makes it possible to disregard quantitatively all complications due to side effects. In transition from infinitely dilute to concentrated solution, it is necessary to account not only for the long-range electrostatic forces but also for short-range forces as well. In the general case, the theory of solution of electrolyte must account for the nature and interaction of all particles in the solution.

The modern state of our knowledge of the structure of atoms, ions, and molecules leads to the conclusion that the further development of the theory of electrolyte solution (the theory of ionic solvation included) should proceed along the path of incorporating quantum mechanical concepts and the elements of quantum statistics. At the present time limitations to the development of the theory are imposed by the extremely complicated mathematical means used for the purpose.

THE FUNCTION OF DISTRIBUTION AND POTENTIAL OF THE IONS

In order to describe an electrolyte solution thermodynamically, it is necessary to know the inner potential energy of this system. This value, in turn, is defined via the energy of interaction between the ions, and the function of their radial distribution in solution (for details see Chapter 2).

The attraction between the ions is usually defined as a sum of potentials of pair interactions which depend only on the interionic distance. The distribution of ions and molecules in electrolyte solutions is characterized by competition between the long-range Coulomb forces and the heat motion. This distribution is orderly even at considerable distances. For very concentrated solutions, the distribution function becomes similar to the distribution function of ionic crystals, which indicates the presence of long-range order in them.

One of the first and most successful approximations in the calculation of the potential of ions interaction in solution is the Debye-Hückel theory. It suggests that each ion in solution is surrounded by an atmosphere of ions of the opposite charge. The charge density of the ionic atmosphere decreases with the distance from the ion, the total charge of the atmosphere being equal to the charge of the ion but taken with the opposite sign. The theory helped establish quantitative relationships between the radius of the ionic atmosphere and the electrolyte concentration and determine the time of relaxation of the ionic atmosphere, etc. This theory does not include the solvation processes and the picture of interaction between separate ions is over-simplified.

THE THEORY OF LONG-RANGE FORCES

The originators of a theory tend to consider systems in which one type of interaction dominates.

LIMIT PROPORTIONS

The activity coefficient of a solute is an important factor in developing a theory. The meaning of the activity coefficient of an electrolyte can better be understood by comparing it with the activity coefficient of a non-electrolyte. Such a comparison is shown in Fig. 15. It gives the dependence of the logarithm of the activity coefficient of a solute on its molar fraction for aqueous solutions of two non-electrolytes and three electrolytes. The figure shows that the activity coefficient of non-electrolyte solutions can both increase o rdecrease with decreasing concentration, but in either case $\ln f$ tends to zero according to the law close to a linear one, while the tangent of the angle of slope of curves *1* and *2* tends to a certain constant value. The other limit proportion is characteristic of electrolyte solutions. As the concentration decreases, the tangent of the angle of slope tends to minus infinity. The static theory can be used to show that short-range forces act in solutions where the first limit proportion is observed. On the other hand, long-range forces must be effective in

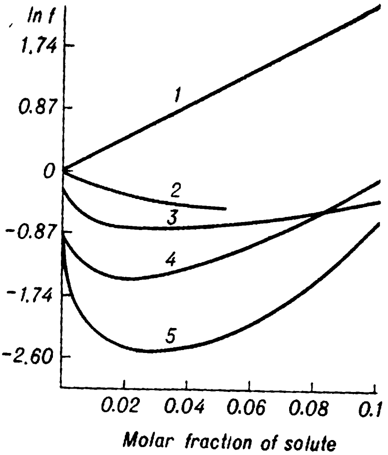

Fig. 15. Dependence of activity coefficient of solute on concentration in aqueous solution of electrolyte and non-electrolyte:

1 — saccharose; 2 — glycine; 3 — NaCl; 4 — $CaCl_2$; 5 — $LaCl_3$.

solutions where the second limit proportion is observed between the solute particles. Thus, Figure 15 proves the presence of short-range forces in the solution of non-electrolyte. As the concentration of electrolytes approaches zero, their curves are characterized by the predominance of long-range forces. As the concentration increases, the curves straighten out and become linear. This region is characterized by the appearance of short-range forces. These play a decisive role at higher concentrations.

LONG-RANGE INTERACTIONS IN SOLUTIONS

In the account of long-range action in solutions of electrolytes according to the Debye-Hückel expression for the electrostatic potential of an ion, the mean activity coefficient I—I of electrolytes is defined by the equation

$$\log f_{\pm} = -\frac{A\,|z_1 z_2|\,\sqrt{I}}{1 + Ba\sqrt{I}}$$

where A and B are constants depending on temperature and dielectric constant of solution, and z_1 and z_2 are ion charges.

The Debye-Hückel equation for the activity coefficient includes, in addition to the temperature, concentration, and dielectric constant, an invariable parameter a, known as the "distance of the maximum approach" of ions. For very dilute solutions, the term $Ba\sqrt{I}$ becomes negligibly small compared with unity, and the approximate equation takes the form

$$\log f_{\pm} = -A\,|z_1 z_2|\,\sqrt{I}$$

This dependence is called the limit Debye-Hückel law according to which log $f_{\pm}$ as a function of $\sqrt{I}$ or $\sqrt{C}$ approaches a straight line with significant dilutions. This equation is very important in the study of solutions.

It follows from the Debye-Hückel equation that the numerator $(-A\ |z_1 z_2|\sqrt{I})$ characterizes the long-range Coulomb effects, while the denominator $(1 + Ba\sqrt{I})$ is actually a correction for the short-range interionic effects. However, the short-range forces are given here in rough approximation since the ions are considered non-deformable spheres, all with the same radii, whereas the interactions occurring in any real solution cannot be described as the interaction of solid spheres.

The short-range interionic effects, and also forces acting between the ions and molecules of the solvent are described by a non-linear dependence of log $f_\pm$ on the ionic strength. An additional term has thus been introduced to account for the short-range effects in the Debye-Hückel equation:

$$\log f_\pm = -\frac{A|z_1 z_2|\sqrt{I}}{1+Ba\sqrt{I}} + DI$$

In this form the equation is suitable for a qualitative description of activity coefficients of electrolytes in the absence of experimental data.

Later, the thermodynamic theory of ion interaction with the solvent was combined with the Debye-Hückel theory for interionic actions. As a result, an equation for the activity coefficient taking into account the ion solvation, was derived. This model has certain indisputable advantages over the Debye-Hückel model, and it agrees more closely with the real picture. In the first instance, this is because the rough approximation made when incorporating the dielectric constant ε of a pure solvent into the equation is to a certain extent justified in this case. Some authors have shown that a lowering of the dielectric constant due to the presence of solute ions occurs in the first layer of solvent molecules surrounding the ions. If this layer is regarded together with the ion as an entity, then the description of the liquid outside 'ions' by the dielectric constant of pure solvent will undoubtedly be a less rough approximation.

THE THEORY OF SHORT-RANGE FORCES

We already know that an electrolyte solution is a complicated system characterized by various interactions. On the one hand, there are the interionic actions that slowly weaken with distance, i.e. long-range forces, and on the other hand, there are the interactions between ions and molecules of preferably ion-dipole character, which weaken more quickly with distance, and finally, there are the interactions between the solvent molecules (by the van der Waals forces or by the formation of the hydrogen bond). As the distance increases, the interactions of the third type weaken sharply and turn into a typical case of short-range forces.

THE ROLE OF SHORT-RANGE EFFECTS

As we compare the values of full energies of the interaction of particles in electrolyte solutions, i.e. the energies required to separate the interacting particles an infinitely long distance from one another, one can come to the erroneous conclusion that the state of a liquid electrolyte system always depends on the interaction between the solvent molecules with the ions, while the liquid solvent is only a donor of molecules which solvate the ions. In fact, the full energy of interaction of water molecules, for example (the energy of the hydrogen bond) is 21 kJ/mole, while the energy of interaction of water molecules with ions is 10-100 times higher. But the destruction of the water structure by many ions in an aqueous solution is not always compensated for by the formation of bonds between the ions and water molecules. The explanation to this experimentally proved fact should be looked for in the short-range interactions between solvent molecules. The concept of the heat motion of particles in liquids, developed by Y. I. Frenkel, can be used in this case. According to this concept, the behaviour of particles in liquid solutions depends on the contribution to the magnitude of the potential barrier which the particle overcomes as the transient equilibrium state in the solution structure is shifted. This contribution does not depend on the full energies of interaction, but depends only on how the interaction force diminishes with distance. The higher the rate at which the energy decreases with increasing distance between the particles, the higher the potential barrier. Because of this, weak though they may be, the interactions quickly diminishing with increasing distance (short-range effects) are very important for the properties of solutions.

EXPERIMENTAL CONFIRMATION

In aqueous solutions of electrolytes the water-water interaction depending on the hydrogen bonding which in its nature is a short-range interaction, is very important for the behaviour of ions, and in many respects determines their properties. The interaction becomes more apparent in dilute solutions containing 'free' water, i.e. water whose molecules are outside the immediate vicinity of the ions. The formation of bonds between water molecules diminishes hydration of ions. On the contrary, the cleavage of the water-water bonds intensifies ion hydration in solution. Thus, the hydration of ions is intensified to a certain extent as the temperature increases and the structure of water is destroyed. Numerous experiments confirm this. For example, the study of the infra-red absorption spectra of the oxygen-containing anions ClO_4^- and SO_4^{2-} in crystal hydrates and aqueous solutions of salts has shown that during the transfer from crystal hydrate to aqueous solution the hydrogen bonds between water molecules and the oxygen of these ions are broken. Of course, in this case the anion hydration weakens due to the formation of the water-water bond.

These considerations are equally valid for non-aqueous and mixed solvents. Small quantities of the second component molecules can produce their effect on the liquid structure, the effect depending on the relative size of molecules of the main component and the additive, and also on the character of bonds formed. For example, small admixtures of methyl alcohol to ethyl alcohol stabilize the structure of the latter. Small quantities of ethyl alcohol added to methyl alcohol destroy the structure of methyl alcohol. Stabilization of solvent structure should decrease solvation and hence reduce solubilsty of salts. The destruction of solvent structure should produce the opposite effect. This is verified expeirimen tally. Thus, the state of the solvent during solvation of ions in dilute solutions is closely connected with the marked effect that short-range forces produce on the properties of liquid solutions.

Chapter Eight

Instead of Conclusion

As we widen our knowledge of solutions, we may go on to consider new problems. Among them are the study of the electron state in solution, the action of a magnetic field, radiation, etc., on a solution, and so on. We shall look at some of them.

SOLVATED ELECTRON

The discovery of the solvated electron is one of the most important discoveries in modern chemistry. Solvated ions are the simplest and the strongest reducing agents. They can be used, for example, to obtain ions of abnormal valency and ion radicals. They are an important intermediate product in radiation, photochemical, electro-chemical and other processes. These particles offer great possibilities for the study of the mechanisms and rates of reactions involving electron transfer. The special interest to the state of electrons in solution is also because the electron is considered by all investigators as one of the main constituents of matter.

IT IS LIKE AN ANION

By "solvated electrons" we mean an electron surrounded by oriented molecules of solvent. In aqueous solutions these formations are called hydrated electrons. Electrons captured by the solvent differ from free electrons in their lesser mobility and higher thermodynamic stability, and resemble solvated anions. Their characteristic feature is their short lifetime. Solvated electrons are also characterized by single negative charge. The radius of a hydrated electron varies from 0.25 to 0.3 nm, its equivalent conductivity e_{aq} is significantly higher than that of all ions except H_3O^+ and OH^-, and in this connection its diffusion mechanism differs from that of other ions. It has been conjectured that the electron moves in solution by very fast jumps from one 'trap' to another. The trap is a cavity in the mass of water formed by the electron itself. The tetrahedral structure comprising four molecules of water and an electron has been calculated theoretically. This structure explains the main experimental results. It does not require the suggestion of the presence of vacant sites. Electron diffusion is explained by 'tunnelling' into the neighbouring tetrahedrons.

TRANSFER OF SOLVATED ELECTRONS

Electrons are especially readily solvated in polar liquids. Many properties of solvated electrons in ammonia, amides, alcohols, etc. are known. The reactions of hydrated electrons with water and the products of its dissociation and ionization, with many inorganic and organic compounds, and with substances entering the composition of biological systems, are studied in detail today. All these data are discussed in detail in special literature.

Owing to their simplicity, solvated electrons, being singly charged ions, are ideal models for studying the electron transfer processes and serve as perfect tools in kinetic and spectroscopic studies. It should be noted that the development of many branches of chemistry depends on the advances made in the study of solvated electrons. Many problems concerning the processes occurring in a living organism are connected with the solution of problems of the electron transfer from one particle to another. The process of the regeneration and propagation of nerve pulses can serve as a good example.

MAGNETIC TREATMENT OF ELECTROLYTE SOLUTIONS

The fact that a magnetic field has an effect on the living matter and some chemical reactions has been known for long. But the detailed scientific investigation of the problem of the magnetic treatment of solutions has been only recently started. The main difficulty is the absence of coordinated experimental data that could give a definite answer to the question: on *what* and *how* do magnetic fields produce their effect? They can produce different effects on the solvent and the solute, and on all components of the solution as a whole.

ATTEMPTS OF EXPLANATION

Various hypotheses, such as the 'colloidal', 'ionic', 'aqueous' hypotheses and so on, have been offered to explain the mechanism of the processes occurring during magnetic treatment of aqueous solutions.

The 'colloidal' hypotheses are based on the suggestion that magnetic fields act on colloidal particles characterized by a rather high magnetic susceptibility (para- or ferromagnetism). Supporters of these hypotheses think that only para- and ferromagnetic particles of submicroscopic impurities, which are always present in water, can interact with magnetic fields during magnetic treatment.

The 'ionic' hypotheses are based on the conjecture that magnetic fields produce their effect on the movement of ions. Most supporters of the 'ionic' hypotheses emphasize the effect of magnetic field on the transitory change in the ion hydration. One of the explanations is that as the ion quickly passes a magnetic field with a sufficiently high gradient, it is displaced abruptly with a considerable acceleration, the hydrate shells of such ions being deformed for a period of time. This facilitates the mutual attraction of ions which make contact through a smaller number of solvent molecules, and hence accelerates the formation of crystals as the salt is precipitated from solution. Another explanation of the possible role of ions in magnetic treatment of water is connected with the formation of electric current, which in turn can produce a marked effect on ion hydration. There are some other explanations of the possible action of ions in magnetic treatment of water, for example, hydrodynamic oscillations of variable frequency, etc.

'Aqueous' hypotheses suggest that magnetic fields act on water itself, and that water properties change depending on the degree and character of association of its molecules. These hypotheses suggest also that structural changes in water could be maintained in time. The structural changes themselves, produced by the action of magnetic fields, are connected with the destruction or deformation of hydrogen bonds due to the resonance of field oscillations and own oscillations of the associates with their dispersing action on the associates of water molecules, with the possible role of water structures formed by single ions, with the changes in the H—O—H angles, etc.

It should be noted that the 'aqueous' hypotheses seem to disagree with the main physical concepts. Pure water relates to diamagnetic substances and the time of its structural relaxation is so small that the idea of 'structural memory' of water seems irrational.

These hypotheses are the first attempts to understand the processes occurring in solutions under the action of magnetic fields, and they are far from being perfect. It is necessary to find objective quantitative characteristics of this influence, and they should be obtained by properly formulated experiments. It is necessary to find out how magnetic treatment affects pure solvents and solutions free from impurities, especially free from air gases. It is necessary to compare these effects with controlled variation of all components of the solution and environmental factors. As to our own opinion, we think that impurities produce an appreciable effect on the structure of water.

INDUSTRIAL USES

Despite the fact that the development of the theory of magnetic treatment of electrolyte solutions is now only beginning, magnetic treatment is widely used now in industry. It is used to control scale deposition in boilers. Magnetic treatment proves effective in the control of deposition of not only mineral salts but organic substances as well. Positive results were obtained by mixing concrete with magnetically treated water, in the purification of water from colloidal particles, in the concentration of minerals, in trapping dusts, in dyeing synthetic fibres, and in the manufacture of soda and storage batteries. It has been established that magnetic treatment produces an effect on the corroding properties of aggressive solutions, the effectiveness of coolants and lubricants, etc. And it is only the beginning...

BIOLOGICAL ACTION

The action of magnetic fields on biological objects (a field of special investigations) is the subject matter of special science, magnetobiology. A magnetic field does affect biological activity, and its effect has been established at the cell level. Recent studies show that an artificial magnetic field acts on the human body and especially on its central nervous system, the sex glands, lungs, and kidneys. Through further studies man may consciously control the action of magnetic field on the human organism, thereby widening the field of its application.

RADIATION EFFECTS

Other physical actions can also produce effects on the properties of electrolyte solutions. Radiation, light, ultrasound, and electric current are among these important physical factors.

EFFECT OF IONIZING RADIATION

Ionizing radiation, such as X-rays, currents of alpha-, beta-, and other charged particles, are especially effective means of action on solutions. There is a special branch of chemistry known as radiation chemistry of water and aqueous solutions. Radiation processes produce profound chemical transformations giving rise to new substances. The amount of new substances is characterized by the radiochemical yield, i.e. the number of molecules that undergo changes per 100 eV of consumed energy of ionizing radiation. In the radiolytic decomposition of water, this value is approximately equal to four decomposed molecules.

The energy of the ionizing particle, as it passes through liquid water, is consumed to ionize and excite the water molecules. The process gives an electron (whose energy is from 0 to several hundred electronvolts) and the ion H_2O^+. The electron quickly looses its excess energy to ionize and dissociate other molecules of water. The resultant energy of this electron is less than the energy required to excite water. This electron can be called an 'underexcited electron'. Such an electron looses its energy comparatively slowly (probability 10^4 times less than the probability of ionization and dissociation processes). The energy is consumed to generate oscillations in water molecules. Then, in the lapse of time of the order of 10^{-11} second, the electron is hydrated and becomes a hydrated electron. In the absence of impurities, the transition of the 'underexcited electron' into the hydrated electron is not accompanied by chemical processes. The ion H_2O^+ is turned simultaneously into OH. The overall reaction of ionization under the action of radiation can be written as this

$$2\,H_2O \rightarrow H_3O^+ + OH + e^-_{aq}$$

The rapid dissociation of other excited water molecules gives the radicals H and OH in a lapse of time of the order of 10^{-13} second. Thus, the irradiation of liquid water gives, in addition to e^-_{aq}, also H and OH, which perform the role of the main primary active particles known as free-radical products. As a result of the secondary interactions, the molecular products H_2 and H_2O_2 are also formed:

$$OH + OH \rightarrow H_2O_2$$
$$H + H \rightarrow H_2$$
$$e^-_{aq} + H \rightarrow H_2 + OH^-$$
$$e^-_{aq} + e^-_{aq} \rightarrow H_2 + 2\,OH^-$$

These reactions are accomplished usually in the lapse of time measured by 10^{-9} second. At the same time they are not the only sources of H_2 and H_2O_2. Free radicals are then recombined to give water as the final product

$$H + OH \rightarrow H_2O$$
$$e^-_{aq} + OH \rightarrow OH^-$$
$$H_3O + OH \rightarrow 2\,H_2O \text{ and others.}$$

RADIOLYSIS OF SOLUTIONS

Radiolysis of water becomes complicated if water contains dissolved substances. For example, the presence in water of dissolved oxygen increases the quantity of hydrogen peroxide formed. It can be determined quantitatively by chemical methods. At the present time, radiolysis, or as it is also called, the radiation chemistry of aqueous solutions of various substances (including solutions of complicated organic compounds of great biological importance) is well studied. Radiolysis of non-aqueous solution is being studied as well.

EFFECT OF ELECTROSTATIC FIELD

An electrostatic field also produces an important effect on the properties of solutions. The prototype of this action is the effect that the surface of ionic crystals produces on the properties of superficial layers of the solvent. For example, water in thin films freezes at lower temperatures and in frozen soils it can exist in the liquid state at temperatures as low as minus 50°C.

* * *

To end our discussion, we should like to point out again that the history of research into solutions is rich in sensational discoveries. These are, for example, the discoveries of the 'structural memory' of water, and superdense (abnormal) water. We think that a more critical approach to the interpretation of the observed phenomena is required. This should rest on the foundation of the modern science. Though our knowledge of electrolyte solutions is vast, it is only a minute portion of what we shall find out in future. There is a vast field of activity for the future generations.

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