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BY

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PREFACE.

This little book is intended principally for the use of Students preparing for the First and Second Stage Examinations of the Board of Education (South Kensington) in Practical Organic Chemistry (Subject XI.P.). It is hoped, however, that it may also be found useful by general students. In working through this book, I would suggest the following mode of procedure :—

The student should first perform all the tests that are given for each substance. He should then make up for himself mixtures containing compounds which are difficult to detect in the presence of each other. Thus, after performing all the tests in Chapter III., he should make a mixture containing an Oxalate, Tartrate and Citrate, and endeavour by means of the table given, to detect the presence of each of these bodies.

After having worked through the book in this way, he should test his skill on unknown mixtures supplied by the teacher.

I trust that the large number of equations expressing the various reactions, and the full directions that are given concerning the performing of any difficult experiment or test, may minimize the work of the teacher.

It should be pointed out that the most characteristic tests are those marked thus *.

In conclusion, I beg to acknowledge with thanks the help given me by the Assistants in the Chemical Laboratories of Allan Glen's Technical School, viz., Messrs. J. Dewar, R. Gilliespie, W. Guthrie, and R. Henderson.

G. G.

Glasgow,
May, 1898.

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PRACTICAL ORGANIC CHEMISTRY

CHAPTER I

DETECTION OF CARBON, HYDROGEN, NITROGEN, CHLORINE, BROMINE, IODINE, SULPHUR, AND PHOSPHORUS, IN ORGANIC COMPOUNDS

CARBON and HYDROGEN.

(a) The presence of **Carbon** in many organic substances may be shown by simply heating a small quantity of the body on platinum foil over the Bunsen flame, when it may take fire and burn clearly, or with a sooty flame; or first char and then burn completely away; or act in a variety of other ways.

(b) Again, when heated with concentrated sulphuric acid, a number of organic substances are *blackened*, and in some cases *carbon dioxide* is evolved, and is detected by lime-water. If it is required simply to ascertain whether a given substance contains *carbon*, the above preliminary experiments (*a* and *b*) may be performed, but if the compound has also to be examined for the presence of **Hydrogen,** time and trouble may be saved by proceeding straight away as directed in (*c*).

(c) A hard glass tube about 20cm. long and 1cm. internal diameter, closed at one end, is required. To the open end is fitted a cork through which passes a small glass tube connected with a delivery-tube. A small quantity of the substance under examination is *quickly* and intimately mixed in a perfectly *dry* mortar with **fine freshly ignited** cupric oxide. The mixture, when placed in the combustion tube, should occupy about 4cm. at the closed end. The tube is filled up to about 6cm. from the end, with *granular* oxide of copper, which is kept in its place by means of a small coil of copper gauze about 1cm. long, and is then supported in a horizontal position with a piece of sheet asbestos about 10cm. square slipped over it, and placed about 3cm. from the cork to prevent it from burning. Inside the tube, between the cork and the asbestos shield, a small quantity of **anhydrous**[1] copper sulphate is put, and finally the combustion tube is closed by the cork, whilst the delivery tube dips into a test tube containing lime or baryta water. Heat is gently applied, first near the copper coil, and then as the granular oxide becomes red hot, it is extended towards the mixture at the closed end.

The *Carbon* in the substance combines with the oxygen in the copper oxide to form *carbon dioxide*, which renders the lime (or baryta) water milky, whilst *water* is formed by the oxidation of the *Hydrogen*, and can generally be seen condensed in the end of the tube, but in some cases the quantity present is so small that it could not be distinguished were it not for the anhydrous copper sulphate, which however is turned **blue** by the slightest trace of moisture.

When volatile substances are being examined, they should be placed in the end of the tube alone (liquids being enclosed in a small bulb with a capillary), and should not be heated until the oxide in front is quite red hot, and then only very gradually. The tube used in this case must of course be much longer than when non-volatile compounds are being tested.

NITROGEN in an organic compound is recognized—

(**a**) By the unpleasant smell resembling burnt hair, noticed when heating certain organic substances on platinum foil.

---

[1] Obtained by heating finely-powdered cupric sulphate in a crucible over the Bunsen flame until all the water is driven off and the powder is quite white.

(b) By **ammonia** being liberated when the substance is heated with **soda-lime.** To perform this test, the body is intimately mixed with excess of soda-lime, and heated in a hard glass test tube. The ammonia evolved may be distinguished by its smell, and also by holding near the mouth of the tube a paper moistened with **mercurous nitrate** solution. If ammonia is present, the paper is turned **black.**

Some organic substances (*e.g.* nitro-compounds) do not evolve ammonia when thus treated.

(c) By being converted into **cyanide** when heated with **potassium or sodium.**

A piece of hard glass tubing about ·5cm. diameter and 10cm. in length, is closed at one end. A bit of potassium about the size of a pea is cut into three or four thin slices, and introduced together with a small quantity of the substance into the tube, which is then drawn out to a capillary. The mixture is first gently heated, and finally, to redness. While still hot the tube is dipped into a small quantity of water contained in an evaporating basin. Care must be taken in performing this last operation, otherwise an accident may occur. If nitrogen is present in the original substance, the aqueous solution will contain **potassium cyanide.** This liquid is filtered, a little caustic potash, ferrous sulphate, and ferric chloride solution added, and the mixture boiled for two or three minutes. When cold, the liquid is acidified with hydrochloric acid, when a precipitate of **Prussian blue** will be formed.

$$(1)\ Fe_2Cl_6 + 6KHO = 6KCl + Fe_2(OH)_6.$$

$$(2)\ FeSO_4 + 2KHO = K_2SO_4 + Fe(OH)_2.$$

$$(3)\ Fe(OH)_2 + 6KCN = \underset{\textbf{Potassium Ferrocyanide.}}{K_4Fe(CN)_6} + 2KHO.$$

$$(4)\ 3K_4Fe(CN)_6 + 2Fe_2(OH)_6 + 12HCl = \underset{\textbf{Prussian Blue.}}{Fe_4[Fe(CN)_6]_3} + 12KCl + 12H_2O.$$

Substances which evolve nitrogen at moderate temperatures (*e.g.* diazo-compounds) cannot be tested by this method.

CHLORINE, BROMINE, AND IODINE.

Since the presence of chlorine, bromine, or iodine in organic compounds can only in a few cases be detected by the formation of the silver haloid salt on treatment with silver nitrate, other means have to be adopted for the recognition of these elements. The following are some of the best known methods—

(**a**) The simplest test for the halogens is that known as **Beilstein's**. A small piece of **cupric oxide** held by means of a platinum wire, is heated in the oxidizing flame of the Bunsen, until the latter is no longer coloured. It is then allowed to cool and a small quantity of the substance to be tested is placed upon it. On again heating in the outer flame, a **blue** or **green** coloration is produced, if a *halogen* is present. This test succeeds even with volatile compounds (*e.g.* chloroform), but it does not give any definite information as to which halogen is present.

(**b**) On heating most organic substances containing halogens with quicklime, the haloid salts of calcium are formed, and can be detected in the usual way.

A small quantity of the substance is mixed with about ten times its weight of **pure quicklime**, and placed in a hard glass tube about 20cm. long and 1cm. internal diameter. The tube is then filled to within about 5cm. of its end with lime and heated, the heating commencing near the open, and gradually extending to the closed end. Whilst still hot, it is dipped into water contained in a beaker, pure nitric acid added till all the lime has dissolved and the liquid has an acid reaction, and the solution then filtered. A portion of the solution may be tested with silver nitrate, when if a precipitate is formed, the remainder can be neutralized, evaporated to dryness, and a part of the residue heated with manganese dioxide and sulphuric acid. The particular halogen present can thus be distinguished. If more than one is present, separation is effected as in inorganic analysis.

(**c**) The halogens may also be tested for by heating with a small quantity of **potassium** in the manner described under the detection of nitrogen (*c*). In this case, potassium chloride, bromide, or iodide is formed. The alkaline filtrate is acidified with nitric acid, and a portion treated with silver nitrate solution. If a precipitate is produced, the remainder of the solution is examined just as in (*b*) above.

SULPHUR.

(a) The presence of **Sulphur** may sometimes be detected in organic substances by boiling with an alkaline solution of lead oxide, when the mixture darkens owing to the formation of lead sulphide. Sulphur may be recognized in albumen, hair, etc., by this method.

(b) If a small quantity of a carbon compound containing sulphur, is gradually added to a fused mixture of **potassium nitrate** and **carbonate** on a piece of platinum foil, potassium sulphate is formed. The residue is dissolved in water, filtered if necessary, and tested for sulphate in the usual way by means of barium chloride.

(c) The best method of testing for sulphur, is to heat the substance with **potassium** or **sodium** as described under nitrogen (*c*). The metal combines with the sulphur to form a sulphide. A small quantity of the alkaline filtrate is placed on a **silver coin**, when the presence of sulphur is at once shown by the production of a **black** *stain*. To another portion of the filtrate, a small quantity of freshly prepared solution of **sodium nitroprussiate** is added, when a **violet** *coloration* is produced. To a third portion acidified with acetic acid, **lead acetate** is added. A **black** precipitate of lead sulphide is thrown down.

PHOSPHORUS.

(a) By treating an organic compound containing phosphorus in the way described under sulphur (*b*), the phosphorus is oxidized to a phosphate, which may be recognized in the usual way by heating the clear solution obtained by filtration, with nitric acid and ammonium molybdate solution, when a *yellow* precipitate is produced.

(b) Magnesium phosphide is formed when certain organic compounds containing phosphorus are strongly heated with powdered magnesia. On treating with water, phosphoretted hydrogen is liberated, and is recognized by its smell and spontaneous inflammability.

In reviewing the above methods for the detection of nitrogen, chlorine, bromine, iodine, and sulphur in carbon compounds, it is at once noticed that a great deal of time may be saved, by at once heating the substance with potassium in the manner described. Various portions of the filtrate are treated according to what substance is being tested for. It should be noted, however, that when the compound contains **sulphur** as well as **nitrogen**, the latter cannot always be detected by the usual test, viz. conversion into ferrocyanide. This is due to the fact that *potassium sulphocyanide* is formed, so that a portion of the filtrate should always be tested for *sulphocyanic* acid by acidifying with hydrochloric acid, and adding ferric chloride solution, when a *blood-red* colour results if this acid is present. On the addition of mercuric chloride, the colour is destroyed. If sulphocyanide is found to be present, it shows that the original compound contained both *nitrogen* and *sulphur*. However, if a large amount of potassium is used, the ferrocyanide test for nitrogen succeeds even in the presence of sulphur. Great care must be taken in this case, when treating the residue with water, as a considerable quantity of potassium may have been left unacted upon.

Again, when volatile substances are being tested in this way (*i.e.* by heating with potassium), a much longer tube is used. This is supported in an almost vertical position, and heated only at the closed end. By this means, if the body volatilizes, it will condense on the cold upper portion of the tube, and on the heating being stopped for a short time, will flow back again on the potassium. This alternate heating and cooling is repeated, until all the substance has been decomposed.

EXERCISES. CHAPTER I.

1. Show that the following bodies contain **Carbon**: (1) *Starch* by method (*a*); (2) *citric acid* by (*b*).

2. Prove that Benzene contains both **Carbon** and **Hydrogen** by method (*c*).

3. Heat a small quantity of *Uric acid* on a piece of platinum foil. Notice smell of burnt hair. Prove that it contains **Nitrogen** by treating another portion by method (*c*).

4. Prove presence of **Nitrogen** in *Morphia* by heating with soda-lime.

5. Show that *Methyl Iodide* contains a halogen, by Beilstein's test (*a*).

6. Demonstrate the presence of **Chlorine** in *Monochloracetic acid* by heating with potassium (*c*).

7. Heat a small quantity of *Ethyl Bromide* with *pure lime*, and show that it contains **Bromine** (*b*).

8. Show that *Ethyl Mercaptan* contains **Sulphur**, by heating with potassium (*c*).

9. Prove that **Sulphur** is contained in *white-of-an-egg*, by heating with alkaline solution of *Lead oxide*.

10. How much **Prussian blue** can theoretically be obtained from 10 grams of *Urea* (CON_2H_4)?

11. Find what elements there are in Sugar, Chloral, Albumen.

CHAPTER II

STANDARDIZING THERMOMETERS—DETERMINATION OF MELTING AND BOILING POINTS

STANDARDIZING THERMOMETERS.

In the determination of melting and boiling points, it is absolutely essential that the thermometer used should be correct, or that its inaccuracies should be known. The cheap thermometers that are commonly used in laboratories are seldom accurate, so that before using one for the determination of any physical constant, the student should test it for himself.

In most laboratories there is at least one accurate instrument, and when this is the case, the work of correcting an unstandardized one is comparatively easy. The thermometer to be tested is placed by the side of the standard one, with the bulbs close together, in a bath of sulphuric acid. The liquid is slowly heated, and the readings for every 10 degrees taken. That is to say, when the normal thermometer registers 10°, 20°, 30°, etc., the corresponding reading on the other is noted. A curve should then be drawn on squared paper, with the readings on the standard instrument as ordinates, and those on the other thermometer as abscissæ. A small label with a certain number upon it, is now attached to the corrected thermometer, whilst the same number is written upon the paper on which the curve is drawn, so that whenever this thermometer is being used, the correct temperatures can be at once found.

If, however, a standard instrument is not at hand, the fixed points of the uncorrected thermometer must be re-determined.

The **zero-point 0°** is found as follows:—

A boiling tube is fitted with a two-holed cork, through which the thermometer and a wire stirrer pass. Sufficient distilled water is placed in the tube to cover the reading 0°. The tube is then immersed in a freezing mixture of salt and ice (or if this is not at hand, strong hydrochloric acid and sodium sulphate). The water is constantly agitated, and the temperature at which crystals of ice are first formed is noted. This is taken as the correct zero.

The **correct 100° point** is obtained as follows:—

The thermometer is placed in a distilling flask (Fig. 1) containing distilled water. The instrument should be suspended so that when the water is boiling, the whole of the mercury column is in the vapour. The reading that the thermometer gives is noted, also the height of the barometer.

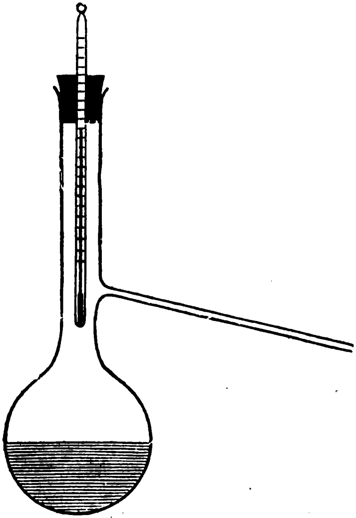


FIG. 1.

Pure water boils at 100° C. only when the atmospheric pressure is 760mm., so that if the barometer at the time of the experiment registers a different pressure to this, a table of boiling points must be consulted to see at what temperature the water is now boiling. Thus a second fixed point on the thermometer will have been found, and in the same way others can be obtained by using various liquids, as ether (b.p. 35° at 760mm.), benzene (b.p. 80·5° at 760mm.), naphthalene (218° at 760mm.), and benzophenone (306° at 760mm.). The correct temperature corresponding to intermediate readings can then be obtained by interpolation. Every thermometer before being used for the first time, should be carefully tested in one of these ways, and the results noted for future reference in the manner suggested.

DETERMINATION OF MELTING POINTS.

Any pure substance which passes from the solid into the liquid state without decomposition, does so at a definite temperature, known as the **Melting Point.** In almost all cases, any impurities present in a substance tend to lower its melting point, although in the case of some derivatives of camphor it has been found that the impurities there have an opposite effect. This constant then (the melting point), when accurately determined, not only affords a valuable criterion of the purity of the body, but also serves as a means of identifying it.

There are two general methods used for finding the melting point of a solid.

FIRST METHOD.—This is the only thoroughly reliable one, but is not made use of in the laboratory so often as the second method, owing to the large quantity of the substance (from 15 to 20grms.) required for the experiment.

The mode of procedure is as follows:—

Not less than 15grms. of the solid is placed in a test tube which is about 2·5cm. in diameter, and 15cm. long. This is fitted inside a longer tube about 3·5cm. diameter and 18cm. long. The inner tube is closed by a cork through which a wire stirrer and a thermometer pass. The thermometer is so placed that the bulb is almost touching the bottom of the tube and is surrounded by the substance. The whole apparatus is then let down inside a glass cylinder which is open at both ends. Underneath this is placed an Argand burner, by which heat is supplied. As soon as the solid commences to melt, it is well stirred by means of the wire. The temperature at which melting begins is observed, and also that at which it is complete. The burner is then removed, the liquid allowed to cool down, and the temperature of re-solidification noted. These observations are repeated several times and the mean taken.

SECOND METHOD: **Heating in a Capillary Tube.**—As but a small quantity of the solid is required for the determination of the melting point by this method, it is the one most generally employed. Usually, however, the results obtained by it are too high, especially when very narrow tubes are used.

The **melting-point tube** is made by drawing out in the Bunsen flame, a thin-walled test tube of about 5mm. diameter. The drawn-out tube should have an internal diameter of about 1 to 1·5 mm. and be about 4 cm. long. One end of this tube is closed by holding it in an almost upright position in the Bunsen flame.

The substance whose melting point is to be determined, is finely powdered, and a small quantity of it introduced into the capillary tube by thrusting the open end of the latter into the powder, inverting it, and by means of a platinum wire causing the substance to form a somewhat tight layer about 2mm. high in the bottom. The charged tube is now attached to the stem of a thermometer by means of a couple of rubber bands (or by capillary attraction, induced by placing a drop of sulphuric acid on the bulb of the thermometer and sliding the tube down the stem), so that the substance is situated near the middle of the bulb. The thermometer, with the melting-point tube attached, passes through a cork which fits in a test tube. The latter is used as air-bath, so that a second hole is made in the cork to allow the air to escape as it expands. This apparatus is supported in a tall beaker (Fig. 2), containing some liquid which is heated up to melt the solid.

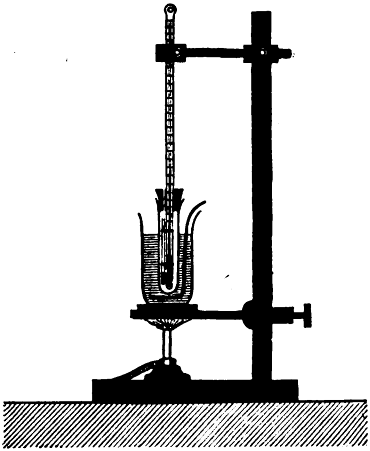


FIG. 2.

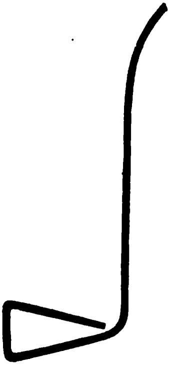


FIG. 3.

If the melting point of the body is below 100°, water may be used; if between 100° and 290°, strong sulphuric acid or glycerine is generally employed. The liquid is gently heated by means of the Bunsen, and at the same time it is well stirred by an up-and-down motion of the stirrer. This stirrer is shown separately in Fig. 3, and can be easily made from a piece of glass rod. The base of it is an equilateral triangle, of such a size that it easily slips over the test tube.

Once the melting point has been roughly determined, the substance is allowed to solidify, and the bath heated rapidly until the temperature registered is about 10° below that at which the solid was observed to melt. The heating is then continued very steadily, and the liquid well stirred so that the rise of the mercury from degree to degree can be readily seen. The **exact** temperature at which liquefaction takes place is noted. The substance should then be again allowed to solidify, and the melting point re-determined. If widely different results are obtained, a freshly charged capillary should be taken for each determination, the discrepancies being probably due to the substance not having remained long enough in the solid state.

In the case of some fats a capillary tube open at both ends is used, otherwise the exact point at which liquefaction takes place is seen with difficulty. To fill one of these tubes, it is placed in the melted fat, when a sufficient quantity enters by capillary attraction. Since, however, some substances only regain their true melting point after having been allowed to remain in the solid state for some time, this mode of procedure does not always lead to accurate results.

It should be noted, that most text-books state that the **true** melting point is obtained by adding a certain correction to the observed temperature (as in the case of boiling points when the whole thread of the thermometer is not in the vapour of the liquid).

While this correction works out on the right side in a few cases, in the majority it makes the result less accurate, because, as stated above, it has been found that the melting point obtained by this method is usually already too high. Obviously then, it is generally better not to correct the observed reading.

DETERMINATION OF BOILING POINTS.

In the same way that a solid is frequently identified by its melting point, so the boiling point of a liquid is often of use for the recognition of that liquid. There is this difference, however, between a melting point and a boiling point. Whilst the former is practically unaffected by the variations of atmospheric pressure, the latter changes considerably. Thus water, which boils at 100° C. under a pressure of 760mm., when placed in an atmosphere in which the barometer stands at 733mm., boils at 99° C. It will thus be seen, that when speaking of the boiling point of a liquid, it is necessary to refer to some particular pressure. The **boiling point of a liquid** is usually defined as, "the constant temperature registered by a thermometer immersed in the vapour of the boiling liquid, the height of the barometer being 760 mm. at the time of the experiment."

Three methods are here given for the determination of boiling points. The *first* is the most general one, but cannot be made use of, when the quantity of liquid at the disposal of the operator is very small; the *second* can be utilized with only a single *drop* of liquid; while the *third* is also sometimes useful in cases of small quantities, but is somewhat tedious to perform.

FIRST METHOD.—The liquid whose boiling point is required, is placed in an ordinary distilling flask (Fig. 1), into the neck of which is fitted an ordinary cork. Through the cork passes the thermometer, which should be so arranged that its bulb is situated just below the opening into the side tube, while the top of the mercury column, when the liquid is boiling, is just below the cork. The bulb of the thermometer should **not extend** into the bulb of the flask, and **never** on any account should it dip into the liquid. The correct arrangement is shown in the figure.

At first sight these conditions may seem a little difficult to obtain, but in reality, only a little manipulative skill is required. The flask is firmly clamped, and the liquid gently heated by means of the Bunsen burner. If the liquid under investigation is a very volatile one, or has an objectionable smell, the side tube of the flask had better be connected with a condenser. If, when the liquid is boiling, the above conditions regarding the position of the thermometer are satisfied, then the correct boiling point will have been determined. However, if it is found that the column of mercury extends above the cork, two methods of procedure are open to the experimenter. He can either add to the observed reading the correction given below, or, since the boiling point has now been roughly determined, another thermometer may be chosen such that when placed in position in the neck of the flask, the required conditions are fulfilled.

Thus, supposing it was found that a certain liquid boiled at about 153°, it would probably be convenient in this case to use a thermometer the graduations on which began at 100°. The advantage of this method of procedure will be at once apparent. Since the whole column of mercury is immersed in the vapour of the boiling liquid, the temperature registered by the thermometer will be the correct boiling point of the specimen, at that particular pressure.

Correction to be applied to observed boiling point (T) when the column of mercury extends above the cork:—A second thermometer is taken and clamped with its bulb close to the stem of the first at a point midway between the top of the projecting column of mercury and the middle of the cork. It should be protected, by means of a screen, from the heat of the burner below. The reading on it is then noted (t).

Let the number of degrees on the stem between the middle of the cork and the top of the column (T) be N.

Then the *true* boiling point T′ will be given by the formula—

$$T' = T + N(T - t) \times \cdot000154.$$

It will be seen that this operation is a very tedious one, so that whenever practicable, the method by which no correction is needed, should be used.

SECOND METHOD.—A **thin-walled** test tube is drawn out by means of the blow-pipe, and a tube made from it about 6cm. long and 7mm. in diameter. This is closed at one end and fastened to the stem of a thermometer by a couple of rubber bands or platinum wire. In it is placed a few drops of the liquid whose boiling point is to be determined, and a small capillary sealed near the end at A. The tube and the capillary is shown in its exact size in Fig. 5.

The thermometer with the accompanying tube (Fig. 4) is then placed in a bath of liquid (*e.g.* sulphuric acid), and the latter gently heated, being constantly stirred meanwhile. When the liquid in the small tube has become heated nearly to its boiling point, small bubbles of air rise up through the liquid from the end of the capillary. At this point, the burner should be removed from under the beaker, and the liquid thoroughly agitated, so that a uniform temperature may be obtained. The burner is replaced for a short time, and then removed again. These operations are repeated so that the rise of temperature can be easily noted from one degree to the next. As the boiling point is neared, the bubbles of vapour rise more quickly, until, when the liquid is just boiling, they come off in a continuous chain. The thermometer at *that* point is read. The liquid should then be allowed to cool down a few degrees, the capillary removed, a fresh one placed in the tube, and the heating again continued. Several observations should be made and the mean taken. Of course a fresh capillary is required each time.

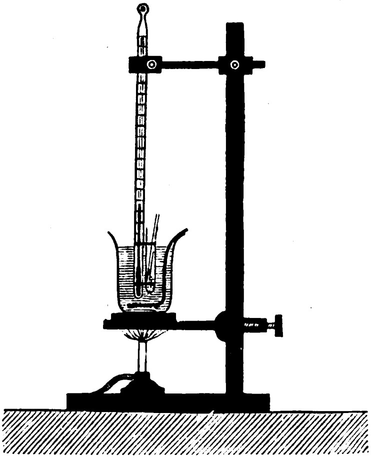


FIG. 4.

FIG. 5.

With ordinary care this method is capable of yielding exceedingly accurate results. The great point to observe, is that the heating must be conducted very slowly, and the bath constantly stirred when the temperature is near the boiling point, so as to make sure that the whole of the liquid in the tube is actually at the temperature recorded by the thermometer.

Third Method.—The principle of this method depends upon the fact that when a liquid boils, the pressure exerted by its vapour is the same as the pressure of the atmosphere in which the boiling is taking place. A piece of *thin-walled* glass tubing is sealed at one end and bent into the shape shown. A small quantity of the liquid whose boiling point is required, is poured into it, and caused to take up its position at the closed end. The tube is then bound to a small beaker containing mercury, into which the open limb dips. The whole is then suspended from a glass rod, and placed in a beaker containing some liquid whose boiling point is higher than that of the specimen under examination. The bath is heated up, and as the liquid in the tube boils, all the air is driven out. When the tube contains nothing but vapour, the apparatus hanging from the glass rod is removed from the bath and allowed to cool. As the vapour condenses, the mercury will rise in the tube and finally fill it, with the exception of a small space at the top of the bend, where the condensed liquid will gather (Fig. 6). If any air bubbles are present the experiment must be repeated.

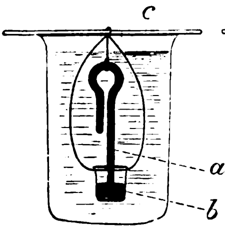


Fig. 6.

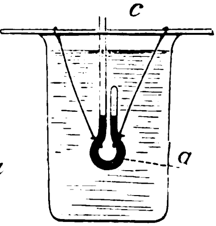


Fig. 7.

The tube is now removed from the small beaker, by placing the finger over the open end while it is still under mercury, and is gradually inverted in such a way that the liquid ascends from the bend into the closed end. Great care must be exercised in this proceeding, otherwise the liquid will suddenly rush up into the *long* limb. The tube having been inverted, mercury is removed by pushing a thin glass rod down the long limb. This is done until the column of mercury is shorter in the open, than in the closed limb of the tube. The tube is removed to the beaker (Fig. 7), the liquid in which is constantly stirred whilst being heated. (A convenient form of stirrer is that shown in Fig. 3.) Gradually as the temperature becomes higher, the mercury rises in the open limb and falls in the closed one. When it is at the same level in both, the thermometer is read, as the pressure now exerted by the liquid in the tube, is the same as that of the atmosphere, *i.e.* the liquid boils. Heating is continued for a short time longer, and then the bath is allowed to cool, being meanwhile constantly stirred. When the columns of mercury are again at the same height in each limb, the temperature is once more noted. These operations are repeated several times, and the mean of the observed temperatures taken as the boiling point.

In performing this experiment, it is obvious that if a correct result is to be obtained, the temperature denoted by the thermometer must be the same as that of the liquid in the closed limb. Consequently, the bulb of the thermometer should be placed as near the enclosed liquid as possible; the bath should be constantly stirred; and the change of temperature when near the boiling point should be very gradual.

EXERCISES. CHAPTER II.

1. Correct the thermometer supplied to you by comparing it with the given standard thermometer.

2. On the thermometer used in Exercise 1, redetermine the 0° and 100° points by the melting and boiling points of water, and see how your results agree with those obtained in Exercise 1.

3. Determine the melting point of **Anthracene** by Method I., and the melting point of **Acetanilide** by Method II.

3. Determine the boiling point of the given liquid (**Alcohol**) by all *three* methods given, and compare your results.

CHAPTER III

ORGANIC ACIDS—OXALIC, TARTARIC, AND CITRIC ACIDS

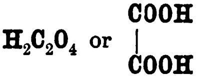
ORGANIC, like inorganic acids, may be divided into groups according to their behaviour with certain reagents. The two most general group reagents, are **neutral** solutions of *calcium chloride, and ferric chloride* respectively.

The acids with which we shall deal in this chapter, viz.—oxalic, tartaric, and citric—in neutral solutions give **white** precipitates with calcium chloride, either in the cold or on heating, but *no* precipitate or coloration with ferric chloride.

In testing for organic acids, it must be first ascertained whether they are present in the free state or as salts. If free acids are found, the systematic examination can be straightway proceeded with by simply neutralizing. If however, they are present as salts of metals, the metals (except in the case of the alkali metals potassium, sodium, and ammonium) must be first removed. This can generally be effected by boiling the substance with a fairly strong solution of sodium carbonate, when most of the metals are converted into insoluble carbonates, whilst the organic acids pass into solution as sodium salts. The precipitate is then filtered off and the filtrate neutralized by dilute hydrochloric acid, and caustic soda in the usual way. Certain metals however cannot be removed by this treatment. For example, *mercury* when present as mercuric cyanide, *antimony* in tartar emetic (potassium antimony tartrate), *copper*, *chromium*, *nickel*, etc., in the presence of tartaric and citric acids, etc. When any of these metals are present then, a solution of the substance in dilute hydrochloric acid should be made, and sulphuretted hydrogen passed into it whilst warm, until no more precipitate is produced. The sulphides are then filtered off and more gas passed into the warm filtrate to ensure complete precipitation. When this is the case, add ammonium hydrate and ammonium sulphide to the filtrate. If a precipitate is produced, filter off. To filtrate add dilute hydrochloric acid in very slight excess and boil until all smell of sulphuretted hydrogen has disappeared. The liquid is then treated with *sodium carbonate* till alkaline and boiled. (*Solid* sodium carbonate is generally preferable, as this prevents the liquid from becoming too bulky.) If a precipitate is produced, it is filtered off and the filtrate neutralized as above.

A neutral solution having been thus obtained, the various group reagents are added in order, as in inorganic analysis.

OXALIC ACID.



$$H_2C_2O_4 \text{ or } \begin{array}{l} COOH \\ | \\ COOH \end{array}$$

Oxalic acid crystallizes in colourless rhombic prisms containing two molecules of water ($H_2C_2O_4.2H_2O$). It is readily soluble in alcohol and in water, but ether only dissolves it sparingly. When the crystals are first heated, they melt at 100°, and the water of crystallization is driven off. At about 150°, the anhydrous acid sublimes, but it decomposes on rapid heating into *carbon dioxide* and *formic acid;* or into *carbon dioxide*, *carbon monoxide*, and *water*.

$$H_2C_2O_4 = CO_2 + H.COOH = CO_2 + CO + H_2O.$$

Oxalic acid is dibasic and forms two classes of salts—**acid** salts, in which only *one* hydrogen atom is replaced by a metal or radicle, as—Acid sodium oxalate, $NaHC_2O_4$, ethyl oxalic acid $C_2H_5HC_2O_4$—and **neutral** salts, in which *both* hydrogen atoms are replaced by metals or radicles, or by one metal and one radicle, as—neutral sodium oxalate, $Na_2C_2O_4$, ethyl oxalate $(C_2H_5)_2C_2O_4$, and potassium ethyl oxalate, $K(C_2H_5).C_2O_4$. We are also aquainted with salts termed **quadroxalates**, which we may look upon as compounds of equal molecules of the acid salt and of oxalic acid, thus—$HKC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$ (salts of lemon).

The oxalates, with the exception of those of the alkali metals, are mostly *insoluble* in water.

1. All oxalates are decomposed on heating, **without blackening**. Oxalates of metals whose *oxides* decompose on heating, leave the metal (*e.g.* silver). Oxalates of the alkalies leave *carbonates*. Oxalates of the alkaline earths (*e.g.* barium, calcium, strontium) leave the carbonates if not too strongly heated, but if great heat is applied, the oxides are left.

*2. On heating an oxalate (or the acid) with **strong sulphuric acid**, it is decomposed, a mixture of **carbon dioxide** and **carbon monoxide** gases being evolved, but no blackening takes place. While the mixture is being heated, the test tube should be held in as nearly a horizontal position as possible, whilst a second test tube containing lime or baryta water is placed beneath, to catch the carbon dioxide as it pours out. The monoxide can be detected by applying a light to the mouth of the tube that is being heated.

$$Na_2C_2O_4 + H_2SO_4 = CO_2 + CO + Na_2SO_4 + H_2O.$$

3. If a soluble oxalate is strongly acidified with sulphuric acid, gently warmed, and a solution of **Potassium Permanganate** added to it gradually, the latter will be **decolorised,** and at the same time carbonic acid gas is disengaged and may be detected in the usual way.

$$5Na_2C_2O_4 + K_2Mn_2O_8 + 8H_2SO_4 = 10CO_2 + K_2SO_4 + 2MnSO_4 + 5Na_2SO_4 + 8H_2O.$$

*4. **Calcium chloride,** when added to a neutral or alkaline oxalate solution, produces a **white** *precipitate* of *calcium oxalate,* **insoluble** in *acetic acid* or ammonia, but **soluble** in dilute nitric or hydrochloric acids. If this precipitate is dried and heated in a crucible over a Bunsen, carbon monoxide is evolved and a residue of *calcium carbonate* left behind, which effervesces on the addition of acetic acid.

$$(1)\ Na_2C_2O_4 + CaCl_2 = \underset{\text{Calcium oxalate.}}{CaC_2O_4} + 2NaCl.$$

$$(2)\ CaC_2O_4 + \text{Heat} = CaCO_3 + CO.$$

5. **Silver nitrate** gives in neutral oxalate solutions, a **white** precipitate of silver oxalate, soluble in *nitric acid*, and in *ammonia*.

$$2AgNO_3 + Na_2C_2O_4 = \underset{\text{Silver oxalate.}}{Ag_2C_2O_4} + 2NaNO_3.$$

The silver oxalate does not darken on being heated, but *carbon monoxide* is given off with a slight explosion, and silver carbonate is left behind. On further heating this is decomposed and metallic silver is produced.

$$Ag_2C_2O_4 = Ag_2CO_3 + CO.$$

$$Ag_2CO_3 = Ag_2 + O + CO_2.$$

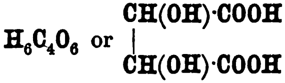
6. When a freshly prepared **Ferrous sulphate** solution is added to a neutral *oxalate* solution, a yellowish colour is produced, and after standing for some time, a bright *yellow crystalline precipitate* of ferrous oxalate is thrown down.

$$K_2C_2O_4 + FeSO_4 = \underset{\text{Ferrous oxalate.}}{FeC_2O_4} + K_2SO_4.$$

7. On strongly heating a dry neutral oxalate with **soda lime**, *hydrogen* is evolved and a carbonate is produced.

$$Na_2C_2O_4 + 2NaHO = 2Na_2CO_3 + H_2.$$

TARTARIC ACID.



$$H_6C_4O_6 \text{ or } \begin{array}{l} CH(OH){\cdot}COOH \\ | \\ CH(OH){\cdot}COOH \end{array}$$

Tartaric acid crystallizes in colourless transparent rhombic prisms, very *soluble* in *water* and *alcohol*, but *insoluble* in *ether*. It melts, with decomposition, at about 167°. Like oxalic acid, it forms both neutral and acid salts, a number of which are soluble in water, whilst *all* are soluble in dilute hydrochloric acid.

*1. Heated in a dry tube, **tartrates** *swell up*, giving off an odour of **burnt sugar**, and leaving a black residue of carbon behind.

2. Heated in a test-tube with **strong sulphuric acid**, tartrates at **once** blacken. Carbon monoxide is evolved and can be burnt at the mouth of the tube. Carbon dioxide and sulphur dioxide are also given off, the latter being recognized by its smell. In order that carbon dioxide may be identified in the presence of this gas, the apparatus shown in Fig. 8 is used.

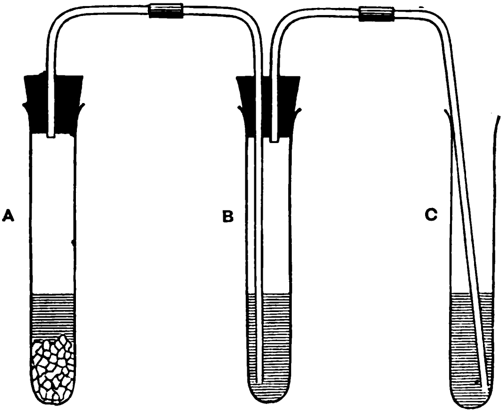


FIG. 8.

In test tube A is placed the tartrate and sulphuric acid; in B a saturated solution of Potassium Bichromate, which absorbs the sulphur dioxide; and in C some lime water, which is rendered milky by the carbon dioxide.

*3. If a little solid tartrate is gently heated to about 120°, with concentrated **sulphuric acid** containing one per cent. of **resorcin**, a beautiful **reddish violet** colour is obtained. This test is conveniently performed on a small piece of porcelain. (Distinction from citrates.)

*4. To a tartrate solution, add a few drops of **Ferrous sulphate** solution, one or two drops of **hydrogen peroxide**, and finally excess of **caustic potash**, when a deep **blue** or **violet** colour is obtained. (Distinction from citrates.)

*5. **Silver nitrate** solution gives with **neutral** tartrates, a *white* precipitate of *silver tartrate*, soluble in ammonia and in nitric acid. If the precipitate is allowed to settle, the supernatant liquid poured off, just sufficient dilute ammonia to dissolve the residue added, and finally a gentle heat applied, the inside of the vessel will be coated with a *mirror* of *silver*. The experiment is best performed in a test tube, which must be *perfectly clean*, and this should be heated in a beaker of water, to obtain a *bright mirror.*

$$2AgNO_3 + Na_2H_4C_4O_6 = 2NaNO_3 + \underset{\text{Silver Tartrate.}}{Ag_2H_4C_4O_6}.$$

*6. **Calcium chloride** produces in **neutral** tartrate solutions, a white precipitate of *calcium tartrate*, soluble in *cold caustic potash* or *soda.* (Distinction from calcium citrate.)

$$CaCl_2 + Na_2H_4C_4O_6 = 2NaCl + \underset{\text{Calcium Tartrate.}}{CaH_4C_4O_6}.$$

Unless the tartrate solution is very concentrated, this precipitate only comes down after long standing or shaking. The precipitate is allowed to settle, the supernatant liquid poured off, a few drops of ammonia and a crystal of silver nitrate added. On gently heating the tube in a beaker of water, a silver *mirror* is produced.

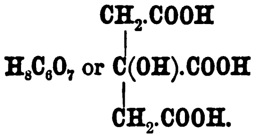
*7. To a solution of tartaric acid (or neutral tartrate), add a solution obtained by dissolving potassium carbonate in acetic acid. On vigorous shaking or stirring, a heavy white precipitate of *potassium hydrogen tartrate* comes down. If alcohol is added, it furthers precipitation.

$$H_6C_4O_6 + \underset{\text{Potassium acetate.}}{CH_3.COOK} = \underset{\left\{\begin{array}{l}\text{Potassium}\\ \text{Hydrogen tartrate}\end{array}\right.}{KH{\cdot}H_4C_4O_6} + CH_3COOH.$$

8. Tartaric acid, or alkaline tartrates, prevent the precipitation by the alkalies, of the oxides of copper, nickel, cobalt, chromium, iron, etc., even on boiling. This property is well seen in Fehling's Solution, which is made by dissolving copper sulphate, Rochelle salt (a tartrate), and caustic soda in water. No precipitate is formed.

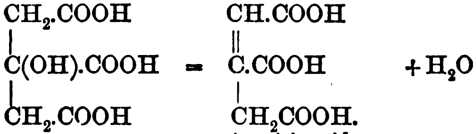
9. A saturated solution of potassium permanganate is slowly turned **brown** by tartaric acid. (Distinction from citric acid.)

CITRIC ACID.



$$H_8C_6O_7 \text{ or } \begin{array}{l} CH_2.COOH \\ | \\ C(OH).COOH \\ | \\ CH_2.COOH. \end{array}$$

Citric acid crystallizes in transparent rhombic prisms containing one molecule of water of crystallization ($H_8C_6O_7 \cdot H_2O$). It is very soluble in water, fairly so in alcohol, but only sparingly so in ether. It melts at 100°, and soon after commences to lose water of crystallization, which, however, is not completely driven off till about 130°. On being heated in a test tube, the acid melts and afterwards blackens, and irritating fumes of *aconitic acid* are given off.



$$\begin{array}{l} CH_2.COOH \\ | \\ C(OH).COOH \\ | \\ CH_2.COOH \end{array} = \begin{array}{l} CH.COOH \\ \| \\ C.COOH \\ | \\ CH_2COOH. \end{array} + H_2O$$

Aconitic acid.

On being more strongly heated, however, it splits up into itaconic acid, citraconic acid, acetone, and the oxides of carbon. As seen by its structural formula above, citric acid is a tricarboxylic acid, and forms three classes of salts as—$C_6O_7H_7 \cdot K$, $C_6O_7H_6K_2$, and $C_cO_7H_5K_3$. A good number of citrates are freely soluble in water, especially those of the alkali metals

*1. Citric acid, or its salts, when heated with **strong sulhpuric** acid is decomposed, carbon monoxide being evolved, and at a further stage carbon dioxide. After continued heating, blackening takes place and sulphur dioxide is evolved (*vide* Tartaric acid).

*2. **Calcium chloride** when added to a *neutral* solution of a citrate, gives **no** precipitate in the **cold**, even after much shaking and long standing, but on warming, the precipitate of calcium citrate comes down. If the solution is very dilute, it will need concentrating somewhat. The precipitate of calcium citrate is not formed in the presence of *free* citric acid even on boiling, but excess of an alkali favours its production. Calcium citrate is soluble in *ammonium chloride*, but *not* in *caustic soda* or *potash.* It is also distinguished from *calcium tartrate*, by being heated in a test tube with a crystal of silver nitrate and a drop of ammonia. No mirror is formed, but after prolonged heating, reduction sets in.

$$2C_6O_7H_5K_3 + 3CaCl_2 = \underset{\text{Calcium citrate.}}{Ca_3(C_6O_7H_5)_2} + 6KCl.$$

*3. Lime water in excess gives no precipitate in the cold with citric acid or citrates, but on boiling, calcium citrate is thrown down. On cooling, the precipitate is re-dissolved.

4. In neutral solutions of citrates, **silver nitrate** gives a precipitate of *silver citrate,* soluble in ammonia. On heating, the silver is reduced, but without the formation of a mirror.

$$C_6O_7H_5Na_3 + 3AgNO_3 = \underset{\text{Silver citrate.}}{C_6O_7H_5Ag_3} + 3NaNO_3.$$

5. Citrates, like tartrates, prevent the precipitation by the alkalies, of the oxides of copper, nickel, cobalt, etc.

6. When caustic potash in excess, and then a few drops of potassium permanganate are added to a solution of a citrate, a green coloration is produced which remains unaltered on heating. (Distinction from a tartrate.)

<table>
<tr><td colspan="4">SEPARATION OF OXALIC, TARTARIC, AND CITRIC ACIDS.
To a neutral solution add *Calcium Chloride;* shake well and allow to stand for twenty minutes. **Filter.**</td></tr>
<tr><td colspan="2">**Precipitate =**
Calcium Oxalate and Tartrate.
Wash well on the filter paper. Remove a small portion of the precipitate for confirmatory tests **C** and **D** below. Make a hole in the filter paper and wash residue through into a boiling tube. Boil with a little *Acetic Acid.* Filter.</td><td colspan="2">**Filtrate.**
Add more calcium chloride and boil for some time. *Filter* at once and test filtrate by re-boiling.</td></tr>
<tr><td>**Residue =**
Calcium oxalate.
Wash well and dry. Divide into two parts **A** and **B**.
A. Place on a piece of platinum foil and heat over the Bunsen to convert into calcium carbonate. Allow to cool, and add *Acetic Acid.*
Carbon dioxide evolved with effervescence.
Presence of **Oxalic Acid** confirmed.
B. Heat in a test tube with strong *sulphuric* acid. *Carbon dioxide* and *monoxide* evolved, without blackening.
Presence of **Oxalic Acid** confirmed.</td><td>**Filtrate**
Evaporate just to dryness and heat with a little strong sulphuric acid. Carbon monoxide and dioxide, and sulphur dioxide evolved, with immediate blackening.
Presence of **Tartaric Acid.**
Confirm as follows—
C. Heat one portion of residue (see above) on a piece of porcelain, with strong *sulphuric acid* containing *resorcin.*
Reddish-Violet *Coloration.*
D. Place second portion in a test tube with a drop or two of ammonia, a crystal of silver nitrate, and a little water. Heat gently.
Mirror of **metallic silver** produced.</td><td>**Precipitate =**
Calcium Citrate and perhaps a little *calcium tartrate.*
Wash well, and pour **cold** dilute caustic soda upon the precipitate to dissolve out any Calcium Tartrate present.
Wash well to remove caustic soda, and divide into two portions **E** and **F**.
E. Place in a clean test tube with a drop or two of ammonia, a crystal of silver nitrate, and a little water. *Heat gently.*
Reduction after some time, but *no mirror.*
Presence of **Citric Acid** confirmed.
F. Heat with strong sulphuric acid.
Blackening after some time. Carbon monoxide and dioxide, and sulphur dioxide evolved.
Presence of **Citric Acid** confirmed.</td><td>Filtrate = remaining organic acids.</td></tr>
</table>

CHAPTER IV

BENZOIC, FORMIC, ACETIC, SALICYLIC, CARBOLIC, AND HYDROCYANIC ACIDS

After calcium chloride, the most important group reagent for organic acids, is a solution of *ferric chloride* made *neutral* by the addition of a dilute solution of *ammonia.* This reagent gives either a precipitate or coloration, with a large number of organic acids. Of these, we shall only deal with five in this chapter, viz.—benzoic, formic, acetic, salicylic, and carbolic acids. The first named gives a precipitate with ferric chloride in the cold, while the other four produce colorations.

BENZOIC ACID.

$H_6C_7O_2$ or $C_6H_5.COOH$.

Benzoic acid crystallizes in white lustrous flat plates or needles, which melt at 121°, and boil at 249°. It is volatile at 100°, but at 140° it sublimes rapidly. It is very slightly soluble in cold water, but readily so in hot. Alcohol also dissolves it freely, but in ether it is only fairly soluble. On boiling an aqueous solution, the acid distils over with the steam. Crystals of benzoic acid when heated on platinum foil, burn with a *blue smoky* flame.

When heated in a dry tube, benzoic acid melts and sublimes on the upper colder portion of the tube. On further heating, no charring takes place, but a pleasant aromatic vapour is given off, which produces a tickling in the throat, and causes coughing. All benzoates of the metals, with the exception of iron benzoate, are more or less soluble in water.

*1. Heated in the dry state with **soda lime**, benzoates evolve **benzene**. This test is conveniently performed, by placing the dry mixture of the benzoate and soda lime in a test tube fitted with a cork and delivery tube. On heating, the benzene distils over and can be collected in a second test tube. To this distillate small quantities of strong nitric and sulphuric acids are added, when the well-known odour of nitrobenzene is recognized.

$$(1)\ C_6H_5COONa + NaHO = \underset{\text{Benzene.}}{C_6H_6} + Na_2CO_3.$$

$$(2)\ C_6H_6 + HNO_3 = \underset{\text{Nitrobenzene.}}{C_6H_5NO_2} + H_2O.$$

*2. Heated with **strong sulphuric acid**, benzoates do not char, but the characteristic odour of benzoic acid is noticed, and a white sublimate of the acid is formed on the upper portion of the tube.

3. **Silver nitrate** gives a white precipitate of silver benzoate in neutral benzoate solutions. On heating, this precipitate dissolves, but comes down in crystalline form when the solution is allowed to cool again.

$$C_6H_5COONa + AgNO_3 = \underset{\text{Silver benzoate.}}{C_6H_5COOAg} + NaNO_3.$$

*4. Benzoic acid is thrown down as a white crystalline precipitate when *hydrochloric acid* (or other mineral acid) is added to a neutral benzoate solution. If a sufficient quantity of liquid is present the precipitate will disappear on boiling, but the crystals again separate out on cooling.

$$C_6H_5COONa + HCl = C_6H_5.COOH + NaCl.$$

*5. In neutral benzoate solutions, a solution of **ferric chloride** which has been rendered neutral by the addition of ammonia, gives a pale buff-*coloured* precipitate of *basic ferric benzoate* $(C_7H_5O_2)_3 \cdot Fe_2(OH)_3$. On the addition of dilute hydrochloric acid, this precipitate dissolves, and at the same time benzoic acid crystallizes out.

$$(C_7H_5O_2)_3.Fe_2(OH)_3 + 6HCl = Fe_2Cl_6 + 3H_2O + 3H_6C_7O_2.$$

6. On heating a benzoate with **strong sulphuric acid** and **ethyl alcohol**, the pleasant and characteristic odour of *benzoic* ether is given off.

$$C_6H_5COONa + H_2SO_4 + C_2H_5(OH) = \underset{\text{Benzoic ether.}}{C_6H_5.COO(C_2H_5)} + NaHSO_4 + H_2O.$$

7. In neutral solutions of benzoates, **lead acetate** gives a white precipitate of *lead benzoate*, soluble in excess of lead acetate and in acetic acid.

$$2C_6H_5.\ COONa + (CH_3.COO)_2Pb = \underset{\text{Lead Benzoate.}}{(C_6H_5COO)_2Pb} + 2CH_3.COONa.$$

8. Solutions of benzoic acid and its salts, and even the salts in the solid state, when mixed with magnesium powder yield on addition of hydrochloric acid a smell of bitter almonds due to reduction to benzaldehyde :—

$$C_6H_5.COOH + \underset{\text{Nascent.}}{2H} = C_6H_5.CHO + H_2O.$$

FORMIC ACID.

H_2CO_2 or $H\cdot COOH$.

Formic acid is a colourless, slightly fuming liquid, having a pungent and characteristic odour. When cooled down it solidifies, melting again at 9°, and boiling at 99°. It is miscible in all proportions with water, alcohol, and ether. It has strong antiseptic properties, and is a powerful reducing agent. The formates as a rule are readily soluble in water, lead formate being the least so.

*1. On heating a formate (or formic acid) with **strong sulphuric acid**, it is decomposed. **Carbon monoxide** is evolved, and may be burnt at the mouth of the tube, but no charring takes place.

$$2H.COONa + H_2SO_4 = 2H_2O + 2CO + Na_2SO_4.$$

But if a formate is heated with **dilute** sulphuric acid, *formic acid* itself is liberated, and can be recognized by its characteristic smell.

$$2H.COONa + H_2SO_4 = 2H.COOH + Na_2SO_4.$$

2. When dry formates are heated with **soda lime**, hydrogen is evolved.

$$H.COONa + NaHO = Na_2CO_3 + H_2.$$

*3. On gently heating a *formate* with **strong sulphuric acid** and **ethyl alcohol**, the fragrant and characteristic odour of formic ether, somewhat resembling the smell of rum, is noticed.

$$H.COONa + H_2SO_4 + C_2H_5(OH) = \underset{\text{Formic ether.}}{H.COO(C_2H_5)} + NaHSO_4 + H_2O.$$

*4. When **mercuric oxide** is added to cold dilute formic acid, it dissolves, forming *mercuric* formate.

$$HgO + 2HCOOH = H_2O + (H.COO)_2Hg.$$

On gently heating, this **mercuric formate** is converted into *mercurous* formate (a white substance), and carbon dioxide is evolved.

$$2(H.COO)_2Hg = (H.COO)_2Hg_2 + H.COOH + CO_2.$$

On further heating, the **mercurous formate** is reduced, and a grey precipitate of metallic *mercury* is produced.

$$(H{\cdot}COO)_2Hg_2 = H.COOH + Hg_2 + CO_2.$$

It will be seen on reference to the above equations, that *free formic acid* is produced at each of these stages. This is capable of dissolving more mercuric oxide, and consequently a repetition of the above reactions takes place, until finally all the formic acid is oxidized. The final state of affairs may be represented by the following equation:—

$$H{\cdot}COOH + HgO = CO_2 + H_2O + Hg.$$

This reaction may be made use of with **formates**, by adding mercuric oxide to the formate solution, warming, and then adding dilute sulphuric acid, drop by drop, to liberate the *formic acid*, which acts upon the *mercuric oxide*.

*5. **Mercuric chloride** gives with formic acid, or formates, on boiling, a **white** precipitate of *mercurous chloride*, or a **grey** precipitate of *metallic* mercury.

(1) $2HgCl_2 + H.COOH = Hg_2Cl_2 + 2HCl + CO_2.$

(2) $HgCl_2 + H.COOH = Hg + 2HCl + CO_2.$

6. In strong solutions of formates, or free formic acid, **silver nitrate** gives a *white* precipitate of *silver formate*, which on warming, or standing, is reduced to a **grey** precipitate of metallic silver, and carbon dioxide is evolved.

$$H.COOH + AgNO_3 = \underset{\text{Silver formate.}}{H.COOAg} + HNO_3.$$

$$2H.COOAg = H.COOH + CO_2 + 2Ag.$$

It will be seen that here again formic acid is re-formed. The final state of affairs may be represented as follows:—

$$H.COOH + 2AgNO_3 = 2Ag + CO_2 + 2HNO_3.$$

7. In neutral solutions of formates, **ferric chloride** gives a **red** coloration, but no precipitate in the cold. To a portion of this red solution, add a little hydrochloric acid, when the colour will be destroyed. If the rest of the solution is boiled, a reddish precipitate of a basic iron salt will be produced.

ACETIC ACID

$H_4C_2O_2$ or $CH_3.COOH$.

Acetic acid is a pungent-smelling, strongly-acid liquid. When anhydrous, it is known as "glacial acetic acid." It solidifies in the cold, forming large crystalline plates, which melt at 17°, and boil at 118°. It attacks the skin, and its vapour burns with a pale blue flame. With water, alcohol, and ether, it is miscible in all proportions, and it is largely used as a solvent in organic chemistry. All neutral acetates are soluble in water, and on ignition in the dry state yield inflammable vapours, consisting chiefly of acetone.

$$2CH_3COONa = \underset{\text{Acetone.}}{CH_3.CO.CH_3} + Na_2CO_3.$$

*1. On heating an acetate with **strong sulphuric acid,** *acetic* acid is set free, and can be recognized by its smell (cf. Formic acid).

$$2CH_3.COONa + H_2SO_4 = 2CH_3COOH + Na_2SO_4.$$

*2. When a mixture of equal parts of **arsenious oxide** and an *acetate* is heated, the intensely obnoxious and highly characteristic smell of **cacodyl oxide** is noticed.

$$As_2O_3 + 4CH_3.COOK = \underset{\text{Cacodyl oxide.}}{As_2(CH_3)_4O} + 2K_2CO_3 + 2CO_2.$$

This is one of the best tests for the presence of an acetate, but only small quantities of the substances should be used. As the liquid (cacodyl oxide) is exceedingly poisonous, the experiment should be performed in a stink cupboard, and care should be taken not to inhale the fumes.

*3. In neutral acetate solutions, **ferric chloride** gives a **red** coloration. To a portion of this red liquid, add a drop of hydrochloric acid; it will be turned **yellow.** If the rest of the solution is boiled, a brownish precipitate of basic ferric acetate will be thrown down, the solution become colourless, and at the same time the smell of acetic acid will be noticed.

(1) $6CH_3.COONa + Fe_2Cl_6 = 6NaCl + (CH_3.COO)_6Fe_2.$

Ferric acetate.

(2) $(CH_3.COO)_6.Fe_2 + 4H_2O = \left.\begin{matrix}(CH_3.COO)_2\\ (OH)_4\end{matrix}\right\}Fe_2 + 4CH_3.COOH.$

Basic ferric acetate.

4. **Silver nitrate** gives in concentrated neutral solutions of acetates a white crystalline precipitate of silver acetate, but no precipitate is formed with free acetic acid. Silver acetate is not reduced to metallic silver, even after prolonged heating. (Distinction from silver formate.)

$$CH_3.COONa + AgNO_3 = NaNO_3 + CH_3.COOAg.$$

Silver acetate.

*5. When an acetate is gently warmed with **alcohol** and **strong sulphuric acid**, a pleasant smell of *acetic ether*, somewhat resembling the smell of formic ether, is produced.

$$CH_3.COONa + C_2H_5.OH + H_2SO_4 = CH_3.COO.C_2H_5 + NaHSO_4 + H_2O.$$

Acetic ether.

6. On strongly heating a dry acetate with *soda lime*, marsh gas (methane) is evolved.

$$CH_3.COONa + NaHO = CH_4 + Na_2CO_3.$$

7. When **mercuric oxide** is dissolved in acetic acid, *mercuric acetate* is formed. On prolonged boiling, no reduction takes place, and when the solution is allowed to cool, white shining crystals of mercuric acetate separate out. (Distinction from formic acid.)

$$HgO + 2CH_3COOH = H_2O + (CH_3COO)_2Hg.$$

Mercuric acetate.

Detection of **Formic** and **Acetic Acids** in the **presence** of **each other.**

Heat substance supposed to contain formate and acetate, with dilute sulphuric acid in a boiling tube fitted with a cork and delivery tube (a small retort is better). The formic and acetic acids will be liberated, and should be collected in a second tube kept immersed in cold water. Divide distillate into two portions **A** and **B**.

Portion A.	**Portion B.**
Add yellow *mercuric oxide* and shake till no more dissolves. Warm gently; *reduction* will take place. **Formic acid present.** Add more mercuric oxide and heat till all the formic acid is destroyed. Filter. *Neglect precipitate.*—**Filtrate = Mercuric Acetate.** Evaporate to dryness and grind in a mortar with strong sulphuric acid. **Smell** of **acetic acid.**	Neutralize with $NaHO$ and evaporate to dryness. Divide into two portions **C and D.** **C**. Heat with strong sulphuric acid; *carbon monoxide* evolved and burns at mouth of tube. **Presence** of **formic acid** confirmed. **D**. Heat with arsenious oxide in stink cupboard: indescribable odour of **cacodyl oxide. Presence** of **acetic acid confirmed.**

SALICYLIC ACID.

$$H_6C_7O_3 \text{ or } C_6H_4\begin{matrix}.OH\\.COOH\end{matrix}$$

Salicylic acid crystallizes in colourless prisms, melting at 159°. It sublimes when gently heated up to 200°, but if rapidly heated to 220°, it breaks up into carbon dioxide and phenol.

$$C_6H_4(OH)COOH = C_6H_5.OH + CO_2.$$

Cold water dissolves salicylic acid sparingly, but in hot water it is readily soluble. Owing to its powerful antiseptic properties, salicylic acid is largely used as a food preservative. Its mono-metallic salts, as calcium salicylate $[C_6H_4(OH).COO]_2Ca$, are as a rule soluble in water, whilst the di-metallic ones, as $C_6H_4{<}\begin{matrix}O\\COO\end{matrix}{>}Ba$, are, with the exception of those of the alkali metals, insoluble.

*1. Heated in a dry tube, salicylates **char** and **phenol** is given off.

*2. Heated with **soda lime**, salicylates are decomposed and **phenol** is liberated.

$$C_6H_4(OH)COONa + NaHO = C_6H_5OH + Na_2CO_3.$$

3. On gently heating a salicylate with **strong sulphuric acid**, the mixture readily darkens, and sulphur dioxide and carbon monoxide gases are evolved.

*4. In neutral solutions of salicylates, **ferric chloride** gives a **violet** coloration, destroyed by hydrochloric acid but *not* by *acetic* (cf. Phenol).

5. **Bromine** water gives a **white** precipitate of tribromosalicylic acid, similar to the precipitate produced in the case of phenol, but the reaction is not so delicate.

$$C_6H_4\,(OH)COOH + 3Br_2 = \underset{\text{Tribromosalicylic acid.}}{C_6HBr_3(OH)COOH} + 3HBr.$$

*6. On heating salicylic acid, or a salicylate, with **strong sulphuric acid** and **methyl alcohol**, the fragrant and characteristic odour of *methyl* salicylate (oil of winter green) is noticed. (Distinction from phenol.)

$$C_6H_4(OH)COONa + H_2SO_4 + CH_3OH = \underset{\text{Methyl salicylate.}}{C_6H_4(OH)COO.CH_3} + NaHSO_4 + H_2O.$$

7. Since salicylic acid is sparingly soluble in cold water, if an acid is added to a strong solution of a salicylate, the latter is decomposed, and the free salicylic acid is precipitated (cf. Benzoic acid).

8. **Silver nitrate** gives in **strong** neutral salicylate solutions a white precipitate of *silver salicylate.* On the addition of dilute nitric acid, the precipitate appears to be insoluble, but this is due to its having been decomposed (*see* 7 above), and the insoluble substance is really salicylic acid, which, however, disappears on boiling. *Silver benzoate* acts in a similar manner.

9. If a small quantity of **copper sulphate** solution is added to a neutral salicylate solution, an *apple-green* coloration is produced. On the addition of *caustic soda* a *green* precipitate is thrown down, which, however, dissolves on a large quantity of the alkali being added, forming a *dark blue* solution.

CARBOLIC ACID OR PHENOL.

H_6C_6O or $C_6H_5(OH)$.

Carbolic acid, or phenol, is not an acid proper, but owing to its reactions being very similar to those of salicylic acid it is treated at this stage. Phenol is an aromatic hydroxy-compound, and when pure, has a neutral reaction, but in so far as it combines with bases it is of an acid character. Thus, when it is dissolved in potash, and the solution evaporated, potassium phenate, C_6H_5OK, is obtained.

Phenol crystallizes in colourless prisms, which melt at 42°, and boil at 182·3°. It is exceedingly deliquescent, and on exposure to air and light is turned pink. It is freely soluble in benzene, alcohol, ether, etc., but only slightly so in cold water. It is volatile in steam, possesses a very characteristic odour, is very poisonous, blisters the skin, and is largely used as a disinfectant.

*1. Heated in a dry tube **phenol** completely volatilizes, giving off its characteristic odour of tar.

*2. When **bromine** water in excess is added to a solution of phenol, a **pale yellow** precipitate of *tribromophenol* is thrown down. This reaction is extremely delicate.

$$C_6H_5.OH + 3Br_2 = \underset{\text{Tribromophenol.}}{C_6H_2Br_3.OH} + 3HBr.$$

*2. Phenol gives a **violet** coloration with **ferric chloride,** which is destroyed by acids, including *acetic* (cf. Salicylic acid).

3. Concentrated sulphuric acid poured beneath a solution containing phenol and nitric acid (about one per cent.) gives an intense *red* tinge.

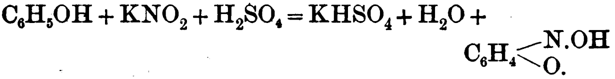
*4. Warm an aqueous solution of phenol with a quarter of its volume of **ammonia,** and then add a little **bleaching powder** solution. A **blue** coloration will be produced, which is turned **red** on the addition of acids. The solution of bleaching powder should be clear, and is made by shaking up the powder with cold water and then filtering.

5. A pine shaving moistened with hydrochloric acid is turned *greenish-blue* by phenol.

6. On boiling phenol with **Millon's reagent,** a *yellow precipitate* is obtained, which dissolves in *nitric acid* forming a *deep red* liquid. If sufficient nitric acid is present in the first place, the red coloration will be obtained at once, instead of the yellow precipitate. Salicylic acid also shows this reaction.

7. Phenol added to **strong sulphuric acid** containing a small quantity of **potassium** or **sodium nitrite**, produces a **green colour**, which on being diluted with water becomes **red**. If this liquid is made alkaline with caustic potash or soda, a beautiful **blue** liquid is obtained.

This is due to some of the phenol being converted by the nitrous acid into *para-nitrosophenol* or *quinonoxime.*



$$C_6H_5OH + KNO_2 + H_2SO_4 = KHSO_4 + H_2O + C_6H_4\!\begin{smallmatrix}\diagup N.OH\\ \diagdown O.\end{smallmatrix}$$

Para-nitrosophenol.

The para-nitrosophenol thus formed reacts with the rest of the phenol and sulphuric acid, and the dark green coloration is the result. This latter reaction is known as **Liebermann's nitroso-reaction.**

Detection of **Phenol** or **Salicylic Acid** in the **presence of Acetic** or **Formic Acids.**

The violet colour produced by ferric chloride with *phenol*, and with *salicylic acid*, is somewhat difficult to distinguish when a formate or acetate is present, owing to the deep reddish colour produced by either of these bodies with the same reagent.

If the preliminary examination leads one to suppose that phenol or a salicylate is present, the following method of procedure should be adopted—

(**a**) To a small portion of the liquid obtained after the addition of ferric chloride, add a *drop* or *two* of dilute hydrochloric acid. This will destroy the *red* colour and the violet will show up more plainly. Of course on the addition of more acid, the violet colour too is destroyed.

(**b**) To another portion of liquid obtained after the addition of ferric chloride, add acetic acid. If **salicylic acid** is present, the violet colour will show up plainly. If **phenol** only is present, the violet colour will be destroyed. In this way phenol or salicylic acid can be detected, but not both.

Detection of Phenol and Salicylic Acid in the presence of each other.

Dissolve substance in water, neutralize if necessary with *sodium carbonate*, and shake up with *ether*, which will dissolve the phenol. Remove ethereal liquid by means of a pipette.

Ethereal solution contains **Phenol.**	Aqueous solution contains **Salicylic Acid.**
Gently evaporate the liquid and the phenol will be left behind. Divide into three portions, **A**, **B** and **C**.	Divide into two portions, **A** and **B**.
A. Dissolve in water and add ferric chloride, **violet coloration**; add **acetic acid**, colour **destroyed.**	**A.** Add ferric chloride, **violet coloration**; add **acetic acid**, **no** change in colour.
B. Dissolve in a little water, add a third its volume of **ammonia**, heat gently, and add solution of *bleaching powder*. **Blue coloration**, turned **red** by acids.	**B.** Evaporate nearly to dryness, and heat with strong sulphuric acid and methyl alcohol. Pleasant smell of **methyl salicylate.**
C. Add to strong sulphuric acid containing sodium nitrite, **green colour**; dilute with water, **red colour**; add soda, **blue colour.**	

HYDROCYANIC ACID.

HCN.

Hydrocyanic, or prussic acid, is a colourless liquid, and when anhydrous evaporates rapidly, producing a solid which melts at —15° and boils at 26°, giving off a vapour which burns with a pale blue flame. It is a feeble acid, scarcely reddening blue litmus, has a smell somewhat resembling that of bitter almonds, and is one of the most deadly poisons known. It dissolves readily in water, forming a solution which on exposure to light is decomposed, a brown substance being deposited, whilst among other products, ammonium formate is found in the solution.

$$HCN+2H_2O=H.COO.NH_4.$$

Prussic acid forms salts with a large number of metals; those of the alkali metals are easily decomposed by water, and by carbonic acid, hydrocyanic acid being liberated. This is the reason why potassium cyanide always smells of the acid when exposed to the air.

$$2KCN+H_2CO_3=K_2CO_3+2HCN$$

A large number of cyanides are soluble in water.

1. Heated in the dry state, cyanides (with the exception of those of the alkali metals) are decomposed; no blackening takes place and a smell of ammonia and prussic acid is given off.

In the case of silver and mercuric cyanides, cyanogen and the free metal are produced.

$$Hg(CN)_2=Hg+\underset{\text{Cyanogen.}}{C_2N_2}.$$

2. When strongly heated with **soda lime**, *cyanides* give off ammonia.

*3. On adding **dilute** sulphuric acid to a cyanide (not silver or mercury cyanides) hydrocyanic acid is liberated and is recognized by its smell. If a little of the cyanide is placed in an evaporating basin, a little water and a few drops of dilute sulphuric acid added, and the basin covered with a clock glass, the under side of which has previously been moistened with a solution of **silver nitrate**, after a few minutes the glass will become opaque from the formation of silver *cyanide.*

4. If a cyanide is heated with **strong sulphuric acid**, *carbon* monoxide is evolved.

$$2KCN + 2H_2SO_4 + 2H_2O = K_2SO_4 + (NH_4)_2SO_4 + 2CO.$$

5. **Silver nitrate** gives with cyanide solutions (except mercuric cyanide) a white precipitate of *silver cyanide,* soluble in ammonia and potassium cyanide, but insoluble in nitric acid.

When the silver nitrate is first added to the cyanide solution, a double cyanide is formed, which is soluble. On adding more silver nitrate the double cyanide is decomposed, and silver cyanide is thrown down.

$$(1)\quad 2KCN + AgNO_3 = \underset{\text{Double cyanide.}}{AgCN.KCN} + KNO_3.$$

$$(2)\quad AgCN.KCN + AgNO_3 = \underset{\text{Silver cyanide.}}{2AgCN} + KNO_3.$$

If the silver cyanide is filtered off, washed, and ignited, cyanogen is evolved and metallic silver left behind.

$$2AgCN = 2Ag + C_2N_2.$$

*6. Place a small quantity of a cyanide solution in an evaporating basin with a couple of drops of **ammonia** and a little **yellow ammonium sulphide** solution. The solution is evaporated until the yellow colour disappears, when ammonium thiocyanate will have been produced. On the addition of a little hydrochloric acid and ferric chloride, a **blood red** *colour,* due to the formation of ferric thiocyanate, is observed. On the addition of mercuric chloride, this colour disappears.

$$(1)\quad HCN + (NH_4)_2S_2 = \underset{\text{Ammonium thiocyanate.}}{NH_4.CNS} + NH_4.HS.$$

$$(2)\quad 6NH_4.CNS + Fe_2Cl_6 = 6NH_4Cl + \underset{\text{Ferric thiocyanate.}}{Fe_2(CNS)_6}.$$

*7. To a solution of a cyanide, add a little **ferrous sulphate** solution and **caustic potash,** and boil for two or three minutes.

When cold, acidify with hydrochloric acid and add a few drops of ferric chloride. A **blue precipitate of Prussian blue** will be produced.

(1) $FeSO_4 + 2KHO = K_2SO_4 + Fe(OH)_2$.

(2) $6KCN + Fe(OH)_2 = \underset{\text{Potassium Ferrocyanide.}}{K_4Fe(CN)_6} + 2KHO$.

(3) $3K_4Fe(CN)_6 + 2Fe_2Cl_6 = \underset{\text{Prussian blue.}}{Fe_4[Fe(CN)_6]_3} + 12KCl$.

The addition of ferric chloride is generally unnecessary, as some of the ferrous sulphate is usually oxidized to the ferric salt.

7. Neither calcium chloride, nor ferric chloride, produces any precipitate or coloration with a cyanide solution.

Note.—Cyanide solutions nearly always give a white precipitate with calcium chloride solution. This is due to the presence of carbonate in the cyanide.

When a substance is given for analysis, if, on heating it in a dry test tube, a horrible-smelling gas is given off, which burns at the mouth of the tube with a pinkish flame edged with green, it may be pretty well assumed that mercury or silver cyanide is present, the obnoxious and inflammable gas being cyanogen.

$$Hg(CN)_2 = Hg + C_2N_2.$$

A fresh portion of the solid should then be taken, and placed in a dry test tube fitted with a cork and delivery tube, the latter dipping into a little caustic potash solution contained in a second test tube. On heating, the cyanogen is given off and is absorbed by the potash, cyanide and cyanate of potassium being formed.

$$C_2N_2 + 2KHO = \underset{\text{Cyanide.}}{KCN} + \underset{\text{Cyanate.}}{KO.CN} + H_2O.$$

The hydrocyanic acid can then readily be detected by adding dilute sulphuric acid to a portion of the alkaline liquid till it becomes acid, and then gently warming, when the smell of bitter almonds will be at once apparent. Other portions of the liquid may be tested by tests 6 and 7.

Mercuric cyanide is soluble in water, but silver cyanide is not.

CHAPTER V

METHYL AND ETHYL ALCOHOLS, GRAPE AND CANE SUGARS, STARCH, GLYCERINE, ANILINE, MORPHINE, AND UREA

METHYL ALCOHOL

CH_4O or $CH_3.OH$.

METHYL alcohol, or wood spirit, is a colourless liquid, having a faint peculiar odour, and boiling at 66° C. It is very inflammable, and burns with a pale blue flame. Many fats and resins are dissolved by it, consequently it is largely used in organic chemistry as a solvent. The commercial alcohol usually contains acetone, from which it may be freed by heating with fused calcium chloride, when the latter combines with the methyl alcohol to form a crystalline compound $CaCl_2.4CH_4O$. This body is stable at 100°, so that on heating to this temperature the acetone is driven off. The $CaCl_2.4CH_4O$ is then treated with water in a retort and distilled. Water and methyl alcohol pass over, and the latter can be obtained in an anhydrous condition by being placed in contact with quicklime, and re-distilled. Methyl alcohol is easily oxidized to formaldehyde and formic acid.

1. When heated in an open dish over a free flame, methyl alcohol volatilizes, takes fire and burns with a pale blue flame, and leaves no residue.

*2. To a small quantity of **strong sulphuric** acid in a test tube, add a little powdered **potassium bichromate** and finally a small quantity of methyl alcohol. A vigorous action will at once ensue and the solution will be turned green owing to the formation of chromium sulphate. The solution will now contain *formic* acid. A little formaldehyde may be produced, but the heat of the reaction will be sufficient to drive this off If the formic acid is present in the solution, the latter must be neutralized and the methyl alcohol distilled off from it, before this test is performed.

$$2K_2Cr_2O_7 + 8H_2SO_4 + 3CH_3.OH = \underset{\text{Formic Acid.}}{H.COOH} + \underset{\text{Formaldehyde.}}{H.CHO} + 2K_2SO_4 + CO_2 + 2Cr_2(SO_4)_3 + 12H_2O.$$

(In reality only a very small quantity of formaldehyde is produced, the equation given having more a *qualitative* than a quantitative significance.)

After the mixture has been allowed to stand for *ten* minutes, it is distilled. The distillate, which will contain the *formic acid*, is neutralized with caustic soda, boiled to drive off any *acetaldehyde* (if ethyl alcohol was also present), and the various tests for a *formate* applied. (Distinction from ethyl alcohol.)

*3. On heating *methyl alcohol* with **strong sulphuric acid** and a **salicylate**, the characteristic odour of methyl salicylate (oil of winter green) is produced.

$$C_6H_4(OH).COONa + CH_3OH + H_2SO_4 = NaHSO_4 + H_2O + \underset{\text{Methyl Salicylate.}}{C_6H_4(OH)COOCH_3}.$$

4. When methyl alcohol is shaken up with **caustic soda**, the latter dissolves, and a solution is produced which on exposure to air turns brown.

5. Methyl alcohol does not give the "iodoform" reaction. (Distinction from ethyl alcohol.)

6. When a mixture of **strong sulphuric acid, sodium chloride**, and **methyl alcohol** is heated, *methyl chloride* is produced. This gas has a pleasant smell, and burns with a *green-edged* flame.

$$CH_3OH + NaCl + H_2SO_4 = NaHSO_4 + H_2O + \underset{\text{Methyl Chloride.}}{CH_3Cl}.$$

This test is best performed by placing a small piece of *rock-salt* in a test tube with a little methyl alcohol, and carefully adding a few drops of concentrated sulphuric acid. On gently warming the mixture, the methyl chloride is given off and can be burnt at the mouth of the tube, when the *green-edged* flame will be noticed.

ETHYL ALCOHOL

C_2H_6O or $C_2H_5.OH$.

Ethyl alcohol is a colourless liquid having a characteristic odour and a burning taste. It boils at 78·3°, and when a light is brought near its surface, it takes fire and burns with an almost colourless, smokeless flame. It is miscible with water and ether in all proportions, and owing to the great readiness with which it absorbs moisture, it is largely used in the preservation of animal and vegetable substances. Next to water, alcohol is the most important solvent, and consequently is largely used in the laboratory. On oxidation, it is converted first into aldehyde, and then into acetic acid.

1. Alcohol, or its solution in water, when evaporated to dryness leaves no residue.

*2. To an aqueous solution of alcohol, a small quantity of **iodine** is added. The solution is gently warmed and then **caustic potash** added drop by drop till the yellow colour disappears. A yellow crystalline precipitate of *iodoform* is thrown down, and at the same time the characteristic smell of that body is noticed.

$$C_2H_5.OH + 6KHO + 4I_2 = \underset{\text{Iodoform.}}{CHI_3} + H.COOK + 5KI + 5H_2O.$$

*3. On heating ethyl alcohol with **strong sulphuric acid** and a **benzoate, acetate,** or **formate,** the characteristic odours of the respective ethers are noticed.

$$(1)\ C_2H_5.HO + H_2SO_4 + C_6H_5COONa = \underset{\text{Ethyl Benzoate.}}{C_6H_5.COO.C_2H_5} + NaHSO_4 + H_2O.$$

$$(2)\ C_2H_5OH + H_2SO_4 + CH_3.COONa = \underset{\text{Ethyl Acetate.}}{CH_3COOC_2H_5.} + NaHSO_4 + H_2O.$$

$$(3)\ C_2H_5OH + H_2SO_4 + H.COONa = \underset{\text{Ethyl Formate.}}{H.COO.C_2H_5} + NaHSO_4 + H_2O.$$

*4. A little powdered **potassium bichromate** is added to a small quantity of **strong sulphuric acid.** On pouring alcohol carefully into the mixture, a vigorous action ensues, the liquid is turned green and the characteristic odour of aldehyde is noticed.

$$K_2Cr_2O_7 + 4H_2SO_4 + 3C_2H_5.OH = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + \underset{\text{Aldehyde.}}{3CH_3.CHO}.$$

The mixture is then allowed to stand for ten minutes, after which it is distilled. The distillate will be chiefly *aldehyde.* A dilute solution of rosaniline is prepared, and to this, sulphurous acid is added drop by drop until a colourless liquid is obtained. On pouring the aldehyde into this liquid, the latter is at once coloured **reddish-violet.** (Schiff's detection of aldehydes.)

Before testing for ethyl alcohol by tests 3 and 4, it should be separated from water as completely as possible. This is done by distillation. To the distillate, dry solid potassium carbonate is added, to remove water not got rid of by distillation. The alcohol is then re-distilled and the treatment repeated if necessary.

Detection of Ethyl and Methyl Alcohols in the **presence of each other.**

Ethyl Alcohol may be detected in the presence of *Methyl Alcohol* by the following tests :—

1. By the production of *iodoform* on treatment with iodine and caustic potash.
2. By the formation of *acetaldehyde* on oxidation with strong sulphuric acid and potassium bichromate.

Methyl Alcohol may be detected in the presence of *Ethyl Alcohol* by the following reactions :—

1. By the production of *methyl salicylate* on heating with strong sulphuric acid and a salicylate.
2. By being converted into *formic acid* on treatment with bichromate of potash and concentrated sulphuric acid.

GRAPE SUGAR.

$C_6H_{12}O_6$ or $CH_2(OH).[CH.OH]_4.CHO$.

Grape sugar, also known as **glucose**, and **dextrose**, crystallizes from water, with one molecule of water ($C_6H_{12}O_6.H_2O$), in granular masses, which melt at 86°. From ethyl alcohol it crystallizes in anhydrous prisms which melt at 146°. It is almost insoluble in absolute alcohol, but water dissolves it readily, forming a sweet solution, which, however, is not quite so sweet as that of cane sugar. It rotates the plane of polarization to the right hand, hence its name of dextrose. In the presence of alkalies, glucose is a powerful reducing agent. When a solution of glucose is mixed with sodium chloride, it deposits crystals of $2C_6H_{12}O_6.NaCl.H_2O$. With the oxides of the alkaline earths, it combines to form glucosates, such as $C_6H_{12}O_6.CaO$, etc.

1. Heated in a dry test tube, glucose melts, evolves water and gradually blackens. The oxides of carbon and hydrocarbons are given off, and the pungent smell of burnt sugar is noticed.

2. Heated in the dry state with **strong sulphuric acid, pure** grape sugar does not blacken, but after a time a yellowish colour is produced. Ordinary samples of grape sugar, however, usually blacken when so treated.

*3. When a solution of grape sugar is heated with a strong solution of **caustic potash or soda,** the liquid becomes dark brown. (Cf. cane sugar.)

*4. When a solution of grape sugar is gently heated with **Fehling's solution,** a **yellow** precipitate of *cuprous hydrate* is thrown down, which on further heating is converted into **red** *cuprous oxide.* (Distinction from cane sugar.)

*5. To a solution of grape sugar add a few drops of **copper sulphate** solution and excess of **caustic potash** or soda. The copper is not precipitated, but the solution becomes **deep blue.** On gently heating, *yellow* cuprous hydrate, and finally *red* cuprous oxide, is thrown down. In performing this experiment, *great* excess of caustic alkali should be avoided, otherwise, on heating, the solution will become a *dark brown* owing to the action of the alkali on the sugar.

*6. If a solution of grape sugar is mixed with **cupric acetate** solution and the liquid allowed to stand, reduction takes place and cuprous oxide or hydrate is thrown down. The precipitation may be hastened by adding a few drops of acetic acid and gently warming the mixture. (Cf. cane sugar.)

7. If a solution of grape sugar, to which a little **caustic potash** or **soda** has been added, is heated up nearly to boiling point, and a few drops of **picric acid** solution added, a **red** coloration is produced, due to the formation of *picramic* acid. (Distinction from cane sugar.)

The solution sometimes requires to be heated after the addition of the picric acid, before the coloration appears.

8. When a few drops of **litmus** solution and a little **sodium carbonate** are added to a solution of grape sugar, and the mixture gently heated, it turns first **greenish** and then **yellow.** On allowing the liquid to cool and shaking it up with air, the *blue colour* returns. (Distinction from cane sugar.)

9. On the addition of yeast to a solution of grape sugar, fermentation soon sets in if the mixture is kept in a warm place, the grape sugar being converted into alcohol and carbon dioxide.

$$C_6H_{12}O_6 = 2C_2H_5.OH + 2CO_2.$$

10. To a dilute solution of grape sugar made alkaline with caustic soda add methylene blue solution and warm. The colour is at once discharged. (Distinction from cane sugar.)

11. To a dilute solution of grape sugar add an acetic acid solution of phenyl hydrazine and put the test-tube in boiling water for half an hour. A yellow precipitate of glucosazone is produced even in dilute solutions. (Distinction from cane sugar.)

CANE SUGAR.

$C_{12}H_{22}O_{11}$ or $C_{12}H_{14}O_3(OH)_8$.

Cane sugar, also known as **saccharose** and **sucrose**, crystallizes from water in large monoclinic prisms, the shape of which is well seen in sugar-candy. It has a very sweet taste, is freely soluble in water, but only sparingly so in alcohol. Cane sugar melts at 160°, and if heated to this temperature and then allowed to cool, an amorphous mass known as barley-sugar, is produced. Like grape sugar, it combines with the oxides of the alkaline earths, yielding saccharates, as $C_{12}H_{22}O_{11}.CaO.2H_2O$, $C_{12}H_{22}O_{11}.2CaO$, etc.

1. When cane sugar is heated in a dry test tube, it first melts, and then decomposes, with the production of a peculiar aromatic smell (smell of burnt sugar), and a residue of porous glistening charcoal remains.

2. Heated with strong sulphuric acid, cane sugar rapidly blackens, and carbon and sulphur dioxides are evolved. (Cf. grape sugar.)

*3. To a concentrated solution of cane sugar, add an equal volume of **strong sulphuric acid.** The mixture will immediately blacken, and at the same time the disengagement of carbon dioxide, steam and sulphur dioxide will cause the blackened liquid to swell up and pour out of the tube as a black froth. This test should be performed in the sink, the test tube containing the sugar solution standing in a beaker.

4. On heating with caustic **potash** or **soda**, cane sugar solutions do not turn brown. (Cf. grape sugar.)

*5. If a few drops of **copper sulphate** solution are added to a solution of cane sugar, and then excess of **caustic potash** or **soda**, the cupric hydrate is kept in solution and the liquid becomes dark blue. On boiling, no cuprous hydrate or oxide is thrown down, as in the case of grape sugar. If the liquid is now made acid, with hydrochloric acid, boiled for some time, and finally made alkaline again with caustic potash, a *red* or *yellow* precipitate will be thrown down, especially if the liquid is again boiled. This is due to the acid having converted the cane sugar into a mixture of dextrose and levulose, both of which reduce alkaline cupric sulphate solution.

$$\underset{\text{Cane Sugar.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Levulose.}}{C_6H_{12}O_6}.$$

6. Cane sugar does not reduce Fehling's solution, even on boiling. (Cf. grape sugar.)

*7. When a solution of cane sugar is heated with **cupric acetate** solution and a few drops of acetic acid, **no** reduction takes place.

8. Methylene blue solution is not discolorised by cane sugar. (Cf. grape sugar.)

9. Phenyl hydrazine does not yield an osazone. (Cf. grape sugar.)

Detection of Cane and Grape Sugars in the presence of each other.

Dissolve a little of substance in water, add a small quantity of copper sulphate solution, and finally excess of caustic potash (or soda). The liquid should now have a *deep blue* colour. Care should be taken not to have too much caustic potash present, otherwise the solution will darken on heating. Dilute the liquid if necessary, and boil for a few minutes in an open basin. If **grape sugar** is present, *red cuprous oxide* will be precipitated. Filter this off, and test a small quantity of the filtrate for *grape sugar*, by adding more copper sulphate and caustic potash and boiling. If more cuprous oxide is thrown down, the rest of the filtrate must be treated in the same way, until all the *grape sugar* has been destroyed.

When the filtrate is found to be free of grape sugar, add strong hydrochloric acid, and then boil for *five* minutes. Add caustic potash in excess and heat if necessary. A *red* or *yellow* precipitate here indicates the presence of **cane sugar.**

STARCH.

$(C_6H_{10}O_5)n$.

Starch, or amylum, differs in appearance according to the source from which it is obtained. It is a soft, white, velvety powder which always contains moisture. When examined under the microscope, it is seen to consist of round or elongated granules, having a peculiarly striated appearance. The interior of these granules consists of *granulose*, whilst the cell wall is made of *starch cellulose*. When starch is heated with water, these granules burst, and the granulose dissolves, whilst the cellulose remains undissolved. Starch is insoluble in *cold water*, also in alcohol and ether. The actual molecular formula of starch has not yet been determined.

1. Heated in a dry test tube, starch gradually blackens, water and combustible gases are given off, and a smell somewhat resembling burnt sugar is produced.

2. Heated with concentrated sulphuric acid, starch rapidly blackens, sulphur dioxide and carbon dioxide being evolved.

*3. Mix a small quantity of starch into a paste with cold water. Pour this paste into a large quantity of boiling water and boil for a few minutes. When cold, take a portion of this **starch paste** and add a small quantity of a solution of **iodine** in potassium iodide; a *deep* **blue** coloration is produced. On boiling the liquid, the blue colour disappears but reappears on cooling.

In performing this test with a mixture, if free caustic potash or soda is present, it should be neutralized, otherwise, on the addition of iodine, **no blue** coloration will be produced until the iodine is present in excess.

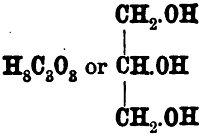
*4. On boiling a small quantity of starch with **dilute sulphuric acid** in a test tube for a few minutes, it is converted into a mixture of **dextrin** and **dextrose.**

$$2(C_6H_{10}O_5)n + n.H_2O = \underset{\text{Dextrin.}}{n.C_6H_{10}O_5} + \underset{\text{Dextrose.}}{n.C_6H_{12}O_6}.$$

To detect the presence **of dextrin,** add a little of the solution to a small beaker of water containing a few drops of **iodine** solution (iodine in potassium iodide), when **a red** colour will be produced.

To confirm the presence of **dextrose,** to a portion of the solution add caustic soda till just alkaline, then acetic acid till just acid, and finally copper acetate solution. On gently warming *cuprous oxide* is thrown down. (Fehling's solution, or alkaline copper sulphate, cannot be used to detect dextrose when dextrin is present, as the latter reduces both of these solutions. It does not, however, reduce copper acetate and acetic acid solution.)

GLYCERINE (*or Glycerol*).



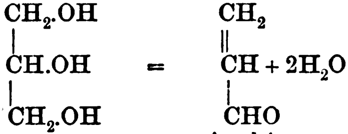
$$H_8C_3O_8 \text{ or } \begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array}$$

Glycerine when perfectly pure is a colourless, sweet-tasted, syrupy liquid, which solidifies in the cold to crystals resembling those of sugar-candy. It melts at 17°, and boils at 290° under atmospheric pressure, without decomposition. If the slightest impurity is present, however, it undergoes partial decomposition at this temperature. It is volatile in steam, and is miscible with water and alcohol in all proportions, but is insoluble in ether.

As seen above, it is really a trihydric alcohol, and as such its behaviour with the metals potassium and sodium, and with the acids, is similar to that of other alcohols.

1. When heated in a dry test tube, ordinary glycerine blackens and an inflammable vapour is given off, having a disagreeable smell. *Pure* glycerine does not blacken on heating.

*2. Heated with **strong sulphuric acid**, glycerine blackens, and the extremely disagreeable and irritating odour of **acrolein** is produced.



$$\begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array} = \begin{array}{l} CH_2 \\ \| \\ CH + 2H_2O \\ | \\ CHO \end{array}$$

Acrolein.

*3. Heated with solid **potassium hydrogen sulphate**, glycerine does not readily blacken as in 2, and *acrolein* is evolved. Here again the potassium hydrogen sulphate acts only as a dehydrating agent.

4. Glycerine, like cane and grape sugars, prevents the precipitation of *cupric hydrate* by *alkalies*. If caustic potash or soda is added in excess to a solution of copper sulphate containing glycerine, no precipitate is produced, even on boiling. (Distinction from grape sugar.)

On acidifying the solution, boiling, and rendering alkaline again, no cuprous oxide is thrown down. (Distinction from cane sugar.)

*5. Glycerine has the peculiar property of forming with **borax** a compound having an **acid reaction**, the borax solution being previously **alkaline**, and the glycerine **neutral.** If a **borax bead** on platinum wire is soaked for a few minutes in a solution of glycerine made just alkaline with sodium carbonate, and then heated in the Bunsen flame, the latter is coloured **green**, showing the presence of *boric* acid.

*6. The property of glycerine mentioned in 5 may be shown in another way.

Prof. Dunstan's test for Glycerine.—Make a solution of borax, by dissolving 1 *part* of borax in 200 parts of water. Take about 2cc. of this solution, and add to it enough **alcoholic** solution of **phenol phthalein** to produce a **rose-red** colour. The solution to be tested for *glycerine* is made *neutral* or very slightly alkaline to litmus, and is gradually added to the borax solution until the *rose* colour is *destroyed.* On the colourless liquid being heated to boiling, the red colour is *restored.* It disappears, however, as the solution cools. *Ammonium* salts also discharge the *red* colour, but it is not restored by heating. This is one of the most delicate and characteristic tests for glycerine in the absence of polyhydric alcohols.

NOTE.—Before testing for glycerine in a solution by tests 1, 2, and 3, it should be concentrated as far as possible on a water-bath.

ANILINE.

$\mathbf{H_7C_6N}$ or $\mathbf{C_6H_5.NH_2}$.

Aniline, or amido-benzene, when freshly prepared is a colourless, oily liquid, having a faint peculiar odour. On exposure to air or light, it turns brown. It is slightly soluble in water (1 in 30), but ether, alcohol, and chloroform dissolve it readily. It boils at 183°, yielding a vapour which burns with a smoky flame. Although neutral to litmus, it combines with one equivalent of acids to form salts, such as aniline hydrochloride, $C_6H_7N.HCl$, aniline sulphate, $(C_6H_7N)_2.H_2SO_4$; etc.

In identifying aniline in a mixture, if it is not present in the free state the following procedure is necessary :—

The salt of aniline is dissolved in water and then treated with caustic potash or soda. This liberates the base, which separates out in oily drops. To dissolve these, ether is added and the mixture shaken. The ethereal solution is removed by a pipette and the ether evaporated off. The free aniline is thus left behind and can be detected by the following tests :—

1. When heated, aniline gives off a vapour which has a very disagreeable smell. If a rod moistened with strong hydrochloric acid is held in the vapour, dense white fumes of aniline hydrochloride are formed.

$$C_6H_7N + HCl = C_6H_7N.HCl.$$

*2. Add one drop of aniline to about 25 cc. of water contained in a small flask. On shaking, the aniline dissolves. Some **bleaching powder** is mixed with water and the solution filtered. A small quantity of the filtrate is now added to the solution of aniline, when a beautiful **violet** coloration is produced. The dirty bluish precipitate that is sometimes produced when a solution of aniline is added to bleaching powder solution, is due to the former solution being *too concentrated.* Only dilute solutions should be used, as this reaction is extremely delicate.

*3. A few drops of aniline are dissolved in a small quantity of dilute hydrochloric acid, and a small quantity of sodium nitrite solution added. If the substances are kept cool, a clear solution of diazobenzene chloride, which has a somewhat peculiar smell, will be formed.

$$C_6H_5.NH_2 + NO.ONa + 2HCl = 2H_2O + NaCl + \underset{\text{Diazobenzene chloride.}}{C_6H_5.N{:}N.Cl.}$$

On warming, a brisk effervescence of nitrogen takes place, and the characteristic smell of phenol is noticed.

$$C_6H_5.N{:}N.Cl + H_2O = \underset{\text{Phenol.}}{C_6H_5.OH} + N_2 + HCl.$$

4. On adding a drop or two of a dilute solution of **copper** *sulphate* to an aqueous solution of aniline, an **apple-green** coloration or precipitate is produced.

*5. Dissolve a small piece of **caustic potash**, about the size of a pea, in a quarter of a test tubeful of alcohol. To this solution, add **one** drop of aniline and *three* or *four* drops of **chloroform**. On gently heating, the highly disagreeable and characteristic odour of *phenylisonitrile* is noticed. This experiment should be performed in a good draught, and care should be taken not to inhale any of the isonitrile.

$$C_6H_5NH_2 + CHCl_3 + 3KHO = 3KCl + 3H_2O + \underset{\text{Phenylisonitrile.}}{C_6H_5.NC.}$$

*6. On a small piece of porcelain, place one drop of aniline and about six drops of concentrated sulphuric acid. The mixture is well stirred and the slightest trace of finely-powdered potassium bichromate added, when a beautiful **blue** coloration will be produced.

MORPHINE.

$C_{17}H_{19}NO_3$.

Morphine crystallizes in prisms containing one molecule of water, which it does not lose till 120°. It is almost insoluble in cold water, and only slightly so in hot. In ether and chloroform it is also insoluble, but in amyl alcohol it is freely soluble, and also fairly so in ethyl alcohol. It is a monatomic base, combining with acids to form *salts*, such as morphine hydrochloride, $C_{17}H_{19}NO_3.HCl$, etc., which are easily soluble in water and alcohol, and are decomposed on the addition of a caustic alkali. Morphine is exceedingly poisonous, has a very bitter taste, and its solution has an alkaline reaction. Its hydrochloride is very largely used in medicine as a soporific.

1. When heated in a dry test tube, morphine melts, and its water of crystallization is driven off. On further heating, a little sublimes, but the greater portion is blackened, and alkaline vapours are evolved.

2. When morphine is fused with **soda lime**, ammonia is liberated.

*3. On the addition of morphine solution to a solution of **iodic acid, iodine** is liberated. In the case of strong solutions, a reddish-brown coloration due to the presence of the free **iodine** is produced, but in dilute solutions the iodine can be detected by means of starch paste.

4. A solution of **iodine** in *potassium iodide* gives with *neutral* morphine solutions a *brown* precipitate of *morphine periodide.* If *starch* is present, it should be removed by shaking up the powder with cold dilute HCl and filtering, before testing for morphia in this way.

$$C_{17}H_{19}NO_3 + 2I_2 = \underset{\text{Morphine periodide.}}{C_{17}H_{19}NO_3.I_4.}$$

If this precipitate is filtered off, well washed and evaporated to dryness with excess of sulphurous acid, on a water-bath, the pure sulphate of morphine remains.

$$2C_{17}H_{19}NO_3.I_4 + 4SO_2 + 8H_2O = \underset{\text{Morphine sulphate.}}{(C_{17}H_{19}NO_3)_2.H_2SO_4} + 8HI + 3H_2SO_4.$$

This is sometimes a convenient method for separating morphine from other substances in a mixture.

5. On the gradual addition of **sodium**, **potassium**, or **ammonium hydrate**, to a solution of morphine salts, the alkaloid is thrown down as a white powder, but on more of the precipitant being added, it readily dissolves, except in the case of ammonium hydrate, in which morphine is only fairly soluble, so that this has to be added in great excess before the liquid becomes quite clear again. If *sodium carbonate* is used instead of either of the above-mentioned alkaline hydrates, the *morphine* is thrown down and does not dissolve in excess of the reagent. If other substances are not present which are also precipitated by sodium carbonate, the morphine may be conveniently separated in this way. The precipitate is filtered off, washed, and the various confirmatory tests applied.

*6. A little solid morphine, or a strong solution of a morphine salt, is added to a freshly-prepared solution of **molybdic** acid in **strong sulphuric acid**. A **violet** coloration is produced, which on exposure to air turns **blue** and then **dirty green**.

*7. Morphine dissolves in strong **nitric acid** with the production of a **red** colour, which is destroyed by stannous chloride. If a solution is being tested, it should be concentrated as much as possible before the addition of the nitric acid. Even then, it is often necessary to heat before the red colour appears.

*8. If a small quantity of morphine is added to **strong sulphuric acid** containing a little **potassium arseniate**, and the mixture gently warmed, a **blue-violet** coloration is produced, which changes to brown-red. On dilution with water, this turns **green**, and chloroform shaken up with it is coloured **violet**.

*9. Concentrated **sulphuric acid** dissolves morphine in the cold without the production of any colour, but on warming, a faint **rose**-coloured tint is developed. On the addition of a minute quantity of **nitric acid** to the cold solution, a deep **red** colour is produced. If a small crystal of potassium bichromate is now placed in the liquid, it is turned a deep **mahogany** colour.

*10. To a small quantity of a solution obtained by dissolving morphine in **strong sulphuric** acid in a porcelain basin, add a crystal of **potassium chlorate** and warm *carefully*. A **grass-green** liquid is produced.

*11. Neutral **ferric chloride** added to solid morphine produces a *deep* **blue** *colour*. If the solution that is to be tested for morphine contains any other substance, it should be neutralized and then a small quantity of ferric chloride added to it. In dilute solutions no *blue* colour will be seen, but on the addition of potassium ferricyanide, a *deep blue precipitate* is thrown down. This is due to one of two things—either the morphine has reduced the ferric chloride to ferrous, and thus the precipitate is one of *Turnbull's blue*, or it has reduced the ferricyanide to ferrocyanide, and thus the precipitate is one of *Prussian blue*. According to Hesse, the latter is the case.

UREA.

H_4N_2CO or $CO(NH_2)_2$.

Urea, or carbamide, is the neutral amide of carbonic acid, and was the first organic body made synthetically. This was done in 1828 by Wohler, who found that on warming an aqueous solution of ammonium cyanate, the salt was changed into urea.

$$NH_4.O.CN = CO(NH_2)_2.$$

Urea, although a neutral body, has basic properties, and combines with one equivalent of acids to form salts. It crystallizes in colourless rhombic prisms or needles, which melt at 132°. It is freely soluble in water and in alcohol, but almost insoluble in ether.

1. When strongly **heated** in a **dry tube**, urea yields ammonia, biuret, cyanuric acid, ammelide and water.

$$8CO(NH_2)_2 = 6NH_3 + \underset{\text{Biuret.}}{NH(CONH_2)_2} + \underset{\text{Cyanuric Acid.}}{N_3C_3O_3H_3} +$$
$$\underset{\text{Ammelide.}}{(CN)_3NH_2(OH)_2} + H_2O.$$

*2. If, however, the urea is gently heated for a short time in a dry test tube just above its melting point, the greater portion of it is converted into ammonia and **biuret.**

$$2CO(NH_2)_2 = NH_3 + \underset{\text{Biuret.}}{NH(CONH_2)_2}.$$

To show the presence of **biuret,** the tube is allowed to cool and the residue dissolved in caustic potash or soda. A *dilute* solution of copper sulphate is added **drop by drop,** when the liquid becomes first *red,* then *violet,* and finally *purple* (Biuret reaction).

3. On heating urea (or its solution) with **soda lime** or **caustic potash,** ammonia is evolved.

$$CO(NH_2)_2 + 2KHO = 2NH_3 + K_2CO_3.$$

4. When urea is heated for some time with strong sulphuric acid, it is converted into ammonium sulphate and carbon dioxide is liberated.

$$CO(NH_2)_2 + H_2SO_4 + H_2O = (NH_4)_2SO_4 + CO_2.$$

*5. Urea is decomposed by **nitrous acid**, nitrogen and carbon dioxide being evolved.

In the **cold** the reaction is as follows :—

$$2CO(NH_2)_2 + 2HNO_2 = (NH_4)_2CO_3 + 2N_2 + CO_2 + H_2O.$$

Whilst if the solution of urea is **hot**, the following changes take place :—

$$CO(NH_2)_2 + 2HNO_2 = CO_2 + 2N_2 + 3H_2O.$$

*6. When an alkaline solution of **hypobromite** (or hypochlorite) is added to a solution of urea, nitrogen is evolved with effervescence. It is best to use freshly-prepared hypobromite.

$$CO(NH_2)_2 + 3NaBrO + 2NaHO = N_2 + 3H_2O + Na_2CO_3 + 3NaBr.$$

*7. **Urea nitrate** is precipitated from strong solutions of urea, by **nitric acid**, in glistening white plates, which are soluble in water but only slightly soluble in nitric acid.

$$CO(NH_2)_2 + HNO_3 = CO(NH_2)_2.HNO_3.$$

8. A strong solution of **oxalic acid** also produces a precipitate in concentrated solutions of urea, the oxalate of urea being almost insoluble in strong oxalic acid solution.

$$2CO(NH_2)_2 + H_2C_2O_4 + 2H_2O = \underset{\text{Urea Oxalate.}}{H_2C_2O_4.2CO(NH_2)_2.2H_2O.}$$

9. In a neutral aqueous solution of urea, **mercuric nitrate** produces a dirty white precipitate having the composition $2CO(NH_2)_2.Hg(NO_3)_2.3HgO$.

10. When **chlorine** is passed into an aqueous solution of urea, the following change takes place :—

$$CO(NH_2)_2 + H_2O + 3Cl_2 = N_2 + CO_2 + 6HCl.$$

CHAPTER VI

EXAMINATION OF MIXTURES CONTAINING ORGANIC COMPOUNDS ENUMERATED IN THE SYLLABUS OF THE ELEMENTARY STAGE

PRELIMINARY EXAMINATION.

I. If the body given for analysis is a solid, notice colour, smell, and form; if a liquid, a small portion should be cautiously evaporated to dryness and the odour of the vapour, changes (if any) in colour of liquid, etc., carefully observed. If there is **no residue**, this points to presence of an **alcohol** or pure **glycerine**; or to presence of **free formic** or **acetic** acid if the original solution was **acid**.

If there is a residue, or if the original solution was acid, and left no residue, then another portion of the liquid (having been first neutralized, if acid) should be evaporated to dryness on the water-bath and the solid, or liquid (*e.g.* glycerine), thus obtained, examined as below.

II. Heat a little of the dry solid (or concentrated liquid) in a hard dry test tube.

Observation.	Inference.
Smell of acetone or vinegar.	**Acetate.**
Smell of tar (phenol).	**Salicylate.**
Smell of burnt sugar and immediate blackening,	**Tartrate.**
White sublimate and no blackening (if pure).	**Oxalate.**
White sublimate, blackening and smell of tar.	**Salicylate.**
Blackens after a time and irritating fumes given off.	**Citrate** or **Glycerine.**[1]

---

[1] *Pure glycerine does not blacken on heating.*

III. Heat a little of the substance with dilute sulphuric acid.

Observation.	Inference.
Acid fumes given off, having a smell resembling that of vinegar.	**Acetate** or **formate.**

IV. Heat a little of the substance with concentrated sulphuric acid.

Observation.	Inference.
No blackening :—	
(*a*) Acid fumes smelling of vinegar.	**Acetate.**
(*b*) CO evolved, and burns at mouth of tube with a blue flame.	**Formate.**
(*c*) CO and CO_2 evolved, the latter being detected by lime-water.	**Oxalate.**
Immediate blackening :—	
(*d*) CO, SO_2, etc., evolved (see Fig. 8).	**Tartrate** or **salicylate.**
Blackening after a time :—	
(*e*) CO, CO_2, SO_2 evolved (see Fig. 8).	**Citrate.**
(*f*) Smell of acrolein (burning fat).	**Glycerine.**

In performing test 4, a small quantity of the substance should be placed in a dry test tube, and a little concentrated sulphuric acid added to it. The tube is then very gradually heated. If an **acetate** is present the smell of acetic acid is readily recognized. A lighted match or taper should be held near the mouth of the tube, so that if any **carbon monoxide** is given off, it will burn. To detect the presence of **carbon dioxide,** a test tube containing lime-water is held beneath the mouth of the other tube while it is being heated. If **sulphur dioxide** is given off, the carbon dioxide cannot be detected in this way. The presence of the former is shown by holding a strip of filter paper, which has been dipped in a solution of potassium bichromate, over the mouth of the tube, when it is turned *green*. If sulphur dioxide is found to be present, a fresh portion of substance may be taken, and the apparatus shown in Fig. 8 used (*see* page 23).

V. Intimately mix a small portion of the substance with excess of soda lime, and heat strongly in a hard glass tube.

OBSERVATION.	INFERENCE.
Smell of *phenol* (tar).	**Salicylate.**
Inflammable gas given off.	**Formate, acetate,** or **oxalate.**

These preliminary tests having been performed, a pretty good idea of what substances have to be looked for will have been obtained.

It must be remembered, however, that the presence of one compound may completely mask the presence of another. Thus, when the substance is heated with concentrated sulphuric acid, if a **tartrate** is present, no information can be obtained in *this test* concerning the presence or absence of **formates, oxalates, citrates,** or **salicylates.** Again, if on heating with strong sulphuric acid for some time, *no* blackening takes place, tartrates, citrates, and salicylates are obviously absent, and any time spent in looking for these bodies would be wasted.

If the mixture given for analysis is a solid, it must not be taken for granted that **glycerine** or **alcohols** are absent. For example, **methyl alcohol** is contained in the white crystalline compound, $CaCl_2.4CH_4O$, from which it may be set free by heating with water. Also, a **methylate** or an **ethylate** may be given. These are deliquescent solids, obtained by dissolving potassium or sodium in *methyl* or *ethyl alcohol*.

On treatment with water, they are immediately decomposed, with the re-formation of the alcohol.

Thus :—

$$\underset{\text{Potassium ethylate.}}{C_2H_5.OK} + H_2O = C_2H_5.OH + KHO.$$

Similar compounds in the case of glycerine likewise may be given.

VI. Examination for presence of alcohols.

Take a small portion of the body under examination.

(a) If a **liquid**, neutralize if necessary, and warm gently. Notice if smell of an **alcohol** is given off.

(b) If a **solid**, dissolve in a little water, and repeat experiment (a) above.

Should the presence of an alcohol be suspected, it is best to separate it from the rest of the mixture by distillation. This can be quickly done as follows :—

Place a portion of the neutral liquid (see **a** and **b** above) in a boiling tube fitted with a cork and delivery tube, the latter dipping into a test tube immersed in a beaker of cold water. On heating the boiling tube, the alcohol will distil over into the test tube. Notice odour of distillate.

In another test tube place a small quantity of strong sulphuric acid and *two* drops of a solution of bichromate of potash, and then add a little of the distillate. If an **alcohol** is present, the solution will be at once turned **green.**

Other portions of the distillate can then be examined for the presence of each alcohol in the usual way (*see* pages 45—48), at least two confirmatory tests being performed.

VII. Detection of Glycerine.

Glycerine is best detected by Prof. Dunstan's test (*see* page 56). To perform confirmatory tests the glycerine should be separated from the rest of the mixture. This can generally be effected in the following manner :—Make the mixture neutral or slightly alkaline, and shake up with a solution made by mixing together **two** volumes of absolute alcohol, and **one** volume of ether. Remove the ethereal liquid, and evaporate off the alcohol and ether on the water-bath, when the glycerine will be left behind. Perform the following confirmatory tests :—

(a) Heat one portion with solid potassium hydrogen sulphate in a dry test tube, when the smell of *acrolein* will be given off (*see* page 55, test 3).

(b) Make another portion just alkaline with sodium carbonate. Immerse in this a transparent borax bead for a few minutes. On heating the bead in the Bunsen flame, the latter will be coloured *green* (*see* page 56, test 5).

SYSTEMATIC EXAMINATION FOR ACIDS.

Before testing for acids in solution, the metals (except alkalies) must be removed, if present.

Take a small portion of mixture, dissolve in water, acidify with hydrochloric acid, warm, and pass sulphuretted hydrogen for some time. If any precipitate is formed, filter off, pass more gas into filtrate to insure complete precipitation, and add ammonium hydrate and sulphide. Filter off any precipitate that may be thrown down. Slightly acidify filtrate with hydrochloric acid, and boil till liquid no longer smells of sulphuretted hydrogen. Add solid sodium carbonate till alkaline and boil for some time. If any precipitate is formed, filter off. The filtrate will now contain the organic acids as sodium salts.

If it is found that any metals other than alkalies are present, a large portion of the mixture should be taken and treated in this way to get rid of them. If no precipitate is formed on treating with sulphuretted hydrogen or ammonium sulphide, but one is produced on boiling with sodium carbonate, obviously the fresh portion taken should be boiled with sodium carbonate only.

The liquid, containing the organic acids as sodium salts, is neutralized by treating the *larger* portion of it with dilute hydrochloric acid, boiling till all carbon dioxide is driven off, and then adding dilute caustic soda till neutral. A small portion is neutralized by *nitric acid* and soda, this being used, if necessary, for confirmatory tests with *silver nitrate.*

EXAMINATION OF ACIDS IN SOLUTION.

To neutral solution, prepared as directed on preceding page, add Calcium Chloride solution; shake well and allow to stand for twenty minutes; filter.

<table>
<tr>
<td rowspan="3">**Precipitate** = **Calcium Tartrate** or **Calcium Oxalate** or both. Examine according to table given on page 28.</td>
<td colspan="3">**Filtrate.**
To filtrate add more Calcium Chloride, and boil for some time. *Filter* **at once** and test filtrate by re-boiling.</td>
</tr>
<tr>
<td rowspan="2">**Precipitate** = **Calcium Citrate** and perhaps a little Calcium Tartrate. Examine according to table given on page 28.</td>
<td colspan="2">**Filtrate.**
To filtrate, which must be **neutral** and cold, add Ferric Chloride solution. **Red coloration** = **Formic** or **Acetic** Acid, **Violet coloration** = **Salicylic** Acid. In the presence of an *acetate* or *formate* the *violet* colour is not very distinct; to a portion of the solution add a drop or two of very dilute *hydrochloric acid*, when the *red* colour will *disappear*, and the *violet* show up more plainly.
Confirm presence of **Salicylic** Acid in the following ways:—
1. Heat a portion of the original solid with *soda lime*, when *phenol* will be given off.
2. Heat a portion of original substance with *strong sulphuric acid* and *methyl alcohol*, when the odour of *methyl salicylate* (oil of winter green) will be noticed.
Place liquid (which has a *red* or *violet* colour) in a boiling tube, and boil for some time, when if an **acetate** or **formate** is present, a *reddish-brown* precipitate of *basic ferric acetate* or *formate* will be thrown down. **Filter.**</td>
</tr>
<tr>
<td>**Precipitate.**—Wash well and dissolve in dilute sulphuric acid. Place in a boiling tube and distil. Distillate = Acetic or Formic Acid. Examine according to table on page 36.</td>
<td>Filtrate (neglect).</td>
</tr>
</table>

CHAPTER VII

EXAMINATION OF MIXTURES CONTAINING ORGANIC COMPOUNDS ENUMERATED IN THE SYLLABUS OF THE ADVANCED STAGE

THE substances for analysis may contain the following constituents:—"Hydrocyanic, formic, acetic, benzoic, oxalic, tartaric, citric, and salicylic acids, cane sugar, glucose, starch, methyl and ethyl alcohols, glycerine, aniline, phenol, morphine and urea; **not more** than **two** *organic* bodies being present in any **one** mixture."

That is to say, a mixture may contain urea oxalate and morphine acetate; phenol and aniline oxalate; etc., since in each of these mixtures mentioned there are but *two* organic bodies. So that, in this stage, it is quite possible for a mixture to contain two acids and two bases; or one acid and two bases; or two acids and one base; etc., but there cannot be *more than two* organic acids and *two organic* bases present.

PRELIMINARY EXAMINATION.

I. Notice colour, smell, form, etc., of substance given for analysis, test whether acid, alkaline, or neutral by means of litmus paper. If a liquid, a small portion should be cautiously evaporated to dryness, and the odour of the vapour, change (if any) in the colour of the liquid, etc., carefully observed. If there is **no** residue this points to the presence of an **alcohol, aniline** or **glycerine**; or to presence of free **formic** or **acetic** acid if the original solution was acid.

If there is a residue, or if the original liquid was acid and left no residue, then a fresh portion (having been first neutralized, if acid) should be evaporated to dryness on the water-bath, and the solid or liquid (*e.g.* glycerine) thus obtained examined as below.

II. Heat a little of the dry solid (or concentrated liquid) in a hard glass test tube.

Observation.	Inference.
(*a*) Smell of acetone or vinegar, *no blackening.*	**Acetate.**
(*b*) Smell of tar.	**Salicylate, phenol.**
(*c*) Smell of ammonia, *no blackening.*	**Urea, cyanide, ammonium salts.**
(*d*) Peculiar characteristic smell.	**Aniline.**
(*e*) Smell of bitter almonds, no blackening.	**Cyanide.**
(*f*) White crystalline sublimate, blackening, and smell of tar.	**Salicylate.**
(*g*) White crystalline sublimate, *no blackening.*	**Oxalate.**
(*h*) White crystalline sublimate, *no blackening*, and aromatic odour.	**Benzoate.**
(*j*) Substance blackens, and has a disagreeable odour.	**Starch, morphine.**
(*k*) Blackening and smell of burnt sugar.	**Tartrate, cane sugar, glucose.**
(*l*) Blackening after some time, and irritating fumes given off.	**Citrate, Glycerine.**[1]

III. Heat a little of the substance in a test tube with dilute sulphuric acid.

Observation.	Inference.
(*a*) Hydrocyanic acid given off, having a smell of bitter almonds.	**Cyanide.**
(*b*) Acid fumes given off, having a smell resembling that of vinegar.	**Acetate, formate.**

---

[1] See note on p. 64.

IV. Heat a little of the substance in a test tube with concentrated sulphuric acid.

OBSERVATION.	INFERENCE.
No blackening:—	
(*a*) Acid fumes smelling of vinegar.	**Acetate.**
(*b*) Acid fumes having irritating aromatic odour.	**Benzoate.**
(*c*) CO evolved, and burns at mouth of tube with a blue flame.	**Formate, cyanide.**
(*d*) CO_2 evolved, and detected by lime water.	**Urea.**
(*e*) CO and CO_2 evolved.	**Oxalate.**
Immediate blackening:—	
(*f*) CO, SO_2, etc., evolved (*see* Fig. 8).	**Tartrate, salicylate, cane sugar, morphine, starch.**
Blackening after a time:—	
(*g*) CO, CO_2 and SO_2 evolved (*see* Fig. 8).	**Citrate.**
(*h*) Smell of acrolein (burning fat).	**Glycerine.**
(*i*) Yellow-coloured liquid, which after prolonged heating becomes brown.	**Glucose.**

In performing the last observation, a small quantity of the substance, together with a little concentrated sulphuric acid, is placed in a dry test tube and very gradually heated. An **acetate** or **benzoate** will be readily detected by the smell of the vapours given off. A lighted match or taper should be held near the mouth of the tube, so that if any **carbon monoxide** is given off it will burn. To detect the presence of *carbon dioxide*, a test tube containing lime water is held beneath the mouth of the other tube while it is being heated. If **sulphur dioxide** is also evolved, the carbon dioxide cannot be detected in this way. The presence of the former is shown by holding over the mouth of the tube a strip of filter paper which has been dipped into a solution of potassium bichromate, when the paper will be turned **green**. If sulphur dioxide is found to be present, a fresh portion of the substance may be taken, and the apparatus shown in Fig. 8 used (*see* page 23).

V. Intimately mix a small portion of the substance with excess of soda lime, and heat strongly in a hard glass tube.

OBSERVATION.	INFERENCE.
(*a*) Ammonia evolved.	**Urea, morphine, cyanides, ammonium salts.**
(*b*) Smell of phenol.	**Salicylate, phenol.**
(*c*) Benzene given off, which condenses in oily drops on the upper portion of the tube.	**Benzoate.**
(*d*) Fumes given off, having characteristic odour.	**Aniline.**
(*e*) Inflammable gas given off.	**Formate, acetate, oxalate.**

VI. Mix a little of the substance into a paste with a small quantity of cold water, in an evaporating basin; add boiling water and stir. When the solution is quite cold, place a little of it in a test tube and add a solution of **Iodine** in potassium iodide.

If **Starch** is present, a beautiful **blue** coloration will be produced. On boiling the liquid, this blue colour will disappear, but reappear on cooling.

The presence of starch may be confirmed by shaking up a fresh portion of the substance with *cold* water, filtering off the undissolved starch and boiling it with dilute sulphuric acid. This converts the starch into a mixture of **dextrin** and **dextrose** (*see* test 4, page 53).

If, instead of a blue coloration, a reddish-brown precipitate is thrown down on the addition of iodine to the above solution, **morphine** is probably present, the precipitate being morphine periodide. If this is filtered off, washed, and evaporated to dryness on the water-bath with excess of sulphurous acid, pure *sulphate* of *morphine* remains.

The presence of morphine may be confirmed by treating various portions of the sulphate according to tests 6, 7, 9, etc., on pages 60 and 61.

If **starch** is present, it must be removed by shaking up the substance with cold very dilute hydrochloric acid, and filtering before testing for morphine in this way. On neutralizing the filtrate and adding iodine solution, the periodide of *morphine* will be thrown down, if morphine is present.

NOTE.—When adding iodine solution to a liquid supposed to contain starch or morphine, if no coloration or precipitate is at once produced the iodine should be added till the liquid has a distinct *yellow* colour, to insure that it (the iodine) is present in excess.

These preliminary tests having been performed, a pretty good idea of what substances have to be looked for will have been obtained. It must be remembered, however, that the presence of one compound may completely mask the presence of another. Thus, when the substance is heated with concentrated sulphuric acid, if a *tartrate* is present, no information can be obtained in this test concerning the presence or absence of *formates*, *oxalates*, *citrates*, *starch*, *cane sugar*, *grape sugar*, *urea*, etc. Notwithstanding this, however, the information obtained by means of these preliminary tests considerably lessens the number of experiments that have to be made.

Thus, if on heating with strong sulphuric acid *no blackening* takes place, *tartrates*, *citrates*, *salicylates*, *starch*, *cane sugar*, and *morphine* are all obviously absent, and any time spent in looking for these bodies would be wasted.

Again, on heating the substance with soda lime, if *ammonia* is not evolved, or if the characteristic smell of *aniline* is not produced, it is at once known that *urea*, *morphine*, and *aniline* are absent, so that observations according to Table IX. need not be performed. These are merely instances, and the student will soon learn how to save himself unnecessary work.

If the mixture given for analysis is a **solid**, it must not be taken for granted that **glycerine, aniline**, or **alcohols** are absent. For example, **methyl alcohol** unites with calcium chloride to form a white crystalline compound $CaCl_2.4CH_4O$, from which it may be set free by heating with water. Also, a **methylate** or an **ethylate** may be given. These are deliquescent solids obtained by dissolving potassium or sodium in methyl or ethyl alcohol.

On treatment with water, they are immediately decomposed with the re-formation of the alcohol.

Thus:— $\underset{\text{Potassium ethylate.}}{C_2H_5.OK} + H_2O + C_2H_5.OH + KHO.$

Similar compounds in the case of glycerine may likewise be given; also salts of aniline (*see* page 57).

VII. Examination for presence of alcohols.

Take a small portion of the body under examination.

(a) If a *liquid*, neutralize if necessary, and warm gently. Notice if smell of an *alcohol* is given off.

(b) If a *solid*, dissolve in a little water and repeat experiment (a) above.

If the presence of an alcohol is suspected, separate it from the rest of the mixture by distillation. Proceed as follows. Place some of the neutral liquid (see **a** and **b** above) in a boiling tube fitted with a cork and delivery tube, the latter dipping into a test tube immersed in a beaker of cold water. Heat the boiling tube, when alcohol will distil over into the test tube.

In another test tube place a little strong sulphuric acid and a few drops of potassium bichromate solution, and then add a little of the distillate. If an **alcohol** is present, the solution will turn **green**. Other portions of the distillate can then be examined for the presence of each alcohol in the usual way. Perform at least two confirmatory tests.

For **Methyl alcohol** the most characteristic tests are 2 and 3, pages 45 and 46.

For **Ethyl alcohol** the most characteristic tests are 2, 3, and 4, pages 47 and 48.

VIII. Table for the Detection of Cane and Grape Sugars.

Place a small quantity of the original substance in a test tube, add cold dilute *caustic soda*, shake well and filter if necessary. The filtrate will contain any sugar present in the mixture. Divide into two portions, reserving the smaller for confirmatory tests. To alkaline solution add a small quantity of copper sulphate solution, and more caustic soda if necessary. The liquid should now be quite clear and have a *deep blue* colour. Excess of caustic soda should be avoided, otherwise the solution may darken on heating. Dilute the liquid if necessary and boil in an open basin for a few minutes. If *grape sugar* is present *red cuprous* oxide will be precipitated. Filter this off, and test a small quantity of the filtrate for grape sugar by adding more copper sulphate and caustic soda and boiling again. If more cuprous oxide is thrown down the rest of the filtrate must be treated in the same way until all the grape sugar has been destroyed. When the filtrate is free from grape sugar, set it aside for testing for cane sugar.

Confirm the presence of **grape sugar** in the following ways:—

Take the alkaline liquid that has been reserved for the purpose and divide into two portions:—

1. Add a small quantity of a *strong* solution of caustic soda and heat. The liquid turns *brown.*

2. Render just acid by means of acetic acid, add cupric acetate solution and warm gently. A **red precipitate** of cuprous oxide is thrown down.

To filtrate free from grape sugar, and which should have a blue colour, add strong hydrochloric acid till acid and then boil for five minutes. Divide into three portions:—

1. Add caustic soda in excess and heat gently. A *red* or *yellow* precipitate **here** indicates the presence of **cane sugar** in the **original** mixture (*see* test 5, page 51).

2. Render just alkaline with caustic soda, add Fehling's solution and heat gently. A *red* or *yellow* precipitate.

3. Render just alkaline with caustic soda, then just acid with *acetic* acid, add copper acetate solution and warm. A *red* or *yellow* precipitate.

IX. Table for Detection of Aniline, Urea, and Morphine.

Treat substance with dilute hydrochloric acid, and filter if necessary. To clear solution, add a dilute solution of **caustic soda**,* *drop* by *drop*, till only *just alkaline*. A *white* precipitate may be **morphine** (also lead, aluminium hydrate, etc., if these metals are present). If a precipitate is formed, filter off, and add more caustic soda to the filtrate and warm. If ammonia is given off, **urea** is probably present (or ammonium salts). If oily drops separate out having a characteristic odour, **aniline** is probably present.

Confirm presence of bodies, in the following ways :—

MORPHINE.	UREA.	ANILINE.
If morphine was detected in the preceding experiment (6), no further confirmation of its presence is needed here. If observation 6 was not performed, then the precipitate on the filter paper should be washed with cold water, and various portions of it treated according to tests 6, 7, 9, etc., on page 60.	Treat a small portion of the original substance with a little warm water ; if it does not all dissolve, filter. The filtrate will contain the *urea*. Divide filtrate into *three* portions, A, B, and C. **A.** To the cold liquid, add about a quarter of its bulk of strong nitric acid and allow to stand, when glistening white plates of *urea nitrate* will separate out (*see* page 63, test 7). **B.** Add an alkaline solution of hypobromite, when *nitrogen* is evolved with effervescence (*see* page 63, test 6). **C.** Evaporate to dryness and perform test 2, page 62.	If *Aniline* is present, shake up with ether, which dissolves the oily drops. Remove ethereal liquid by means of a pipette, and evaporate off the ether. With the *Aniline* left behind, perform the following confirmatory tests :— **A.** Test 2, page 57. **B.** Test 5, page 58. **C.** Test 6, page 58.

---

* If an *alcohol* was not found in the previous experiments, but is now distinguished by its smell on heating with caustic soda, an ethereal salt is probably present. For example, if *methyl oxalate* were present, on treating the solution with caustic soda, *methyl alcohol* would be set free, and be detected by its smell.

$$C_2O_4(CH_3)_2 + 2NaHO = C_2O_4Na_2 + 2CH_3.OH.$$

Methyl oxalate.

X. Detection of Glycerine.

Glycerine is best detected by Prof. Dunstan's test (*see* test 6, page 56). To perform confirmatory tests, the glycerine should be separated from the rest of the mixture. This can generally be effected in the following manner:—Make the mixture neutral or slightly alkaline, and shake up with a solution made by mixing together *two* volumes of absolute alcohol, and *one* volume of ether. Remove the ethereal liquid by means of a pipette, and evaporate off the alcohol and ether on the water-bath, when the *glycerine* will be left behind.

(a) Heat one portion with solid potassium hydrogen sulphate in a dry test tube, when the smell of *acrolein* will be noticed (*see* test 3, page 55).

(b) Make another portion just alkaline with sodium carbonate. Immerse a transparent borax bead in this for a few minutes. On heating the bead in the Bunsen flame the latter will be coloured *green* (*see* page 56, test 5).

Systematic Examination for Acids.

Before testing for acids in solution, the metals (except alkalies) must be removed if present.

Take a small portion of the mixture, dissolve in water, acidify with dilute hydrochloric acid; warm, and pass sulphuretted hydrogen for some time. If any precipitate is formed, filter off, pass more gas into the filtrate to insure complete precipitation, and add ammonium hydrate and ammonium sulphide. Slightly acidify filtrate with hydrochloric acid, and boil till liquid no longer smells of sulphuretted hydrogen. Add solid sodium carbonate till the liquid is alkaline, and boil for some time. If any precipitate is produced, filter off. The filtrate will now contain the organic acids as sodium salts.

If it is found that any metals other than alkalies are present, a larger portion of the mixture should be taken, and treated in this way to get rid of them. If, however, no precipitate is formed on treating with sulphuretted hydrogen, or ammonium sulphide, but one is produced on boiling with sodium carbonate, obviously the fresh portion taken should be boiled with sodium carbonate only.

The liquid containing the organic acids as sodium salts is divided into portions, one being much larger than the other.

The larger portion is treated with dilute hydrochloric acid and boiled till all carbon dioxide is driven off, and then exactly neutralized with dilute caustic soda.

The smaller portion may be neutralized with dilute *nitric acid* and soda, and is used for confirmatory tests with silver nitrate, if necessary. Care must be taken in the preceding operations, if hydrocyanic acid is present, not to inhale any of the fumes, and the treatment of the substance with sulphuretted hydrogen, etc., should be conducted in a good draught.

If the presence of **hydrocyanic acid** is suspected the following tests with the original substance should be made:—

1. Take a small portion and treat according to test 3, page 42.
2. Take a second portion and treat according to test 6, page 43.
3. Treat a third portion according to test 7, page 43.

If, however, mercuric or silver cyanide is present, detect presence of hydrocyanic acid according to Note, page 44.

EXAMINATION OF ACIDS IN SOLUTION.

To neutral solution, prepared as directed on the preceding page, add *Calcium Chloride* solution, shake well, and allow to stand for twenty minutes; filter.

<table>
<tr>
<td rowspan="4">Precipitate = Calcium Oxalate or Calcium tartrate or both.
Also it may consist of Calcium sulphate, phosphate, fluoride, etc., if any of these inorganic acids are present.
Test precipitate, by heating a little of it with strong sulphuric acid in a test tube. If CO and CO_2 are evolved without blackening, Oxalic acid is present. If CO, CO_2, and SO_2 are evolved with blackening, Tartaric <i>Acid</i> is present, and perhaps <i>Oxalic</i> as well.
If <i>no</i> organic acid is present, neglect precipitate.
If an organic acid <i>is</i> present examine according to table given on page 28.</td>
<td colspan="4">Filtrate.
To filtrate, add more Calcium Chloride, and boil for some time. Filter at once and test filtrate, by re-boiling.</td>
</tr>
<tr>
<td rowspan="3">Precipitate = Calcium Citrate, and perhaps a little Calcium Tartrate. Examine according to the table given on page 28.</td>
<td colspan="3">Filtrate.
To filtrate, which must be <i>neutral</i> and <i>cold</i>, add Ferric Chloride solution. Filter.</td>
</tr>
<tr>
<td rowspan="2"><i>Buff-coloured</i> precipitate = Basic ferric benzoate. Wash well, and pour warm ammonium hydrate over it.
Collect the liquid that passes through the filter paper, warm it, and again pour over the residue on the filter paper. Evaporate the clear liquid (which consists of <i>ammonium benzoate</i>) almost to dryness. Cool, and add a few drops of strong hydrochloric acid till acid, when crystals of Benzoic Acid will separate out.
Confirm presence of <i>Benzoic Acid</i> in the following ways:—
1. Filter off crystals of Benzoic Acid, wash with cold water, place in a test tube, add strong sulphuric acid and ethyl alcohol. Heat. Smell of <i>Benzoic ether.</i>
2. Heat original substance with excess of soda lime in a dry test tube. <i>See</i> test 1, p. 30.</td>
<td colspan="2">Filtrate.
<i>Red</i> colour = Formic or Acetic; <i>Violet</i> colour = Salicylic or Carbolic (Phenol). In the presence of an <i>Acetate</i> or <i>Formate</i>, the <i>violet</i> colour is not very distinct; to a small <i>portion</i> of the solution add a drop or two of very dilute <i>hydrochloric acid</i>, when the <i>red</i> colour will disappear and the <i>violet</i> show up more plainly. The <i>violet</i> colour may be due to the presence of <i>Salicylic Acid</i>, or of <i>Phenol</i>. Add acetic acid to a portion of the <i>violet</i> liquid; if the colour disappears, <i>Phenol</i> is present; if the <i>violet</i> colour remains, <i>Salicylic Acid</i> is present and perhaps <i>Phenol</i> as well. If it is suspected that <i>both</i> are present, treat according to table on page 41. If Salicylic Acid alone is present, confirm in the original mixture in the following ways:—1. Test 2, page 37, 2. Test 6, page 38. If Phenol alone is present, shake up some of original neutral substance with Ether, remove ethereal liquid by means of a pipette, evaporate off the ether, and with the remaining <i>Phenol</i> perform the following confirmatory tests:—1. Test 2, page 39, 2. Test 4, page 39, 3. Test 7, page 40.
Having tested for <i>Phenol</i> and <i>Salicylic Acid</i>, the remaining <i>red</i> or <i>violet</i> liquid is placed in a boiling tube, and boiled for some time, when if an <i>acetate</i> or <i>formate</i> is present, a <i>reddish-brown</i> precipitate of basic ferric <i>acetate</i> or <i>formate</i> will be thrown down. Filter.</td>
</tr>
<tr>
<td>Precipitate.—Wash well and dissolve in dilute sulphuric acid. Place in a boiling tube and distil. Distillate = Acetic or Formic Acid or <i>both.</i> Examine according to table on page 36.</td>
<td>Filtrate (neglect).</td>
</tr>
</table>

CHAPTER VIII

PREPARATION OF SOME REAGENTS USED IN ORGANIC ANALYSIS

ALKALINE HYPOBROMITE SOLUTION.

This should be prepared only just before it is required for use. A stock bottle of caustic soda, however, may be made up, and the bromine added to a portion of it as needed. Weigh out 200 grams of caustic soda, and dissolve this in 500cc. of water.

When hypobromite solution is required, take 10cc. of the caustic soda solution, add *one* cc. of *bromine* and mix well. Larger quantities of the hypobromite may be prepared, using the same proportions.

BROMINE WATER.

This is prepared by adding bromine gradually to water in a bottle, and shaking until no more bromine is dissolved. That is, until a saturated solution is obtained.

CALCIUM CHLORIDE SOLUTION.

This is prepared by dissolving 200 grams of the pure crystallized salt in a litre of distilled water. The solution thus obtained should be neutral to litmus.

CHLORINE WATER.

Chlorine gas, prepared by the action of hydrochloric acid upon manganese dioxide, is passed into water, until the liquid is saturated, and has a distinct greenish-yellow colour. If the water is made cold by placing a few pieces of ice in it, the solution of chlorine obtained is much stronger. Chlorine water should be stored in a black, well-stoppered bottle, but even then, after a time it undergoes decomposition.

COPPER ACETATE SOLUTION.

A solution of this salt is prepared when required by dissolving a crystal or two in a small quantity of water.

COPPER SULPHATE SOLUTION.

Dissolve 25 grams of the pure crystallized salt in 500cc. of water.

FEHLING'S SOLUTION.

Weigh out 17·32 grams of pure re-crystallized copper sulphate and dissolve in 250cc. of distilled water. If the solution is not perfectly clear, add a few drops of sulphuric acid.

Then take 87·5 grams of Rochelle salt (potassium sodium tartrate), and 25 grams of caustic soda, and dissolve in water. Make this solution up to 250cc. by the addition of more water.

For **quantitative** work, these solutions are kept in separate bottles, and *equal* quantities of each of them are mixed together immediately before use.

For **qualitative** work, however, the solutions may be mixed together as soon as they have been prepared and stored, in *one* bottle. The solution thus prepared gradually undergoes chemical change.

FERRIC CHLORIDE SOLUTION.

Dissolve 25 grams of the ordinary crystalline salt in 500cc. of water. Make *exactly neutral* by adding ammonium hydrate till a precipitate just begins to form.

SOLUTION OF IODINE IN POTASSIUM IODIDE.

Five grams of iodine and 10 grams of potassium iodide are shaken up with a small quantity of water. When all the iodine has been dissolved the solution is made up to 500cc.

LIME WATER.

Freshly-slaked lime is shaken up with distilled water in a Winchester or other large stoppered bottle. It is then allowed to stand, and the clear liquid syphoned off, and stored in accurately-stoppered bottles.

FERROUS SULPHATE SOLUTION.

This is always prepared just as it is required. Shake up some crystals with a little *cold* water, and then pour off the liquid. This will get rid of any ferric sulphate which may have been formed on the surface of the crystals. Now add more *cold* water, and shake until a saturated solution is obtained.

SOLUTION OF MOLYBDIC ACID IN SULPHURIC ACID.

This solution should only be prepared when required, as the more recently it has been prepared, the better it acts. About the correct proportions to use are, a half-gram of sodium molybdate or molybdic acid, to 100cc. of strong sulphuric acid. For ordinary purposes it is quite sufficient to guess the quantities of each.

PHENOL PHTHALEIN SOLUTION.

Dissolve ·1 gram of the solid substance in 100cc. of dilute alcohol (1 of alcohol to 1 of water).

SOLUTION OF RESORCIN IN SULPHURIC ACID.

This solution is made by dissolving 2 grams of resorcin in 100cc. of strong sulphuric acid.

ROSANILINE SOLUTION—SCHIFF'S REAGENT FOR ALDEHYDES.

Shake up a crystal or two of rosaniline hydrochloride (fuchsine) with water, until a reddish-violet colour is obtained. To the clear solution add sulphurous acid, drop by drop, till the solution becomes just colourless.

SODIUM NITROPRUSSIATE SOLUTION.

This solution is prepared only when required. Shake up a crystal or two of the solid substance with a little water. With *alkaline* sulphide solutions this solution produces a violet coloration.

Sodium Nitroprussiate crystals ($Na_4Fe_2(CN)_{10}(NO)_2.4H_2O$) may be prepared in the following way:—

Dissolve 20 grams of potassium ferricyanide in 250cc. of boiling water. Add 50 grams of glacial acetic acid, and into this solution, whilst still hot, pour a *cold* solution made by dissolving 10 grams of mercuric chloride and 5 grams of sodium nitrite, in water. This solution is kept at a temperature of 60° C. for several hours, until a small quantity of it no longer gives a blue coloration when tested with ferrous sulphate. The mixture is then evaporated down till it forms a thick paste on cooling. This paste is squeezed in a piece of linen, to allow the potassium acetate that has been formed to drain off. The residual substance is removed from the linen, dissolved in boiling water, and then allowed to cool. Crystals of mercuric cyanide now separate out, and may be removed by filtration. The red filtrate is concentrated and allowed to cool, when crystals of sodium nitroprussiate are formed. These may be further purified by re-crystallization from water.

Reaction:—

$$K_6Fe_2(CN)_{12} + 2CH_3{\cdot}COOH + 4NaNO_2 + HgCl_2 =$$

$$\underset{\text{Sodium Nitroprussiate.}}{Na_4Fe_2(CN)_{10}(NO)_2} + Hg(CN)_2 + 2KCl +$$

$$2CH_3{\cdot}COOK + KNO_2 + KNO_3 + H_2O.$$

STARCH SOLUTION.

One gram of starch is mixed into a paste with a little cold water. This is poured into a large beaker, or dish, containing about 100cc. of boiling water, and the boiling continued for two or three minutes. When the liquid has stood for some time, and has settled, the clear liquid is decanted off.

Since starch solution is much more sensitive when freshly prepared, than after it has stood for some time, it is advisable not to make up a large quantity at a time.

MILLON'S REAGENT.

Dissolve a grain of mercury in two grains of nitric acid in the cold, and then add twice the bulk of water to the solution.

EXAMINATION QUESTIONS IN PRACTICAL ORGANIC CHEMISTRY.

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First Stage.

1892.

1. A bottle is supposed to contain one of the following gases:—marsh gas, carbon monoxide, or cyanogen. How could you ascertain which of these gases was present?

2. Give the chemical equations of the reactions employed in testing for formic acid, acetic acid, and salicylic acid.

3. A sample of cream of tartar is suspected to be mixed with oxalic acid. How could you ascertain if such were the case?

1893.

1. Give exact instructions for the preparation of specimens of iodoform, ethyl acetate, and ethylene (ethene) dibromide.

2. Sketch the apparatus required in the production of ether (ethyl oxide) by the continuous process, and state the precautions to be observed.

3. Describe characters and tests (with equations) by which you can distinguish acetamide from ammonium acetate, acetic acid from formic acid, potassium ferrocyanide from ferricyanide.

1894.

1. Sketch the apparatus and name the materials required for the preparation in the laboratory of the following compounds:—Absolute alcohol from rectified spirit, hydrocyanic acid (solution), ethyl oxide.

2. By what reactions could you demonstrate the presence of nitrogen in urea, glycocoll (glycine), and cyanide of potassium?

3. Give exact instructions for the preparation of specimens of any two of the following compounds:—Dextrose from starch, urea from ferrocyanide of potassium, nitro-glycerine from glycerine, succinic acid from ethylene.

1895.

1. Give exact instructions for the preparation of calcium ethyl sulphate, and the method of testing for its impurities.

2. Describe a method for obtaining pure formic acid.

3. A given salt may be an acetate, a formate, or an oxalate; describe and explain the tests by which you would fully identify each acid radicle.

1896.

1. Describe three tests for prussic acid, and explain them.

2. Draw a diagram of the apparatus required in the preparation of ethylene dibromide, and state the method of procedure.

3. Distinguish the sugars according to their action on Fehling's solution (alkaline cupric tartrate).

What is the action of a dilute acid upon cane sugar?

1897.

1. Describe the materials required and all the operations involved in making acetic anhydride.

2. Some lead formate is required; describe the method you would employ for the preparation of the formic acid from which you would produce the salt.

3. An aqueous solution contains either aldehyde, ethyl alcohol, or acetone; how would you distinguish the compound present?

1898.

1. Describe exactly how you would prepare acetic aldehyde. Make a sketch of the apparatus required.

2. You are required to prepare a specimen of pure acetic acid from vinegar. Explain precisely how you would proceed.

3. How would you demonstrate the production of glucose from cane sugar and starch respectively?

1899.

1. Describe the materials required and all the operations involved in making acetyl chloride.

2. How would you proceed to make oxalic acid:—

   (*a*) from common sugar, (*b*) from oxamide, (*c*) from formic acid?

3. What tests can you apply to distinguish (*a*) aldehyde from acetone, (*b*) turpentine oil from paraffin?

1900.

1. By what tests would you distinguish between an amide and an amine?

2. How may the nitrogen and the iron be detected in potassium ferrocyanide?

3. Describe the preparation, properties and decomposition by heat of mercuric cyanide.

4. By what methods could you recognize methyl alcohol in a mixture of ethyl and methyl alcohols?

5. Describe the appearance in the pure state of the following compounds:—Iodoform, ethyl iodide, acetic acid, acetyl chloride, acetamide, and cyanuric acid.

1901.

1. A solution which smells of ammonia is to be tested for methylamine, how would you proceed?

2. How can you recognise the chlorine in chloroform, the nitrogen in acetamide, the iron in prussian blue?

3. How would you detect formic acid in acetic acid?

4. Describe the appearance of the following compounds and state whether each is soluble in water or in alcohol:—Palmitic acid, succinic acid, nitro-glycerin, iodoform.

5. Describe the action, if any, of strong nitric acid on the following substances:—alcohol, urea, acetic acid, oxalic acid.

1902.

1. Give a sketch of the apparatus you would use in order to prepare acetaldehyde, and explain the process usually adopted for obtaining this aldehyde in a pure state.

2. What tests would you apply in order to show the presence of chlorine and nitrogen in an organic substance containing these elements?

3. Describe the processes you have adopted and the products obtained in the preparation of any two organic acids.

You are requested to give your own experience and not any description derived from books.

4. Describe the action of nitric acid on ethyl alcohol under various conditions.

5. By what tests can you distinguish methyl alcohol from ethyl alcohol, and how would you test for the former in a specimen of alcohol?

1903.

1. Describe and explain with a diagram some efficient form of apparatus for fractional distillation.

2. Explain fully, with equations, the Prussian blue test for nitrogen in organic compounds.

3. Describe the processes adopted and the products obtained in the preparation of an amine and an amide.

You are requested to give your own experience, and not any description derived from books.

4. Describe and explain three tests for the recognition of acetaldehyde.

5. How would you proceed to make gun-cotton from cotton-wool?

Second Stage.

1891.

1. You are required to ascertain whether a certain liquid is pure benzene or a mixture of benzene and toluene. What methods would you employ to determine this point?

2. Describe the methods you would employ in preparing formic acid, absolute alcohol, and ethyl iodide.

3. By what experiments would you prove the presence of oxygen in alcohol, of chlorine in chloroform, and of nitrogen in aniline? By what test is aniline commonly recognized?

1892.

1. Give the chemical equations representing the reactions employed in testing for prussic acid, urea, citric acid, salicylic acid, and tartaric acid.

2. Describe tests by which you may recognize cane sugar, glucose, and dextrin.

3. How could you distinguish acetic acid from acetone, glycerine from glycol, carbonyl chloride from carbon tetrachloride?

1893.

1. By what processes and distinctive tests would you recognize the presence of nitrogen, iodine, and sulphur in an organic substance?

2. Describe the operations you would perform upon benzene in order to produce from it specimens of nitrobenzene and aniline.

3. You are required to prepare para-phthalic (terephthalic) acid from para-xylene. What materials and apparatus would you require, and how would you proceed?

1894.

1. Describe with a sketch, the usual method of determining melting points, and state the melting point of any substance you have yourself examined.

2. How would you proceed to obtain pure oxalic acid and pure tartaric acid from a mixture of the two containing no other substances?

3. You are required to prepare specimens of picric acid, diazobenzene chloride, and benzoic acid. Describe the apparatus and materials required, and the method of procedure in each case.

1895.

1. Describe the operation of determining the amount of nitrogen in an organic compound by the process which is based upon the collection and measurement of the nitrogen in the form of gas.

2. To what uses are the following reagents applied in the study of organic compounds, and how are they used?

   (*a*) acetyl chloride, (*b*) phenyl hydrazine, (*c*) dilute nitric acid.

3. Give equations expressing the interaction between

   (*a*) Hydrocyanic acid and silver nitrate solution;
   (*b*) Potassium cyanide and silver nitrate solution;
   (*c*) Oxalic acid and a permanganate mixed with sulphuric acid;
   (*d*) Urea mixed with hypobromite solution.

1896.

1. From a sample of crude naphthalene how would you prepare the hydrocarbon in a pure state?

2. Give instructions for the production of pure picric acid from phenol; and describe the properties of any two picrates.

3. To what uses are the following reagents applied in the study of organic compounds, and how are they used? (*a*) acetic anhydride, (*b*) aluminium chloride, (*c*) phosphoric chloride.

1897.

1. Describe, with sufficient detail, the preparation of picric acid from phenol, and the tests which you could apply to it to ascertain its purity.
2. How would you apply the chloroform test for a primary amine? Explain the interaction.
3. Describe and explain the biuret test for urea.

1898.

1. Explain, with the aid of equations, the Prussian blue test for a cyanide.
2. What tests would you employ in order to distinguish between benzoic acid and salicylic acid? Explain the action of these tests.
3. Describe precisely how you would obtain a pure specimen of benzaldehyde from commerical oil of bitter almonds.

1899.

1. Describe from your own experience the preparation of any one derivative of:—(*a*) phenol, or (*b*) naphthalene.
2. How are the following tests applied? (*a*) the Prussian blue test for cyanide; (*b*) the distinction of methyl cyanide from methyl isocyanide.
3. Give complete instructions for making ethyl iodide.

1900.

1. Describe your own experience in the preparation of any one of the following substances:—(*a*) ethyl oxalate, (*b*) acetyl chloride or acetic anhydride, (*c*) quinone, (*d*) aniline.

   Give a list of any other compounds of which you have made specimens.
2. By what simple tests would you distinguish between ethylamine and ammonia?
3. By what tests and characters would you distinguish benzaldehyde from nitrobenzene?

1901.

1. Describe your own experience in the preparation of *one* of the following compounds.

(*a*) Ethyl acetic.
(*b*) Aniline.
(*c*) Acetamide.
(*d*) Hydrocyanic acid.

Give a list of any other compounds of which you have made specimens.

2. Describe exactly how you would proceed in order to diazotise aniline.

3. How would you detect the chlorine in chlorobenzene, the sulphur in thiophene, the nitrogen in pyridine?

4. Nitrobenzene, benzaldehyde, and benzonitril:—by what characters and tests would you distinguish these three substances from one another?

5. Describe tests for the recognition of any two natural alkaloids.

1902.

1. Describe exactly the process you would employ in order to prepare benzene-sulphonic acid. What are the chief properties of this substance.

2. By what experiments would you demonstrate the difference in stability of the chlórine atom in parachlorotoluene and benzyl chloride?

3. Explain in detail the method you would adopt in order to make a specimen of acetic anhydride. Sketch the apparatus to be employed.

4. Describe the phenomena observed when bromine is added to (*a*) benzene, (*b*) phenol, (*c*) allyl-alcohol, (*d*) turpentine or camphor, and briefly explain them.

1903.

1. What visible effect is produced by adding solution of ferric chloride to solutions of the following substances?—(*a*) hydroquinone (quinol), (*b*) morphine, (*c*) catechol, (*d*) phenol.

2. Describe the operation of determining the total nitrogen in a compound such as dinitrobenzene.

3. Describe the action of concentrated sulphuric acid on (*a*) pure benzene, (*b*) potassium ferrocyanide. Write equations in each case.

4. What precautions would you take in preparing and separating the mononitro derivatives of phenol?

5. By what characters and tests would you detect the presence of invert sugar in common cane sugar.

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