AN EXPERIMENTAL COURSE
OF
PHYSICAL CHEMISTRY

PART II
DYNAMICAL EXPERIMENTS

BY
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Volume I.—Statical Experiments.
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PART II

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PREFACE

The remarks made in connection with Volume I. of this work apply equally to the present volume. The portions of the subject, dealt with here, are somewhat more difficult than those considered in the previous volume, and demand a moderate knowledge of physics. Hence, owing to the large number of chemical students who are insufficiently grounded in physics, it has been deemed well to describe, in detail, methods of measuring the electrical quantities, resistance, capacity, electromotive force, and dielectric constant in the chapters where the physico-chemical relationships of those properties are discussed. The subject of radioactivity is often claimed as a purely physical one, but when the far-reaching importance of the subject upon the fundamental principles of chemistry is considered, this position can hardly be maintained, and no apology should be necessary for introducing a chapter on radioactivity in this volume.

I wish, in conclusion, to express my indebtedness to Ostwald-Luther's *Physiko-chemische Messungen*, and to my colleague, Mr. Holland Crompton, Head of the Chemistry Department of Bedford College, who, both by his advice and criticism, and by reading the manuscript, has rendered me much valuable assistance.

J. F. SPENCER.

PREFACE TO THE SECOND EDITION

As in the first volume, the arrangement and method of treatment adopted in the first edition has been retained. The text has been carefully revised, whereby errors have been corrected and ambiguous passages made clearer. An addition has been made to the chapter on Velocity of Chemical Reactions. A new chapter, on Decomposition Voltage, Discharge Potential and Overvoltage, has been added, and carefully chosen experiments on these subjects described. It is hoped that these additions will increase the utility of the work both to students and teachers. The author takes this opportunity of expressing his thanks to those of his colleagues who have pointed out errors and ambiguities in the previous edition and made suggestions for improvements. It is his hope that this kindly assistance may be continued in the future.

J. F. SPENCER.

BEDFORD COLLEGE,
(UNIVERSITY OF LONDON),
20th April, 1921.

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AN EXPERIMENTAL COURSE OF PHYSICAL CHEMISTRY

PART II

CHAPTER I

MASS ACTION AND VELOCITY OF CHEMICAL CHANGE

(SEE ALSO APPENDIX A)

1. **Mass Action.** Guldberg and Waage (1867) have shown that the velocity of a chemical reaction, at any given time, is proportional to the product of the concentrations of the reacting substances at that moment. Thus if two substances A and B are reacting with the formation of two other substances C and D, and if the concentrations of A and B at the commencement of the reaction are expressed by a and b respectively, the velocity of the reaction at the moment it begins will be expressed by

$$\frac{dx}{dt}=kab,$$

where k is a constant.

After the reaction has proceeded for a time t, and a quantity x of A and B has been changed into C and D. the velocity will be given by

$$\frac{dx}{dt}=k(a-x)(b-x),$$

where k has the same value as in the previous expression. Whence it is obvious that the velocity decreases as the reaction proceeds.

Suppose now the reaction considered is a reversible one, and that

$$A+B \rightleftarrows C+D.$$

Then at the start the concentration of C and D is zero, and consequently the velocity of the reverse reaction is also zero, but after a time t a quantity of A and B represented by x has been changed into C and D. Hence the concentration of these two substances may also be represented by x, and the velocity of the reverse reaction by

$$\frac{dx}{dt}=k'x\,.\,x.$$

At equilibrium the velocity of the reaction in both directions will be the same: if this occurs when a quantity ϕ of A and B have been converted into C and D the velocities of the reactions in the two directions will be given by

$$\frac{dx}{dt}=k(a-\phi)(b-\phi) \text{ and } \frac{dx}{dt}=k'\phi^2;$$

or, irrespective of the original concentrations, if α, β, γ and δ represent the concentrations of A, B, C and D respectively at equilibrium,

$$\frac{dx}{dt}=k\alpha\beta \text{ and } \frac{dx}{dt}=k'\gamma\delta.$$

Since the velocities are the same

$$k\alpha\beta=k'\gamma\delta;$$

or

$$K=\frac{\gamma\delta}{\alpha\beta},$$

where K is a constant which is characteristic of the reaction.

All reversible reactions may be considered in the same way, and all such reactions have a definite constant which depends only on the nature of the reacting substances, and is uninfluenced by their amounts.

Should one or more of the substances in any reaction be a solid, then the active mass, *i.e.* the concentration present in the homogeneous phase in which the reaction is taking place, of this substance is constant. This will be clearer if an actual case is considered, such as the reaction between barium chloride and sodium sulphate.

$$Na_2SO_4 + BaCl_2 \rightleftarrows 2NaCl + BaSO_4.$$

In this case barium sulphate is precipitated, and consequently the concentration of barium sulphate in the solution must be constant, *viz.* the amount determined by its solubility.

If then the concentrations of the four substances be α, β, γ and δ respectively,

$$K = \frac{\alpha\beta}{\gamma^2}.$$

The experimental determination of the reaction constants for reversible reactions is not suitable for this course, for in many cases the equilibria are only established very slowly. A period extending over months often being necessary, and in some cases, according to van't Hoff, a geological period would be required for the establishment of an equilibrium.

2. Velocity of Chemical Change. It has already been shown that the velocity of a reaction at any moment depends upon the product of the active masses of the reacting substances at that moment.

Hence if a reaction is taking place between a number of substances of active masses $a, b, c \ldots$, then **the velocity** of the reaction at that moment is given by

$$\frac{dx}{dt} = kabc\ldots.$$

Consider a reaction in which one substance only is undergoing change, *i.e.* a mono-molecular change. If the original concentration of this substance be indicated by a, then

$$\frac{dx}{dt} = ka$$

represents the initial velocity of the change, where k is the velocity constant. If at a time t, x represents the amount of a changed, then $(a-x)$ gives the active mass at the time t and the velocity is given by

$$\frac{dx}{dt} = k(a-x);$$

on integrating this expression

$$-\log_e(a-x) = kt + \text{constant}. \quad \ldots\ldots\ldots\ldots\ldots(1)$$

At the commencement of the reaction $t=0$, and $x=0$, and on substituting these values in (1)

$$-\log_e a = \text{constant}.$$

Hence
$$\log_e \frac{a}{a-x} = kt.$$

It is generally very difficult to determine exactly the moment at which a reaction commences, so that it is preferable, in determining the velocity constant, to obtain measurements at two different times t_1 and t_2 when quantities x_1 and x_2 have been transformed; the expression then becomes

$$\log_e \frac{a-x_1}{a-x_2} = k(t_2-t_1).$$

Should two substances be participating in a reaction, the expression representing the velocity of reaction takes a somewhat different form. As the simplest case, it may be assumed that the reacting substances have the same initial concentration a, and that at a time t a quantity x of both has been transformed, then the velocity will be given by

$$\frac{dx}{dt}=k(a-x)(a-x),$$

which on integrating becomes

$$\frac{1}{a-x}=kt+\text{constant}. \quad \ldots\ldots\ldots\ldots\ldots(2)$$

As in the last case $t=0$, and $x=0$ at the commencement

hence $$\frac{1}{a}=\text{constant};$$

and substituting this value in (2)

$$kt=\frac{x}{a(a-x)}.$$

Should the substances reacting have different initial concentrations a and b, then at a time t, when x of both has been transformed, the velocity is expressed by

$$\frac{dx}{dt}=k(a-x)(b-x),$$

which on integrating gives

$$\frac{1}{a-b}\log_e\cdot\frac{a-x}{b-x}=kt+\text{constant}, \quad \ldots\ldots\ldots\ldots(3)$$

and as $t=0$, $x=0$ at the beginning of the reaction

$$\frac{1}{a-b}\log_e\frac{a}{b}=\text{constant}.$$

Substituting the value of the constant in (3)

$$kt=\frac{1}{a-b}\cdot\log_e\frac{b}{a}\cdot\frac{(a-x)}{(b-x)}.$$

Expressions similar to the above may be deduced for reactions in which more than two substances are taking part, but such reactions are often very complicated, and are not suitable for the present purpose. It is found, however,—that the larger number of reactions, no matter how complicated they may seem from their chemical equations, are nevertheless chiefly mono- or bi-molecular. This is explained on the assumption that the reaction proceeds in a series of stages which are of the simpler orders. In investigating the velocity of chemical actions it is obvious that they must be stopped instantaneously at a definite time, or the methods of investigation must be such as allow of a definite conclusive observation, which will indicate the extent of the change, being made at a definite time. Where possible, therefore, physical changes, which will indicate the state of the reaction, should be observed, and of these, optical activity and volume may be noted as among the most suitable physical properties for such observations. If chemical methods have to be resorted to, then volumetric determinations are always to be recommended, since the rapidity with which they can be effected amounts almost to an instantaneous stopping of the reaction. When gravimetric methods have to be employed, and indeed also in volumetric operations, care must be taken that only those reagents are used which do not influence the state of the reaction in any way other than completely stopping it.

The velocity of reaction is best considered under the heading of the types of reactions, and will be treated here under:

(1) Mono-molecular reactions,

(2) Bi-molecular reactions.

1. Mono-molecular Reactions

Mono-molecular reactions, as has already been explained, are those in which one molecule only is reacting, but it is customary to consider the saponification of esters by means of acids under the heading of mono-molecular reactions. These, as will be seen from the equation,

$$CH_3\cdot COOC_2H_5+H_2O \rightleftarrows CH_3\cdot COOH+C_2H_5OH,$$

are strictly bi-molecular reactions, and consequently should only give constant values for k when the expression

$$k=\frac{1}{t}\cdot\frac{1}{a-b}\cdot\log_e\frac{b}{a}\cdot\frac{(a-x)}{(b-x)} \;\ldots\ldots\ldots\ldots\ldots(4)$$

is employed. But generally in such reactions the active mass of the water a is so large that $(a-x)\simeq a$. If then $(a-x)=a$ is substituted in equation (4),

$$(a-b)k=\frac{1}{t}\log_e\cdot\frac{b}{b-x}.$$

In any given reaction $(a-b)$, the difference of the original concentrations of the reacting substances, is constant, hence the expression becomes

$$\mathsf{K}=\frac{1}{t}\log_e\frac{b}{b-x},$$

which will be seen to be the expression for mono-molecular reactions, explaining why such reactions may be treated as mono-molecular.

The saponification of esters takes place rather slowly in pure water, but much more quickly in the presence of acids, the velocity being proportional to the concentration of the hydrogen ions. Hence it follows, since the relative strength of acids is also proportional to the concentration of the hydrogen ions, that a determination of the velocity constant for the saponification of an ester by various acids will furnish the relative strengths, *i.e.* avidities, of the acids employed.

EXPERIMENTS

1. *Determine the Velocity Constant for the Decomposition of Hydrogen Peroxide.* Hydrogen peroxide decomposes spontaneously into oxygen and water, but the change occurs too slowly for the purpose of the present experiment. Its velocity may, however, be increased by means of a catalyst, such as Bredig's colloidal platinum.

Prepare a solution of hydrogen peroxide by dissolving 100 c.c. of "20 volume" hydrogen peroxide in a litre of water. Place about 250 c.c. of the solution in a flask, stand it in a thermostat and allow it to take on the temperature of the bath. Remove 5 c.c. of the solution by means of a pipette, add an excess of dilute sulphuric acid, and titrate with $\frac{N}{10}$ potassium permanganate solution. Then add 5 c.c. of a solution of colloidal platinum to the hydrogen peroxide solution. The colloidal platinum is prepared in the following manner: Two short platinum wires, 2 mm. diameter, are welded to two stout copper wires which are inserted into glass tubes so as to leave about 1 cm. of the platinum protruding. The glass tubes serve as insulating handles. The copper wires are connected to the lighting circuit through a resistance, which cuts the current down to about 5 amperes. The platinum ends are then brought together in a dish of conductivity water (see Chapter III.), cooled by ice. As soon as the wires touch they are drawn apart so that an arc 1–2 mm. long is produced. The arc will not persist for more than a few seconds, and must be repeatedly remade, by bringing the wires into contact as at first, for about ten minutes. The solution is then filtered, to free it from platinum dust, and constitutes a solution of colloidal platinum. Note the time at which the platinum solution is added to the hydrogen peroxide, and take this as the commencement of the reaction t_0.

The initial concentration of the hydrogen peroxide is obtained by calculation from the original titration value. When two minutes have elapsed, remove 5 c.c. of the solution and titrate it as quickly as possible, taking as the time t_1, the mean of the time between the beginning and the end of the titration. Repeat the observations every five minutes and record the titration values n_2, n_3, n_4, n_5, ..., etc., and the times t_2, t_3, t_4, t_5, ..., etc. Since the titration values are proportional to the concentration of the hydrogen peroxide, it is unnecessary to calculate the concentrations. The titration values may be inserted in the equation, in place of the concentrations, and k calculated.

Thus since $$k = \frac{1}{t_2 - t_1} \log_e \frac{a - x_1}{a - x_2},$$

$$k = \frac{1}{t_2 - t_1} \log_e \frac{n_1}{n_2} = \frac{1}{t_3 - t_2} \log_e \frac{n_2}{n_3} = \text{etc.},$$

in which the n values are the number of c.c. of permanganate used in the titrations, and the t values the number of minutes which have elapsed from the beginning of the reaction. Calculate the value of k for each determination, and note that it is the same in each case. In the calculation it is not necessary to convert $\log_e$ to $\log_{10}$, and since the experiment is only concerned with the constancy of k ordinary logarithms may be inserted in the expression. The real value of the constant may be obtained from the mean value of the determinations by multiplying it by 2·302.

2. *Determine the Relative Strengths of Sulphuric and Hydrochloric Acids.* This experiment consists in a determination of the rates at which the acids in question saponify methyl acetate. Before commencing the actual determination an approximately $\frac{N}{20}$ *solution* of baryta must be made up. This is best done in the following manner. Fit a four litre narrow-mouthed bottle B (Fig. 1), with a two-holed cork C. Into one hole insert a tube *t* connected to a soda lime tube *d*, and into the other hole a tube *b*, which reaches to the bottom of the bottle and is connected to a burette G. The burette is supported by a stand and clamps *f*, attached to the neck of the bottle as indicated in the diagram. Close the burette at the top by a soda lime tube *s*, to which a length of indiarubber tubing *i* is attached. Now grind up about 60 grams of barium hydrate, place it in a flask containing 500 c.c. of water and boil until the solution is saturated. Close the flask with a cork carrying a soda lime tube and allow to cool. When cold, filter 200 c.c. of the solution into the bottle B and add sufficient water to make 4 litres. The water used here must be freshly boiled distilled water which has been allowed

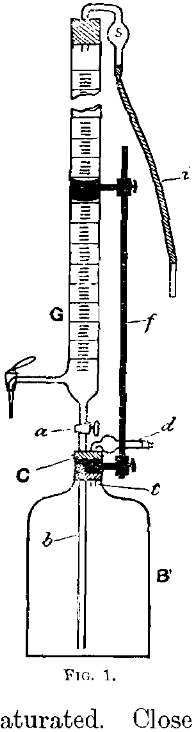

FIG. 1.

to cool in carbon-dioxide free air. Shake the solution and then place the burette and soda lime tubes in position. In this way a solution of baryta is obtained which is permanently out of contact with carbon-dioxide. The burette is filled by opening the tap (a) and drawing at the tube i.

The baryta solution must next be standardised by titration with an $\frac{N}{20}$ solution of oxalic acid, using phenolphthalein as indicator.

Prepare $\frac{N}{2}$ solutions of hydrochloric and sulphuric acids, and titrate 2 c.c. of each of these solutions with the baryta solution. This is for the purpose of obtaining an idea of the quantity of baryta solution to be used in the subsequent titrations. Now take two 8 oz. stoppered bottles, thoroughly clean and dry them, and label them HCl, and H_2SO_4 respectively; place 100 c.c. of $\frac{N}{2}$ hydrochloric acid into one, and 100 c.c. of $\frac{N}{2}$ sulphuric acid into the other, and stand the bottles in a thermostat at 25°. A bottle containing freshly distilled methyl acetate should also be placed in the thermostat. When the solutions have taken on the temperature of the bath add 5 c.c. of methyl acetate to the hydrochloric acid, shake well and immediately withdraw 2 c.c. of the mixture, run it into a Erlenmeyer flask containing 50 c.c. of carbon-dioxide free water. Note the time at which the solution is run into the water, and record it as t_0 the commencement of the reaction. Titrate the solution with baryta, running in nearly the whole of the required quantity at once, remembering that somewhat less, about 5 per cent., will be required than was necessary for 2 c.c. of the acid; record the titration as

n_0. After 10 minutes withdraw a further quantity of 2 c.c. of the acid mixture, and treat it in exactly the same way as the first quantity, noting both the time t_1, and the titration value n_1. Make further titrations at intervals of 10, 20, 30, 40, 60 and 120 minutes, and a final titration about 48 hours afterwards, noting the times t_2, t_3, t_4, ..., t_∞, and the titration values n_2, n_3, n_4, ..., n_∞, where t_∞ and n_∞ represent the final time and titration values.

After the second titration has been made with the hydrochloric acid, start the reaction with the sulphuric acid and carry on both experiments side by side, recording the results in the same way as for hydrochloric acid. Here, as in the last experiment, it is not necessary to calculate the quantity of ester saponified from the titration values, as would appear to be required by the expressions

$$k=\frac{1}{t}\log_e\frac{a}{(a-x)} \quad \text{and} \quad k=\frac{1}{t_2-t_1}\log_e\frac{(a-x_1)}{(a-x_2)},$$

for the initial concentration of the ester is proportional to $(n_\infty-n_0)$, and the concentration at time t is proportional to $(n_\infty-n_t)$ where t is the time counted in minutes from the beginning of the experiment. For the purpose of calculating the value of k the expression then becomes

$$k=\frac{1}{t}\log_e\frac{(n_\infty-n_0)}{(n_\infty-n_t)}.$$

The value of k may also be calculated from titration to titration, instead of always from the commencement of the reaction. If n_y and n_x are the titration values at times t_y and t_x respectively, then

$$k=\frac{1}{t_y-t_x}\cdot\log_e\frac{(n_\infty-n_x)}{(n_\infty-n_y)}.$$

Ordinary logarithms may be used in the calculation of the constant, and the absolute constant obtained from the mean value by multiplying it by 2·302.

Having obtained the constants for both acids, the relative strengths are at once visible, for

$$\text{Strength of HCl} : \text{Strength of } H_2SO_4 :: k_{HCl} : k_{H_2SO_4}.$$

The degree of dissociation of $\frac{N}{2}$ hydrochloric acid is 0·85, and that of $\frac{N}{2}$ sulphuric acid is 0·53, hence the concentrations of the hydrogen ions, and consequently the strengths of the $\frac{N}{2}$ acids are in this proportion.

3. *Determine the Velocity Constant of the Hydrolysis of Cane Sugar by Hydrochloric Acid and Sulphuric Acid.* The disaccharides, *e.g.* cane sugar, are hydrolysed by the action of dilute acids. This change, in some cases, can be followed by observing the change in the optical activity of the reaction mixture. Thus, if a solution of cane sugar is treated with hydrochloric acid it is converted into a mixture of glucose and fructose in equi-molecular quantities.

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6.$$

The three substances, glucose, fructose and cane sugar, rotate the plane of polarised light; cane sugar and glucose to the right, and fructose to the left. The mixture of glucose and fructose, *i.e.* invert sugar, is laevo-rotatory, since fructose is more strongly laevo-rotatory than glucose is dextro-rotatory. Hence, if such an hydrolysis be allowed to take place in the observation tube of a polarimeter, it is obvious that the course of the reaction, and consequently its velocity, may be followed by observing the change in the angle of rotation. If λ_0 is the angle of rotation of the reaction mixture at the moment of mixing, λ_∞ the angle of rotation when the reaction is complete, then $(\lambda_0 - \lambda_\infty)$ is proportional to the amount of cane sugar present at the commencement of the reaction, and if λ_t is the angle of rotation at time t, where t is the time in minutes from the commencement of the reaction, then $(\lambda_t - \lambda_\infty)$ is proportional to the amount of cane sugar present at the time t. Hence the velocity constant k may be obtained from the expression

$$k = \frac{1}{t} \log_e \frac{\lambda_0 - \lambda_\infty}{\lambda_t - \lambda_\infty},$$

or calculating the constant from reading to reading, and not from the commencement of the reaction,

$$k = \frac{1}{t_y - t_x} \log_e \frac{\lambda_x - \lambda_\infty}{\lambda_y - \lambda_\infty},$$

where λ_x and λ_y are the rotations at the times t_x and t_y respectively.

Prepare exactly normal solutions of hydrochloric acid and sulphuric acid, and also a solution of 20 grams of cane sugar (coffee crystals are best to use here), in 100 c.c. of water. Add a small piece of camphor to the solution as a preservative. Place about 50 c.c. of each of these solutions in a thermostat, then fit up a polarimeter as described in Chapter X., Part I., and determine the zero of the instrument. Connect a jacketed observation tube to a water supply at 25°, obtained by passing a slow stream of water through a leaden coil placed in a thermostat, and thence through the jacket of the observation tube. When the temperature of the tube is constant, mix equal volumes of cane sugar solution and hydrochloric acid solution, fill the observation tube as quickly as possible and read the angle of rotation, noting the time of the reading. This may be regarded as the commencement of the reaction, and the time as t_0 and the angular reading as λ_0. Make a second reading 5 minutes after the first, and further readings in 10, 20, 40, 60, and 120 minutes, and a final reading 48 hours later. It is unnecessary to keep the water flowing for the 48 hours' interval, for the observation tube may be kept at the required temperature by immersing it directly in the thermostat. Repeat the measurements with sulphuric acid, and calculate the value of k for both acids, using the formula given above.

It is not absolutely essential to have water circulating round the observation tube if the experiment is carried out in a room whose temperature is fairly constant.

4. *Determine the Velocity Constant of the Decomposition of Diazo-benzene Chloride.* Cain and Nicholl (*J.C.S.* 1902, 81, 1412) have shown that the decomposition of diazo-compounds, between 20° and 60°, is a mono-molecular one, and they have followed the reaction and determined the velocity constant of a large number of diazo-compounds by measuring the volume of nitrogen evolved. The reaction may be represented by

$$C_6H_5N:NCl+H_2O=C_6H_5.OH+N_2+HCl.$$

The quantity of diazo-benzene chloride decomposed is proportional to the total volume of nitrogen liberated. Hence if v_∞ is the volume of nitrogen liberated when the reaction is complete, and v_t the volume liberated in a time t, then

$$k=\frac{1}{t}\log_e\frac{v_\infty}{v_\infty-v_t}.$$

For this experiment the apparatus depicted in Fig. 2 is required. It consists of a stout glass tube T, 15 cms. long and 3 cms. diameter, fitted with a rubber stopper S which carries a rotatory stirrer R working in an air-tight mercury joint **M**. A capillary side-tube **C**, 1 mm. diameter, is attached to **T**.

The mercury joint is made in the following manner: A hole 5 mm. diameter is bored right through the stopper **S** (Fig. 3), and one 12 mm. diameter, concentric with the first, is bored half way through the stopper, as indicated in **A**. A piece of glass tube *g*, about 4 cms. long, passes through the smaller hole, so that 5 mm. project on the under side, and a second piece of tube *h*, 3 cms. long and 12 mm. external diameter, is forced down to the bottom of the half-bored hole, so that an annular cup is formed in the cork. The stem of the stirrer **B** is made of a glass rod, slightly smaller in diameter than *g*, to which a piece of tube, 1·5 cms. long and of the same diameter as *g*, is attached in an air-tight manner by means of a piece of rubber tubing *r*. A piece of tube *k*, of diameter intermediate to those of *g* and *h*, is attached to **B** by a rubber stopper. The two parts **A** and **B** are then put together, as indicated in **C**, the pulley **P** is attached, and the stirring rod bent as in the figure. Mercury is then poured into the annular cup, and thus seals the joint completely.

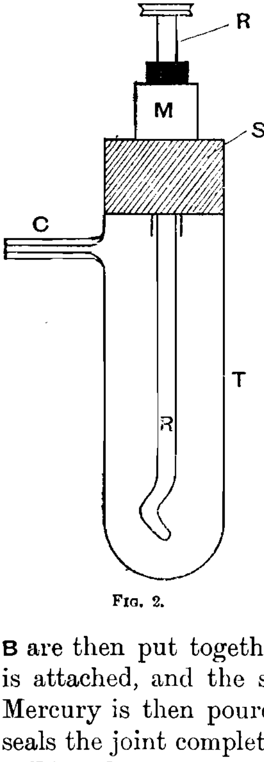

Fig. 2.

Diazo-benzene chloride must be freshly prepared for each experiment, and is best prepared in the following manner: 9·3 grams of redistilled aniline are dissolved in

30 c.c. of hydrochloric acid of sp. gr. 1·16, and the mixture cooled with ice. A solution containing 6·9 grams of sodium nitrite in 100 c.c. of water is slowly added to this, and the solution made up to 1400 c.c. Place 30 c.c. of the solution in the tube T, which has been supported in a thermostat at 25°. Insert the stirrer and set it in motion; after ten minutes have elapsed, connect the side tube to a Hempel gas-burette. Note the time when the connection is made, which serves as the commencement of the experiment t_0. Read the volume of gas evolved every thirty minutes, noting time, temperature, barometric pressure and volume. After about eight measurements have been made, place the reaction vessel in a beaker of hot water for about ten minutes, and then replace in the thermostat. After the normal temperature has been regained, read off the volume v_∞. Calculate the constant as indicated above.

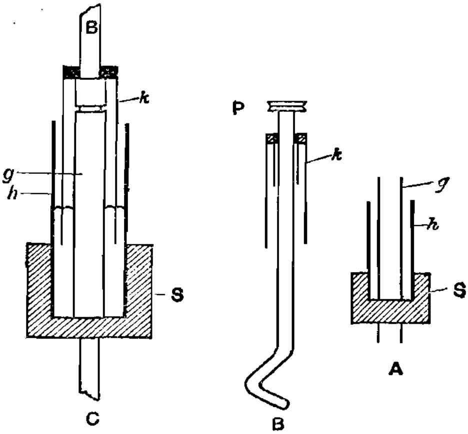

FIG. 3.

2. Bi-molecular Reactions

The saponification of esters by alkalies is one of the most easily followed bi-molecular reactions. The rate of this reaction, as is clear from the equation

$$CH_3.COOCH_3 + NaOH = CH_3.COONa + CH_3OH,$$

depends on the concentration of the hydroxyl ions, and consequently on the concentration of the alkali. Since the amount of alkali decreases as the reaction proceeds, it is obvious that the progress of the reaction may be followed by determining the concentration of the alkali from time to time. Hydrolysis by alkalies occurs much more rapidly than hydrolysis by acids, and consequently the observations are more difficult to make.

The expression representing the velocity constant of a bi-molecular reaction is

$$k = \frac{1}{t} \cdot \frac{1}{a-b} \log_e \frac{(a-x)}{(b-x)} \cdot \frac{b}{a},$$

where a and b represent the original concentrations of the reacting substances, and x is the quantity transformed in time t.

EXPERIMENT

Determine the Velocity Constant of the Saponification of Methyl Acetate by Caustic Soda. Make up solutions of $\frac{N}{60}$ methyl acetate, $\frac{N}{40}$ caustic soda, $\frac{N}{20}$ nitric acid and $\frac{N}{20}$ baryta. The caustic soda solution must be free from sodium carbonate. (See p. 67.) Place 100 c.c. of methyl acetate solution in a 250 c.c. stoppered bottle, and in a second bottle place 102 c.c. of the caustic soda solution. Place both bottles in a thermostat, and while they are reaching the temperature of the bath, measure accurately 10 c.c. of the standard nitric acid solution into a conical flask. When the temperature of the solutions has become constant pour the alkali into the ester, stopper the bottle and shake vigorously, noting the time at which the mixing took place t_0. The concentration of caustic soda is obtained by calculation from the volumes and concentrations of the solutions mixed, the exact amount of alkali added being determined by adding about 30 c.c. of water to the bottle which contained the alkali, and titrating the quantity left behind in the bottle, and subtracting the amount from the quantity originally taken. When the reaction has been proceeding for about 3 minutes, withdraw 10 c.c. and run it into the measured volume of standard nitric acid, which stops the reaction. Note the time at which the pipette has half delivered its contents as the time of stopping the reaction. Titrate the excess of nitric acid by means of the standard baryta solution. Make titrations of further quantities of 10 c.c. in 5, 10, 15, 30, 60 and 100 minutes, and a final titration in 24 hours. In this experiment it is unnecessary to calculate the actual concentrations of the alkali and the ester, since they are proportional to the titration values.

If n_0 is the number of c.c. of nitric acid required to neutralise the alkali at the commencement of the reaction, n_∞ at the end of the reaction, and n_t at a time t, the value of k may be calculated from

$$k=\frac{1}{n_\infty t}\cdot\frac{\log_e n_t+\log_e(n_0-n_\infty)}{\log_e n_0+\log_e(n_t-n_\infty)}.$$

The above expression is derived from the ordinary equation for bi-molecular reactions by substituting the titration values which are proportional to the various factors. n_∞ is proportional to the amount of alkali left after the reaction is complete, *i.e.* $(a-b)$, where a is the original concentration of the alkali, and b that of the ester, n_t is proportional to the concentration of the alkali at time t, *i.e.* $(a-x)$, (n_0-n_∞) to the initial concentration of the ester, *i.e.* b, n_0 to the initial concentration of the alkali, *i.e.* a, and (n_t-n_∞) to the concentration of the ester at time t, *i.e.* $(b-x)$.

This experiment, which depends on the concentration of the hydroxyl ions, may obviously be used to determine the relative strengths of bases, in the same way as described in an earlier experiment for acids (page 10).

Determination of Degree of Hydrolysis

Since the rate of saponification of esters depends on the concentration of either the hydrogen or hydroxyl ions, this process may be used to determine the degree to which salts of weak acids and strong bases, or weak bases and strong acids are hydrolysed. For a salt of a strong acid and a weak base is split up by water into the free undissociated base and the dissociated acid thus:

$$H_2O+CO(NH_2)_2HCl=CO(NH_2)_2+HCl+H_2O,$$

giving the strong hydrochloric acid which furnishes hydrogen ions. A salt of a weak acid and a strong base is hydrolysed by water giving the acid which is practically undissociated, and the dissociated base thus:

$$K_2CO_3+H_2O=2KOH+H_2CO_3,$$

the strong base, caustic potash, furnishing hydroxyl ions.

Consequently by using such salts to bring about the saponification of an ester, the amount of hydrolysis may be obtained by comparing the velocity constant with that obtained when the free acid or alkali are used to effect the saponification.

EXPERIMENTS

1. *Determine the Amount of Hydrolysis of Urea Hydrochloride in Water Solution.* Make up an $\frac{N}{2}$ solution of hydrochloric acid, and place 100 c.c. of it into each of two 250 c.c. stoppered bottles. To one add an equivalent quantity of urea, *i.e.* 0·56 gram, thus forming an $\frac{N}{2}$ solution of urea hydrochloride. Determine the velocity constant for both solutions in the way described on page 10. Calculate the value of k in both cases from the titration values. If k_1 is the value for hydrochloric acid, k_2 that for urea hydrochloride, and h the fraction of the urea hydrochloride hydrolysed, then

$$h=\frac{k_2}{k_1}.$$

The value of h is, of course, only for a half normal solution of the salt. Other concentrations may now be determined and the influence of dilution upon the amount of hydrolysis obtained.

The amount of hydrolysis of sodium carbonate and potassium phenate may be determined in a similar manner, by adopting the method used in obtaining the velocity constant of sodium hydrate. For full details of these experiments see Shields, *Zeit. f. Physik Chemie,* 12, 1893, 167.

Determination of the Order of a Reaction

Study of the velocity of chemical reactions has shown that generally only in the case of the simplest reactions the number of reacting molecules is that represented by the chemical equation. Thus for example the decomposition of phosphine by heat is generally written

$$4PH_3 = 4P + 6H_2.$$

This would indicate that the reaction is quadri-molecular, but experiment has shown that it is only mono-molecular, and must be represented by

$$PH_3 = P + 3H,$$

with subsequent formation of phosphorus and hydrogen molecules.

The order of reaction may be obtained from the type of equation required to give a constant value to the velocity constant. Thus, if the above reaction is quadri-molecular, then the constant would be obtained from the expression

$$\frac{dx}{dt} = k_4(a - ax)^4$$

or

$$k_4 = \frac{1}{t}\left(\frac{1}{(a - ax)^3} - \frac{1}{a^3}\right)$$

where a represents the original concentration of the phosphine and x the fraction which has decomposed at the time t. Kooij (*Zeit. f. Physik Chemie*, 12, 155, 1892) has shown that the value of k_4 is not in any sense constant, but if the values of a and x are inserted in the expression for a mono-molecular reaction, *i.e.*

$$k_1 = \frac{1}{t}\log_e \frac{a}{a - ax},$$

a constant value is obtained, which signifies that the reaction is mono-molecular.

Hence the order of a reaction may be determined by inserting the experimental data in the expressions for the various types of reaction and finding which equation gives a constant value to k.

A second method, due to van't Hoff, is based on the fact that the velocity of a reaction is proportional to the n^{th} power of the concentration of the reacting substances,

i.e.
$$-\frac{dx}{dt}=ka^n$$

where a is the initial concentration and n the number of reacting molecules. If two experiments be made with different initial concentrations a_1 and a_2, then

$$-\frac{dx_1}{dt}=ka_1{}^n;\quad -\frac{dx_2}{dt}=ka_2{}^n;$$

dividing these two expressions and taking logarithms we obtain the value of n,

$$n=\frac{\log\frac{dx_1}{dt}-\log\frac{dx_2}{dt}}{\log a_1-\log a_2}.$$

To use this method, two solutions or quantities of the reacting substance are made up of different concentrations a_1 and a_2, and the initial concentrations carefully determined. They are then allowed to undergo reaction for a given time t and the amount of change in each estimated. Let this be x_1 and x_2 respectively, then the values of $\log\frac{x_1}{t}$, $\log\frac{x_2}{t}$, $\log a_1$ and $\log a_2$ are inserted in the above equation, and n solved.

EXPERIMENTS

1. *Determine the Order of Reaction of the Decomposition of Hydrogen Peroxide.* The decomposition of hydrogen peroxide is generally expressed by the equation

$$2H_2O_2=H_2O+O_2,$$

but it has been shown that it is more correctly expressed by the equation

$$H_2O_2 = H_2O + O.$$

If the former representation is correct the reaction is bi-molecular, but if the latter method is the correct one then the reaction is a mono-molecular one.

Prepare two solutions of hydrogen peroxide, by adding 5 c.c. and 20 c.c. respectively of "20 volume" hydrogen peroxide to 100 c.c. of water. Determine the strength of the solutions in gram molecules per litre by titration with potassium permanganate. Carry out the determination of rate of the reaction as described on page 8. Make about 6–8 determinations in each case, and calculate the mean value $\frac{dx_1}{dt}$ and $\frac{dx_2}{dt}$ from the titration values. Then using the formula given above, calculate the value of n.

2. *Determine the Order of Reaction in the Saponification of an Ester by an Alkali.* Carry out the experiment as described on page 18, and from the results calculate the constant, using the equations for mono- and bi-molecular reactions. In the equation for mono-molecular reactions insert the values of the methyl acetate only, as was done in the case of the hydrolysis by acids. Note that a constant value of k is obtained from the bi-molecular equation, indicating that the reaction is bi-molecular.

CHAPTER II

PARTITION COEFFICIENTS

WHEN a substance, which is soluble in each of two non-miscible or partly miscible solvents, is shaken with a mixture of the two solvents it will distribute itself in a perfectly definite way between them. If the dissolved substance has the same molecular weight in both solvents, then it is found that at equilibrium the ratio of the concentrations of the dissolved substance in the two solvents is constant. Thus, if C_1 and C_2 are the concentrations in the two solvents, then

$$K=\frac{C_1}{C_2}$$

where K is known as the **Partition or Distribution Constant.**

Should the dissolved substance have different molecular weights in the two solvents, *i.e.* it is either associated or dissociated in one of the solvents, then the partition coefficient cannot be obtained by the simple expression given above.

Suppose a substance of molecular weight M is associated in one of the solvents to form molecules which are n times as large as the simple molecules, thus:

$$nM \rightleftarrows (M)_n.$$

Then if C_1 is the concentration of the simple molecules in the non-associating solvent and C_2 the concentration in the associating solvent

$$C_1^n = KC_2,$$

$$\text{or} \qquad K = \frac{C_1}{\sqrt[n]{C_2}}.$$

It will therefore be clear that the study of the distribution of substances between two solvents will furnish information about the molecular weights in those solvents.

Experiments

1. *Determine the Partition Coefficient of Iodine between Water and Benzene.* Place 100 c.c. of water and 100 c.c. of benzene in a 250 c.c. stoppered bottle and add about 5 grams of powdered iodine. Cover the neck of the bottle and stopper with an indiarubber cap and shake for two hours in a thermostat. Allow the contents of the bottle to separate completely, remove 5 c.c. of the benzene solution, and titrate with a standard $\left(\frac{N}{10}\right)$ solution of sodium thiosulphate. Restopper the bottle and shake for an hour more, and then titrate a further 5 c.c. of the benzene solution. If the concentration of the iodine in the benzene solution is constant, the concentration in the water solution may be determined. To do this, insert a 20 c.c. pipette into the aqueous layer, keeping the top closed with the finger, then gently blow out any liquid which may have entered the pipette. Wait until the layers are quite separate again and withdraw 20 c.c. Titrate with an $\frac{N}{50}$ solution of sodium thiosulphate. Repeat the experiment using 2 and 10 grams of iodine. Calculate the partition coefficient in each case.

2. *Determine the Partition Coefficient of Succinic Acid in Water and Ether.* Place 100 c.c. of carbon-dioxide free water and 100 c.c. of ether in each of three 250 c.c. stoppered bottles, add 1·0, 0·5, and 0·25 grams of succinic acid respectively to the bottles. Stopper and close the bottles with indiarubber caps, and shake in a thermostat at 20° for an hour. Allow the layers to separate, and analyse as described in the last experiment by titration with $\frac{N}{20}$ baryta solution, using phenolphthalein as indicator. Calculate the partition coefficient from the titration values.

3. *Determine the Partition Coefficient of Acetic Acid in Benzene and Water.* Shake together for 30 minutes in a thermostat at 25° the following mixtures:

100 c.c. benzene, 100 c.c. water, 10 grams of glacial acetic acid.

100 c.c. benzene, 100 c.c. water, 5 grams of glacial acetic acid.

100 c.c. benzene, 100 c.c. water, 2 grams of glacial acetic acid.

Titrate both layers, and calculate the values of $\frac{C_1}{C_2}$ and $\frac{C_1^2}{C_2}$, where C_1 is the concentration of acetic acid in the water solution and C_2 that in the benzene solution. Note that the factor $\frac{C_1}{C_2}$ increases as the concentration of acetic acid decreases and that $\frac{C_1^2}{C_2}$ is constant, indicating that in benzene solution acetic acid is associated and exists chiefly as double molecules $(CH_3.COOH)_2$.

Determination of the Relative Molecular Weight of Dissolved Substances. If a substance is dissolved in a mixture of two solvents to form two solutions in equilibrium, it follows that if the molecular weight of the dissolved substance in one of the solvents is known, the molecular weight in the other solvent may be deduced from a knowledge of the partition coefficient. Further, if the partition coefficient changes with concentration, the relationship between concentration and the degree of association or dissociation in the second solvent can be calculated.

Consider a dilute solution of an acid in solution in two solvents, water and benzene. Let C_1 be the concentration in the aqueous solution at equilibrium, and C_2 that in the benzene solution. Assume further that α is the degree of dissociation of the acid in the aqueous solution. Then

$$\frac{\mathrm{C}_1{}^2\alpha^2}{\mathrm{C}_1(1-\alpha)}=\mathrm{K},$$

where K is the dissociation constant. If now v is the number of litres containing 1 gram molecule, *i.e.* $\frac{1}{\mathrm{C}_1}$,

$$\frac{\alpha^2}{(1-\alpha)v}=\mathrm{K},$$

from which the value of α may be calculated.

Further, the ratio between concentrations of the simple unchanged molecules in both solutions is constant, hence if β be the fraction of the total acid in the benzene solution which is unassociated,

$$\frac{\mathrm{C}_1(1-\alpha)}{\mathrm{C}_2\beta}=k,\quad i.e.\ \mathrm{C}_2\beta=\frac{\mathrm{C}_1(1-\alpha)}{k}.$$

Applying, now, the law of mass action to the acid in the benzene solution, and assuming that the associated molecules are double, we have

$$2A \rightleftarrows A_2,$$

and

$$\frac{(C_2\beta)^2}{C_2(1-\beta)} = k_2.$$

Hence substituting the value of $C_2\beta$ in this expression, we get

$$k_2 = \frac{C_1{}^2(1-a)^2}{k^2C_2 - C_1(1-a)k}.$$

Since k_2 is not dependent upon concentration, we can obtain the value of a second equilibrium mixture containing a different concentration of acid, *e.g.* C'_1 and C'_2.

Then $$k_2 = \frac{\{C'_1(1-a)\}^2}{k^2C'_2 - C'_1(1-a)k} = \frac{\{C_1(1-a)\}^2}{k^2C_2 - C_1(1-a)k},$$

and since a is known (see Chapter III.), k can be calculated, and by substituting these values in

$$C_2\beta = \frac{C_1(1-a)}{k}$$

the value of $C_2\beta$ is known, *i.e.* the concentration of the unassociated molecules in benzene solution, and consequently the degree of dissociation of the double molecules is known, and k_2, the dissociation constant of these molecules, can be calculated.

EXPERIMENT

Determine the Degree of Dissociation of Bi-molecular Acetic Acid in Benzene Solution. Place into each of four 500 c.c. stoppered bottles 200 c.c. of benzene and 200 c.c. of water, and add 4·0, 2·0, 1·0 and 0·5 grams of glacial acetic acid respectively. Close the bottles with rubber caps and shake for half an hour at 25°. Allow the layers to separate, and determine the concentration of acetic acid in both layers by titration with $\frac{N}{50}$ baryta solution, using 10 c.c. of the aqueous solution and 20 c.c. of the benzene solution for each titration.

In the last experiment it was shown that acetic acid formed double molecules in benzene solution, hence from the data just obtained it is possible to calculate the degree of dissociation of these double molecules by means of the equations given above.

To do this the value of a must first of all be calculated. This is obtained from the dissociation constant K.

$$K = \frac{a^2}{(1-a)v},$$

where v is the number of c.c. of water containing 1 **gram** molecule of acetic acid.

Hence $$a = \frac{Kv}{2}\left\{\sqrt{\left(1+\frac{4}{Kv}\right)}-1\right\}.$$

For acetic acid $K = 1{\cdot}8 \times 10^{-5}$.

The value of the constant k for the ratio between the single simple molecules in both solutions may now be obtained by inserting the concentration values in both solutions for two dilutions in the expression,

$$\frac{\{C'_1(1-a)\}^2}{k^2C'_2 - C'_1(1-a)k} = \frac{\{C_1(1-a)\}^2}{k^2C_2 - C_1(1-a)k},$$

where k is the only unknown. The value of either half of the above equation gives the value of k_2 the dissociation constant of the double molecules.

Hence since $$k_2 = \frac{C_2\beta}{C_2(1-\beta)},$$

the value of β, the degree of dissociation, follows. Calculate β for all four solutions, and plot the results as abscissae against the value of c_2 as ordinates and so obtain a dissociation curve for the molecules $(CH_3COOH)_2$.

This experiment may be repeated with any of the acids given in the table below. The strength of the acid is proportional to the ionisation constant K, hence it will be an instructive experiment to determine the dissociation constant in benzene for two acids of widely differing ionisation constant and see whether there is any relationship between the strength of the acid and the dissociation constant of its double molecules.

Acid.	Ionisation Constant.
Benzoic, - -	$6{\cdot}0 \times 10^{-5}$
Salicylic, - -	$1{\cdot}02 \times 10^{-3}$
Cinnamic, - -	$3{\cdot}5 \times 10^{-5}$
Acetic, - - -	$1{\cdot}8 \times 10^{-5}$

Determination of the Hydrolysis of Salts

It has been shown that if a mixture of two substances is shaken with two immiscible or partly miscible solvents, these substances will distribute themselves between the two solvents independently of one another and each in exactly the same way as it would have done had the other substance been absent. Use is made of this fact to determine the degree of hydrolysis of salts. When a salt is hydrolysed by water, free acid and base are produced according to the equation

$$AB + H_2O \rightleftarrows HA + BOH.$$

In the case of a salt of a weak organic base this may be represented

$$HAB \rightleftarrows B + AH,$$

e.g. in the case of aniline hydrochloride we have

$$C_6H_5NH_2HCl \rightleftarrows C_6H_5NH_2 + HCl.$$

If then aniline hydrochloride is dissolved in water, there will be present in the water a mixture of the salt, base and acid, and if this solution is shaken with another solvent, say benzene, all these substances will distribute themselves between the two solvents as they would have done had they been separately there alone. But as the salt and hydrochloric acid are practically insoluble in benzene the concentrations of these substances in benzene may be taken as zero in this solvent. It is experimentally impossible to determine directly the amount of free aniline in the water solution, but since there is practically nothing but aniline in the benzene solution the concentration of the aniline may be directly determined in this solvent. From the concentration of aniline in the benzene solution and the partition coefficient of aniline between the two solvents, the concentration of the free aniline in the water solution may be calculated, and consequently the amount of hydrolysis determined.

EXPERIMENT

Determine the Amount of Hydrolysis of Aniline Hydrochloride in Water at 25°. Make up solutions of aniline hydrochloride in water, containing respectively 20, 10 and 5 grams of the salt in 1100 c.c. of water. Determine exactly the concentration of the salt by titrating with a standard solution of potassium bromate and bromide. For the method of preparing and using this solution see page 129, Part I. Then place 1000 c.c. of each of these solutions in three large stoppered bottles and add 75 c.c. of benzene to each solution. It is essential here to note that the volumes of these solutions must be carefully measured. Stopper and cover the bottles with rubber caps and shake for an hour at a definite temperature, say 25°. Place in a 500 c.c. stoppered bottle 400 c.c. of water, 75 c.c. of benzene and 5 grams of aniline and shake for an hour. Allow the solution to separate and determine the partition coefficient of the aniline between water and benzene by analysing both layers of the bottle which contains aniline only. This may be done by titrating with the standard bromate and bromide solution. Determine the concentration of aniline in the benzene layer of the other bottles. An alternative method of analysing the solutions consists in withdrawing a measured quantity, saturating it with hydrochloric acid gas, evaporating to dryness and weighing the residue of aniline hydrochloride. The former method is however to be preferred. The calculation is carried out as follows: At equilibrium we have the condition expressed by the equation

$$C_6H_5NH_2HCl \rightleftarrows C_6H_5NH_2 + HCl$$

in the water solution.

Hence from the law of mass action, if α, β, γ and δ represent the concentrations, in gram equivalents per litre, of salt, water, aniline and hydrochloric acid

$$\alpha K = \gamma\delta, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(i)}$$

since β, the concentration of the water, is constant throughout the experiment.

If C be the concentration, in gram equivalents per litre, of aniline hydrochloride in the water solution before the addition of the benzene, and C_1 the concentration of the aniline, in gram equivalents per litre, in the benzene solution at equilibrium, then if L is the partition coefficient of aniline between water and benzene,

$$C_1 = LC_2$$

where C_2 is the concentration, in gram equivalents per litre, of free aniline in the water solution,

$$i.e. \quad \gamma = C_2 = \frac{C_1}{L}.$$

The weight of aniline in the benzene layer is $\frac{93 \times C_1 v}{1000}$ grams, where v is the volume of the benzene and 93 the equivalent weight of aniline; also since the volume of the water is 1000 c.c., $C_2 \times 93$ represents the weight of free aniline in the water layer. The total weight of aniline taken as salt was $93 \times C$ grams, hence

$$93C - 93C_2 - \frac{93C_1 v}{1000}$$

represents the weight of aniline present, combined as hydrochloride. This is only found in the water layer,

hence $$\frac{1}{93}\left(93C - 93C_2 - \frac{93C_1 v}{1000}\right) = C - C_2 - \frac{C_1 v}{1000}$$

gives the concentration, in gram equivalents per litre, of the unhydrolysed aniline hydrochloride,

$$i.e. \quad a = C - C_2 - \frac{C_1 v}{1000}.$$

This factor also represents the concentration of the combined hydrochloric acid, consequently the free hydrochloric in gram equivalents per litre is given by

$$\delta = C - C + C_2 + \frac{C_1 v}{1000}$$
$$= C_2 + \frac{C_1 v}{1000}.$$

Substituting these values in the equation

$$K = \frac{\gamma \delta}{a},$$

we get

$$K = \frac{C_2\left\{C_2 + \frac{C_1 v}{1000}\right\}}{C - C_2 - \frac{C_1 v}{1000}},$$

from which K, the hydrolysis constant, can be calculated. When pure aniline hydrochloride is dissolved in water the concentration of the free aniline and free hydrochloric acid produced by the hydrolysis must be the same.

i.e. $\gamma = \delta$, and $(C - \gamma)$ = the concentration of the unhydrolysed salt.

Hence

$$\gamma \times \gamma = K(C - \gamma),$$

or

$$K = \frac{\gamma^2}{(C - \gamma)}.$$

Since C and K are both known, γ may now be calculated. The degree of hydrolysis h is given by the ratio of the concentration of the free base in water solution to that of the salt originally taken,

$$h = \frac{\gamma}{C},$$

and the percentage hydrolysis by $100h$.

Calculate the value of K for each of the solutions and use the mean of the determinations to calculate the value of γ for other solutions, employing the value of C obtained in the original titrations.

As an additional exercise, the hydrolysis of potassium phenate may be determined, using water and benzene as the solvents, and titrating the phenol in the benzene solution by means of a standard solution of bromate and bromide in the presence of dilute hydrochloric acid, exactly as with aniline.

CHAPTER III

CONDUCTIVITY OF ELECTROLYTES

An electric current passing through an electrolyte obeys the same laws as one flowing along a metallic conductor, the current strength in both cases being directly proportional to the electromotive force driving the current, and inversely proportional to the resistance of the conductor. This is expressed by Ohm's Law,

$$\mathrm{C}=\frac{e}{r},$$

where C is the current strength in amperes, r is the resistance in ohms, and e the electromotive force (E.M.F.) in volts.

At the outset it will be well to define the various electrical units employed, together with their relationships to one another.

The unit of electrical **quantity** is the **Coulomb**. This is that quantity of electricity, which placed at a distance of 1 cm. from an equal quantity repels it with a force of one dyne. It is also that quantity of electricity which will liberate 0·0000104 grams of hydrogen from a solution containing hydrogen ions.

Current strength is defined as the quantity of electricity which flows across a given cross-section in one second. The unit of current strength is the **ampere**, which represents the passage of a current of one coulomb per second across a given cross-section. An ampere, as will be seen from Ohm's Law, is the current which flows in a conductor that has a resistance of one ohm, when the E.M.F. driving the current is one volt.

The unit of **resistance, the ohm,** is defined as the resistance offered to the passage of an electrical current by a column of mercury 106·3 cms. long and 1 mm. cross-section at 0°.

The **volt** is the electromotive force necessary to drive a current of one ampere through a resistance of one ohm.

The **conductivity** of a substance, *i.e.* its power of conducting an electric current, is obviously the reciprocal of its resistance, and since the **specific resistance** of a substance is the resistance of a cube of the substance of 1 cm. edge, the **specific conductivity** of a substance is defined as the conductivity of a cube of the substance of 1 cm. edge. This factor will be designated κ in the present chapter.

Knowledge of the specific conductivity of solutions does not lead very far in physico-chemical work, because the conductivity of a solution is not due to the whole of the material lying between the electrodes, but only to the dissolved substance. Hence, in order to obtain conductivities of solutions which shall be comparable, they must be represented as functions which take account of the amount of the dissolved substance. There are two such quantities in general use: (1) The **equivalent conductivity** and (2) the **molecular conductivity.**

The **equivalent conductivity,** represented by the symbol Λ, is defined as the conductivity of a solution containing one gram equivalent of the dissolved substance when placed between electrodes of an indefinite size situated 1 cm. apart.

Molecular conductivity, designated by the symbol μ, is the conductivity of a solution containing one gram molecule of the dissolved substance, when placed between electrodes of an indefinite size 1 cm. apart.

The relationship between specific conductivity and the derived functions is expressed in equation form thus:

$$\mu = \mathsf{K}v_1 \quad \text{and} \quad \Lambda = \mathsf{K}v,$$

where v and v_1 represent the volume of solution in cubic centimetres, which contains one gram equivalent and one gram molecule of the dissolved substance respectively.

In this section we are only concerned with the conductivity of solutions; the conductivity of solids, liquids other than solutions, and gases belongs to the domain of physics.

One class of solutions only conducts electricity, namely electrolytes. Electrolytes are solutions of substances which are ionised, *i.e.* dissociated into ions on solution, and consist almost entirely of aqueous solutions of acids, bases, and salts.

Measurement of the Resistance of Solutions

Resistance is generally measured by means of a Wheatstone Bridge. This consists of a system of resistances RS*ac* (Fig. 4) connected as in the diagram. A battery B is connected to *a* and *c*, so that the current flows along the two paths *abc* and *adc*. The total fall of potential along the two paths is the same, consequently if R and S are two resistances, one of known value and the other unknown, there must be some point *d* along *ac* at which the fall of potential between *a* and *d* is the same as that between *a* and *b*, where *b* is the point of contact between R and S. This point is found by connecting one terminal of a galvanometer G to *b*, and the other to a sliding contact which can be moved along the wire *ac*. At the point *d*, where the potential is the same as at *b*, no current will flow from *b* to *d*, and consequently there will be no deflection of the galvanometer. When this is the case, the ratio of the resistances R : S will be the same as the ratio of the resistance of *ad* : *dc*, and if *ac* is a wire of uniform resistance, the resistances of *ad* and *dc* will be in the same ratio as their lengths, *i.e.*

$$\mathrm{R} \cdot \mathrm{S} :: \text{length } ad : \text{length } dc;$$

or

$$\mathrm{S} = \frac{\mathrm{R} \times \text{length } dc}{\text{length } ad}.$$

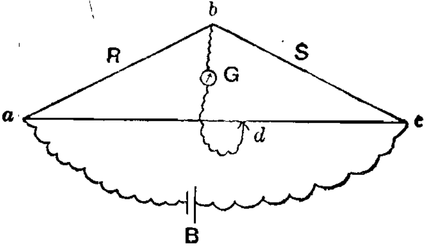

FIG. 4.

To measure the resistance of a solution the arrangement must be slightly changed, for when a current is passed through a solution the electrodes are changed, *i.e.* polarised, and to measure the resistance with constantly varying electrodes means, inevitably, false results. Consequently, instead of a direct current, an alternating current is used; this is obtained from the secondary coil of a small induction coil. A galvanometer of the ordinary type is useless for determining the point of balance, *i.e.* equal potential, when using an alternating current, and is substituted by either a telephone or an electrodynamometer. In general work the telephone is almost always employed, although in many respects the dynamometer is superior to it. The arrangement is now as indicated in Fig. 5. **R** is a box of resistance coils, **W** the cell containing the solution whose resistance is to be measured, **T** the telephone, **I** is a small induction coil which is worked by an accumulator, and *ab* is a uniform wire, along which a sliding contact *c* may be moved until the point is reached at which *d* has the same potential as *c*. When this is the case no current flows through the telephone, and consequently it is silent. It will be noticed here that the positions of the source of current and the indicating instrument have been interchanged from the arrangement usually adopted in the measurement of resistances of metallic conductors. This arrangement is to be preferred, because when the telephone is connected to the slide contact the noises produced in it when the contact is pressed down are apt to interfere with the sharp definition of the point of balance; and, further, when the slide contact is not pressed down no current flows through the cell.

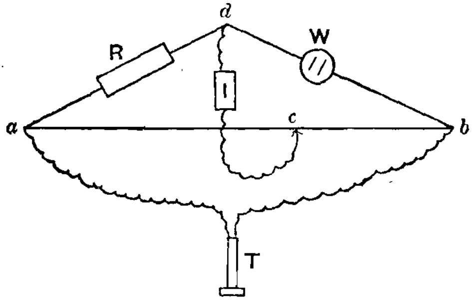

FIG. 5.

Some description of the various parts of the apparatus employed is needed, and this will be given here.

1. **The bridge wire** consists of a uniform wire, 1 metre long and 0·1–0·2 mm. diameter, made of either platinum, iridio-platinum, or constantan. This is fastened to two brass plates A and B (Fig. 6), which are placed 1 metre apart at either end of a piece of wood, which carries a scale graduated in millimetres. The wire is therefore tightly stretched between the metal plates and lies above the graduations, as indicated in the diagram. Terminals *ab* are attached to the brass plates, which serve for making electrical contact with the wire. A sliding contact C is attached to the bridge; this is fitted with a platinum edge, by means of which contact can be made with any point of the bridge wire.

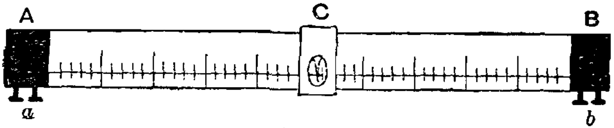

Fig. 6.

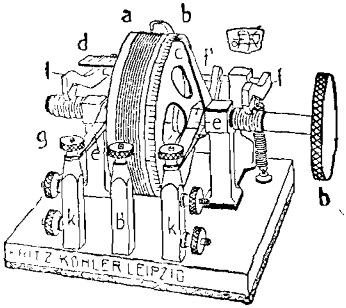

Fig. 7.

Sometimes the bridge wire is coiled round an ebonite drum, as illustrated in Fig. 7. The contact is made by a small platinum point *b*, which slides along the wire, and is connected to the terminal *b′* by means of a stiff support and a flexible lead.

In this arrangement, when the drum is rotated the contact slides along the wire, its position being read on the scale *d*, which gives the number of complete rotations made by the drum. The fractions of rotations are read from the graduations on the drum. The wire is wound round the drum in 10 complete turns, so that each complete turn advances the contact 0·1 of the length of the wire; the drum is divided into 10 large divisions which are each subdivided into 10 smaller divisions, and these can easily be read to a tenth part. The terminals *kk* are connected with the ends of the bridge wire by means of the spring contacts *ee*.

Calibration of the Bridge Wire. A bridge wire, just like any other measuring instrument, must be calibrated before use.

This can be done, easily, in two ways: (1) by means of a resistance box which has been calibrated, and (2) by Strouhal and Barus' method.

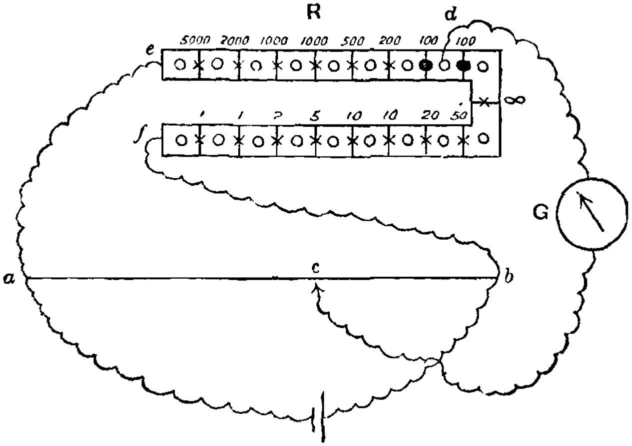

Fig. 8.

(1) *By means of a resistance box.* The two ends of the bridge wire *a*, *b*, Fig. 8, are connected to the two end terminals *ef* of a resistance box R. Two plugs, which place resistances of 100 ohms each in the circuit, are

removed, and the contact *d* between them is connected through a galvanometer G to the sliding contact *c* on the bridge. A battery B is connected across the ends of the bridge wire. The sliding contact is now moved until the galvanometer is not deflected. This should be at the division 500 if the bridge wire is uniform. It will generally be found to be other than this position, say 500·2. Hence a correction of −0·2 mm. is necessary at this point. The corrections necessary at other points are determined by changing the resistances in the box, at either side of the contact *d*. A scheme of such a determination, showing the resistances to be used in the box for the various points on the bridge wire, is given below.

Resistances of Arms of Box.	Correct Bridge Reading.	Actual Bridge Reading.	Correction.
10 : 990	10	10·1	−0·1 mm.
20 : 980	20	19·8	+0·2 „
30 : 970	30	29·9	+0·1 „
50 : 950	50	49·8	+0·2 „
100 : 900	100	101·0	−1·0 „
100 : 400	200	200·0	±0·0 „
300 : 700	300	301·1	−1·1 „
200 : 300	400	400·8	−0·8 „
100 : 100	500	500·0	±0·0 „
300 : 200	600	601·0	−1·0 „
700 : 300	700	700·4	−0·4 „
400 : 100	800	799·8	+0·2 „
900 : 100	900	901·4	−1·4 „

The corrections should then be plotted against the observed bridge readings and a calibration curve drawn which should be used to correct all readings.

(2) *Method of Strouhal and Barus.* This method is very similar in principle to that adopted in calibrating a capillary tube (Chapter IX., Part I.). The method

consists in comparing the resistance of a series of short lengths of the bridge wire. This is done by connecting a second resistance, made up of ten approximately equal resistances, in parallel with the bridge wire to be calibrated. The calibrating resistance consists of a strip of hard wood or ebonite *ab* (Fig. 9) into which 11 mercury cups are bored. The ends of the single resistances dip into these cups and so form a continuous resistance.

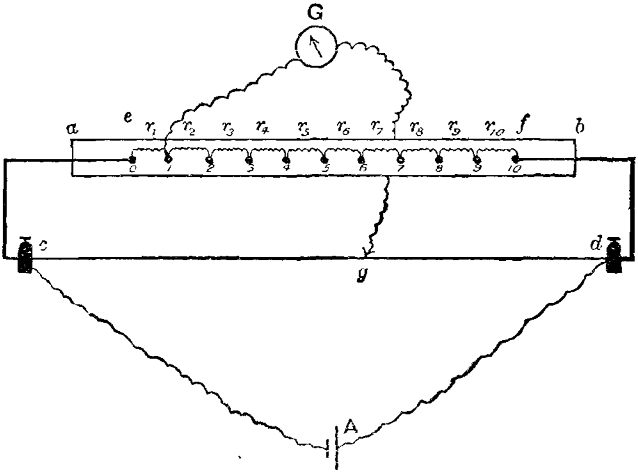

Fig. 9.

The single resistances are made from coils of manganin wire, each of which has a resistance about $\frac{1}{10}$ that of the bridge wire. The manganin wires are soldered to thick copper wires, which are bent at right angles. The resistances are protected by being placed in glass tubes which are closed with sealing wax, leaving only the thick copper ends free. The ends of the calibrating resistance, *e*, *f*, are connected to the ends of the bridge wire, *c*, *d*, which are permanently connected to a single accumulator A. The sliding contact *g* of the bridge wire is connected through a galvanometer G with a long flexible lead which is amalgamated at its free end. To calibrate the bridge wire the free end of the flexible lead is placed in mercury cup 1, and the sliding contact moved until there is no deflection of the galvanometer needle. When this is the case the resistance of the short length of the bridge wire will bear the same relation to the resistance of the whole wire as the resistance of r_1 bears to the sum of the ten resistances. The length of the bridge wire which is proportional to r_1 may be termed l. The resistance r_1 is now interchanged with r_2 and the position of balance again found with the galvanometer lead still in the mercury cup 1, this position is say l_1 on the bridge wire. The galvanometer lead is then moved to cup 2 and the position of balance again found, say l_2.

The difference l_2-l_1 gives a second length of the bridge wire which bears the same relation to the resistance of the whole wire as the resistance r_1 does to the sum of the ten resistances, *i.e.* $l_2-l_1=l$. The resistances r_3 and r_1 are now interchanged, and the position of balance found without changing the position of the galvanometer lead; this gives a length of wire l_3 proportional to the sum of the resistances r_2 and r_3. The galvanometer lead is now placed in mercury cup 3 and a new position of balance l_4 is obtained. The difference l_4-l_3 gives a third length of wire which bears same proportion to the whole wire that r_1 does to sum of the ten resistances, *i.e.* the resistance of l_4-l_3 is equal to the resistance of l. This process is repeated until the galvanometer lead is in the mercury cup 9, the length in this case being subtracted from 1000 to give the tenth length of wire, which has the same resistance as the first piece l. The sum of the ten measured lengths is subtracted from 1000, and one tenth of the difference is added to each of the measured lengths, so that now there are ten lengths which together make up the total length of the bridge wire, and these are successively the lengths which should correspond to the bridge wire readings of 100, 200, 300, etc. The differences between the determined lengths and the scale readings give the corrections that must be applied to the bridge wire at these points. The corrections should be plotted against the bridge readings to give a calibration curve which should be used in all determinations. A series of values is given in the table below, which will indicate the method adopted in the calibration.

Number of mercury cup connected to galvanometer.	Arrangement of the resistances.	Bridge Reading.	Length of bridge wire proportional to r_1.	Corrected length of bridge wire.	Length corresponding to 100, 200, 300, etc.	Correction to be applied.
1	$r_1 : r_2 \dots r_{10}$	100·3	100·3	100·47	100·47	−0·47
1 2	$r_2 : r_1 + r_3 \dots r_{10}$ $r_2 + r_1 : r_3 \dots r_{10}$	100·6 200·2	99·6	99·77	200·24	−0·24
2 3	$r_2 + r_3 : r_1 + r_4 \dots r_{10}$ $r_2 + r_3 + r_1 : r_4 \dots r_{10}$	200·6 299·8	99·2	99·37	299·61	+0·39
3 4	$r_2 \dots r_4 : r_1 + r_5 \dots r_{10}$ $r_2 \dots r_4 + r_1 : r_5 \dots r_{10}$	300·2 401·0	100·8	100·97	400·58	−0·58
4 5	$r_2 \dots r_5 : r_1 + r_6 \dots r_{10}$ $r_2 \dots r_5 + r_1 : r_6 \dots r_{10}$	399·9 500·0	100·1	100·27	500·85	−0·85
5 6	$r_2 \dots r_6 : r_1 + r_7 \dots r_{10}$ $r_2 \dots r_6 + r_1 : r_7 \dots r_{10}$	500·4 599·6	99·2	99·37	600·22	−0·22
6 7	$r_2 \dots r_7 : r + r_8 \dots r_{10}$ $r_2 \dots r_7 + r_1 : r_8 \dots r_{10}$	600·3 700·7	100·4	100·57	700·79	−0·79
7 8	$r_2 \dots r_8 : r_1 + r_9 + r_{10}$ $r_2 \dots r_8 + r_1 : r_9 + r_{10}$	699 3 799·9	100·6	100·77	801·56	−1·56
8 9	$r_2 \dots r_9 : r_1 + r_{10}$ $r_2 \dots r_9 + r_1 : r_{10}$	801·2 899·6	98·4	98·57	900·13	−0·13
9	$r_2 \dots r_{10} : r_1$	900·3 1000·0	99·7	99·87	1000·0	±0·00

The sum of the lengths in column 4 is 998·3, this subtracted from 1000 gives +1·7, *i.e.* 0·17 must be added to each of the ten measured lengths in column 4 to give the lengths represented by the scale readings 100, 200, 300, etc. The corrections in column 7 must be plotted as abscissae against the values in column 6 as ordinates, and a curve drawn. This will show at once the correction to be applied to any reading on the bridge scale. The description above makes use of a galvanometer to detect the point of balance, but a telephone may be used; of course in this case the battery must be substituted by an induction coil and battery.

2. **The Resistance Box** consists of a number of resistances of various values, attached to a series of brass

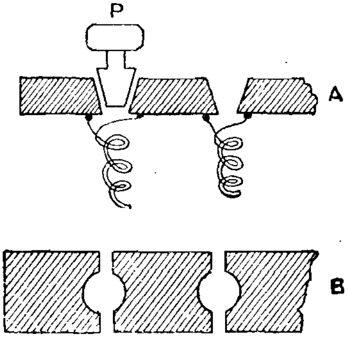

FIG. 10.

blocks which are fastened to an ebonite slab and so insulated from one another (Fig. 10). The spaces between the brass blocks are fitted with well ground brass plugs, which have ebonite handles, and these when in position serve to make metallic contact, of practically no resistance, between the brass blocks and so prevent the current passing through the resistances connected to the brass blocks. The end blocks are connected to terminals (Fig. 8), so that when all the plugs are in position there is practically no resistance between the box terminals. But if a plug is removed, then the resistance, lying between the two blocks connected by that plug, is placed in the circuit. The wire constituting the individual resistances is always wound in double coils, A (Fig. 10), to prevent self induction. The value of the various resistances is always stated on the ebonite slab holding the brass parts. When not in use the plugs should be placed loosely in the holes allotted to them, and when the box is in use they should be given a twist so that a firm and good contact is made. The plugs should never be placed on the laboratory bench, but always either in the lid of the box, or in holes provided in the brass pieces of some resistance sets. It is especially important that the metal part of the plugs should not be touched with the fingers, otherwise they will become greasy and make imperfect contacts. Greasy plugs may be cleaned by washing with light petroleum. Resistance boxes generally contain the following resistances: 1, 2, 2, 5, 10, 10, 20, 50, 100, 100, 200, 500, and 1000 ohms. Larger boxes go up to 10,000 ohms; but for our purpose a box containing resistances up to 1000 ohms will be sufficient.

Calibration of a Resistance Box. A set of resistances, like every other instrument for exact measurement, must be calibrated before use. To calibrate a set of resistances, the arrangement illustrated in Fig. 11 is employed. The ends of the resistance box, *a*, *b*, are connected through a commutator K with the ends of the bridge wire, *c*, *d*. A galvanometer, G, is also connected across the bridge wire. A battery, B, is connected to the sliding contact *s* and the point between the two resistances of the box which are to be compared. All the connecting wires must be thick, so as to have a negligible resistance.

The resistances 1, 2, 2 and 5 are then compared with the 10 ohm resistance, and the position of balance on the bridge wire determined. The commutator is then reversed so that the resistances are interchanged; if now the balance is maintained the resistances are equal, but if the sliding contact has to be moved to regain the point of balance, say n mm., then the ratio of the resistances is given by $\frac{1000 \pm 2n}{1000}$. The two 10 ohms are then compared in the same way, the 20 with the sum of the two 10 ohm resistances, and so on until the whole have been compared. Then it is usual to assume that the sum of 1, 2, 2 and 5 is correct and equal to 10 ohms, and calculate the others on this basis. The real value of the sum of 1, 2, 2 and 5 is given by comparing them with a standard 10 ohm resistance; the true value of the other resistances can then be calculated. The method of calculating the relative values of the different resistances is the same as that given in Chapter II., Part I.,

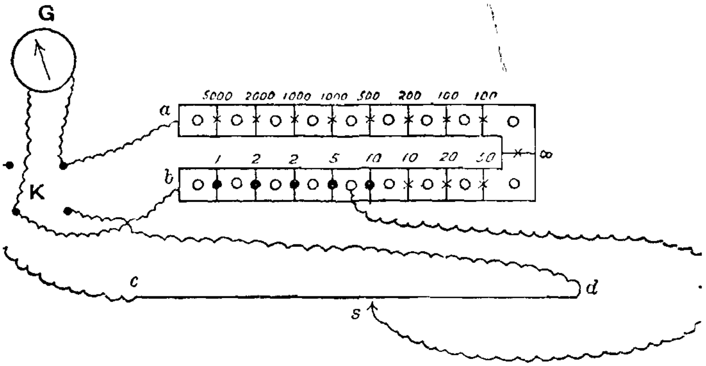

FIG. 11.

for the calibration of a set of weights. For any but the most accurate work, all but the very cheapest resistance boxes are quite accurate enough for use without calibration.

3. **The Induction Coil.** The coil used for the determination of conductivity should be small and of few windings. Should a large coil be used, quantities of electricity which are far too large will be sent through the solutions, producing considerable polarisation of the electrodes, with its attendant inaccurate results. The hammer of the coil should be light, and should vibrate very rapidly,

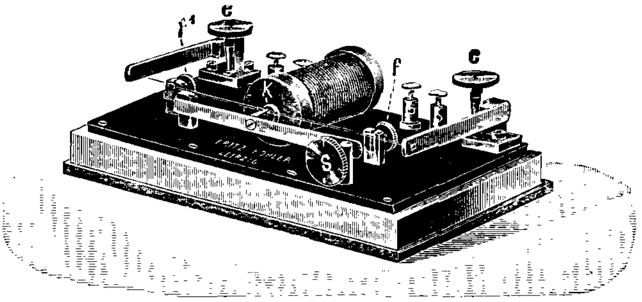

Fig. 12.

thus producing a high-pitched note in the telephone, which is much more easily distinguished than a low-pitched note. An induction coil due to Nernst is very suitable for this work. The hammer is substituted by an oscillating wire, Fig. 12, carrying a soft iron core in the middle. The tone of the note heard in the telephone may be changed readily by means of the screws C C and *f f'*. The current should only be sent through the coil during the actual measurements, and not be kept flowing between the measurements. It should also be only just strong enough to work the coil. Generally, a difficulty is experienced at first in differentiating between the noise of the hammer and the sound in the telephone; this usually disappears after a while, but if it continues the noise of the coil may be damped considerably by standing it on a piece of thick felt and at some distance from the operator.

Conductivity Vessels. The vessels in which the measurement of the conductivity of a liquid is carried out are of various forms and dimensions, depending on the nature of the solution under observation. They are made generally of Jena glass, and are provided with a pair of platinum electrodes, fused into glass tubes and supported by an ebonite stopper which is fitted to the vessel.

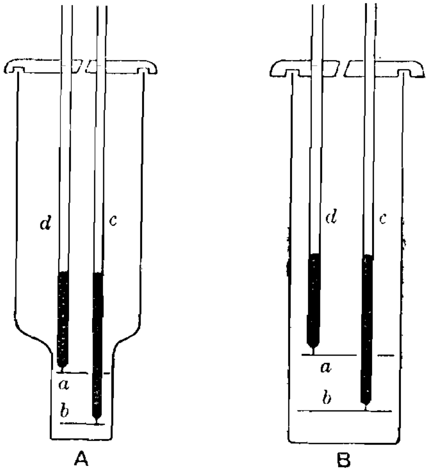

Fig. 13.

For ordinary determinations the most suitable vessels to employ are those represented in Fig. 13; the form A has a tube narrowed down to about 1 cm. diameter, and is used for electrolytes which conduct well. The form

B is used for electrolytes having a poor conductivity. As will be seen in the diagram, the platinum plates, *a*, *b*, are attached to stout platinum wires which are fused into the glass tubes, *c*, *d*. Electric connection between the plates and the rest of the circuit is made by means of a drop of mercury poured into the tubes.

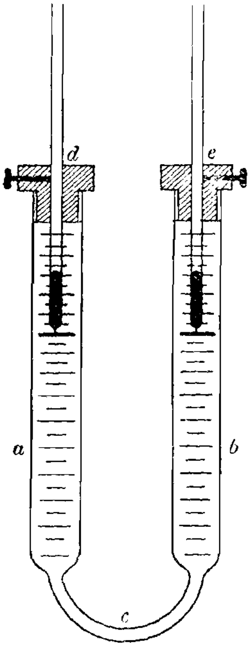

Fig. 14.

For liquids which conduct electricity very well, the form of vessel indicated in Fig. 14 is the most suitable. This consists of two wide tubes, *a*, *b*, connected by a narrower tube *c*. The electrodes, as before, are inserted through ebonite stoppers, *d*, *e*, but in this vessel they are movable, thus making the vessel suitable for solutions of conductivity extending over a wide range.

When saturated solutions have to be measured the forms of conductivity vessel already mentioned are not convenient, and one of the following forms is used. The dipping electrode (Fig. 15) consists of two platinum plates fused into two tubes *a* nd *b*; these are fused to a wider tube *c*, which serves o protect the plates. Connection with the measuring ircuit is made by drops of mercury placed in the tubes , *b*. Such an electrode may be dipped directly into the ottle containing the saturated solution.

The pipette electrode (Fig. 15) consists of a pipette *c* furnished with a stopcock *d*. The electrodes are placed in the bulb of the pipette and connected by the side tubes, *e*, *f*, through a drop of mercury with the rest of the circuit. Such a pipette may be surrounded by a glass jacket containing water at a given temperature. The pipette is then dipped into the solution, filled, and the conductivity determined in the ordinary way.

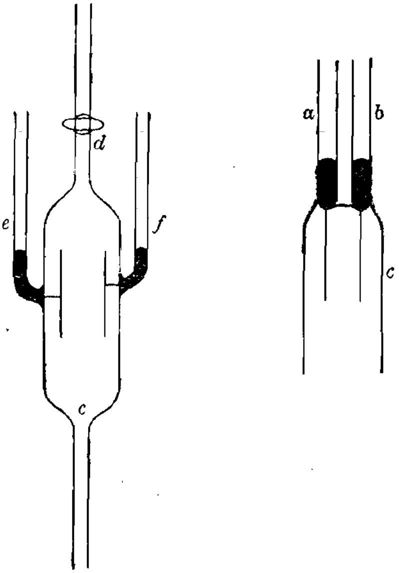

FIG. 15.

It is important in conductivity determinations that the liquid should not exert a solvent action on the glass of the conductivity vessel. This may be prevented by using vessels made of Jena glass; other glassware may be used if it is thoroughly steamed out before use. This is best done by inverting the vessels over a jet of steam for 30–60 minutes. An arrangement for doing this is depicted in Fig. 16; the apparatus consists of a flask A, into the neck of which a funnel B, with a wide stem, is tightly fitted by means of a rubber stopper. A glass tube C is inserted tightly into the stem of the funnel by means of a piece of rubber tubing. The vessel to be steamed is placed on C, and steam from the boiling water in A allowed to play on its surface.

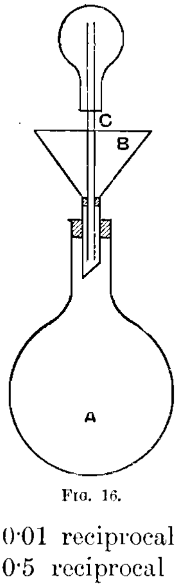

FIG. 16.

All glass vessels, which come directly in contact with the liquids whose conductivity is to be measured, should be steamed out before use.

The electrodes employed in conductivity measurements must be prepared with extreme care. Bright platinum electrodes only give satisfactory results when the conductivity of the solution does not exceed 0·0004 reciprocal ohms, and for solutions of a greater conductivity than this they must be coated with platinum black. Such coated electrodes will give perfect results for solutions having conductivities up to 0·01 reciprocal ohms, and moderately good results up to 0·5 reciprocal ohms. Solutions which have a better conductivity than this should be measured with electrodes coated with palladium black, which enables good results to be obtained with solutions having conductivities up to 0·04 reciprocal ohms, and moderately good results up to 0·2 reciprocal ohms. The measurements with unsuitable electrodes are unsatisfactory on account of the difficulty experienced in finding the position of minimum sound in the telephone.

It is advisable always to use platinised electrodes, but these must not be used where the platinum is likely to have a catalytic action on the solution. The conductivity of the solution can always be brought to within the limits of accurate measurement by a suitable choice of the type of vessel, or by moving the electrodes further apart.

Platinising of Electrodes. Electrodes are best platinised by immersing them, after they have been thoroughly freed from grease by washing with warm chromic acid solution, in a solution consisting of 3 grams of chloroplatinic acid and 0·02–0·03 grams of lead acetate in 100 c.c. of water. The electrodes are placed in an inclined position to facilitate the removal of any gas which may be liberated on them, and connected through a reversing switch to two accumulators, so that they serve as electrodes in the electrolysis of the solution. The current is allowed to flow for 15 minutes, its direction being reversed every half minute, and should be so regulated that the evolution of gas is not very rapid. In this way the electrodes will be coated with a black velvety coherent deposit of platinum. The electrodes, as thus prepared, will contain, occluded in the platinum black, gases and quantities of the platinising liquid. To remove these, it is best to place the electrodes in dilute sulphuric acid and pass a current for about half an hour, reversing it every minute. The electrodes should then be washed several times with warm air-free water, and finally left standing in air-free water until required for use.

Conductivity Water. Ordinary distilled water possesses so large a conductivity that it is rendered quite unsuitable for the preparation of solutions to be used in conductivity determinations. Hence, water has to be specially purified before it is suitable for this purpose.

Such water is termed "conductivity water," and should have a conductivity not greater than 2–3 × 10^{-6} reciprocal ohms. The purest water that has been obtained has a conductivity of 4 × 10^{-8} reciprocal ohms, but it loses this high resistance on standing in the air for a few hours, due to the absorption of carbon-dioxide, and in a day or two when preserved in a closed flask, due to the material dissolved out of the walls of the flask.

Conductivity water good enough for ordinary purposes can be prepared from ordinary tap water by warming it with a few c.c. of potassium permanganate solution acidified with a few drops of sulphuric acid, and then distilling off the water. The distillate is then shaken with a small quantity of caustic soda and redistilled. These two distillations may be carried out with an ordinary glass condenser. The water must then be redistilled, using a tin tube to condense it in, and the first and last thirds must be rejected. To prevent the contents of the distilling flask spurting into the condenser tube, it is well to close the end of the condenser which enters the distillation flask, and pierce a few small holes in the closed end. The final distillation should be carried out in a room free from laboratory fumes. The conductivity water should be stored in a large, thoroughly steamed-out glass bottle, which is fitted with a paraffined cork carrying a soda-lime tube and a syphon. The water thus prepared may be improved by bubbling a stream of carbon-dioxide free air through it for the purpose of removing any carbon-dioxide which it may contain. Conductivity water should not be kept stored for more than a week, and generally it is better to use water which has been freshly prepared.

The Resistance Capacity of the Cell

It has already been noted that the conductivity values which are of use in physico-chemical determinations are the molecular conductivity and the equivalent conductivity. These have been shown to be functions of the specific conductivity, which is defined as the conductivity of 1 c.c. of the solution measured between electrodes of 1 sq. cm. area, and placed 1 cm. apart. If then the electrodes of the vessels do not fulfil these conditions, the conductivity actually measured will have to be multiplied by a factor to convert it into the specific conductivity. If K represents the specific conductivity of a solution, and C its measured conductivity in reciprocal ohms, *i.e.* $\frac{1}{\mathsf{R}}$, where R is the measured resistance of the solution, then

$$\mathsf{K} = \mathsf{CN} = \frac{\mathsf{N}}{\mathsf{R}},$$

where N is the required factor known as the resistance capacity of the cell, or the cell constant.

The value of N may be calculated from the dimensions of the electrodes and their distance apart. If s represents the area of the electrodes in sq. cms. and l the distance apart,

$$\mathsf{N} = \frac{l}{s}; \quad \mathsf{K} = \mathsf{C}\frac{l}{s} = \frac{l}{\mathsf{R}s}.$$

These expressions would be exactly true if the electrodes exactly fitted the vessel in which the conductivity was to be measured. Should this, however, not be the case, then a factor must be introduced to allow for the form of the vessel.

In general, therefore, the cell constant is not determined in this way, but by measuring a solution of known specific conductivity in the cell, and from the observed conductivity calculating the constant. Thus

$$N = \frac{K}{C}.$$

Solutions of potassium chloride of known concentration and known specific conductivity are employed in the determination of the cell constant. It is advisable to use a solution of potassium chloride in this determination whose specific conductivity approximates to the conductivity of the solutions to be subsequently measured in the vessel. A table is given below of the specific conductivities of solutions of potassium chloride of various concentrations at a series of temperatures.

SPECIFIC CONDUCTIVITY OF POTASSIUM CHLORIDE SOLUTIONS

Temperature.	N.	$\frac{N}{10}$.	$\frac{N}{50}$.	$\frac{N}{100}$.
0°	$6{\cdot}54 \times 10^{-2}$	$7{\cdot}16 \times 10^{-3}$	$1{\cdot}522 \times 10^{-3}$	$7{\cdot}76 \times 10^{-4}$
5°	$7{\cdot}41 \times 10^{-2}$	$8{\cdot}22 \times 10^{-3}$	$1{\cdot}752 \times 10^{-3}$	$8{\cdot}96 \times 10^{-4}$
10°	$8{\cdot}32 \times 10^{-2}$	$9{\cdot}34 \times 10^{-3}$	$1{\cdot}996 \times 10^{-3}$	$10{\cdot}19 \times 10^{-4}$
15°	$9{\cdot}25 \times 10^{-2}$	$10{\cdot}48 \times 10^{-3}$	$2{\cdot}243 \times 10^{-3}$	$11{\cdot}47 \times 10^{-4}$
20°	$1{\cdot}02 \times 10^{-1}$	$11{\cdot}67 \times 10^{-3}$	$2{\cdot}501 \times 10^{-3}$	$12{\cdot}78 \times 10^{-4}$
25°	$1{\cdot}12 \times 10^{-1}$	$1{\cdot}289 \times 10^{-2}$	$2{\cdot}768 \times 10^{-3}$	$14{\cdot}12 \times 10^{-4}$
30°	—	$1{\cdot}412 \times 10^{-2}$	$3{\cdot}036 \times 10^{-3}$	$15{\cdot}52 \times 10^{-4}$

EXPERIMENTS

(i) *Determine the Resistance Capacity of a Conducting Cell.* This determination must be carried out at a definite known temperature, for temperature, as can be seen from the table above, has a great influence on the conductivity of solutions, causing an increase in conductivity of about 2 per cent. per degree increase of temperature. Hence the conductivity vessel must be supported in a thermostat during the measurement (see Chapter III., Part I.). This is best done by a spring clip permanently attached to the side of the thermostat. Connect up the bridge wire with a resistance box, conductivity cell, induction coil and telephone, as indicated in Fig. 5, page 40. The connecting wires must be all made of stout insulated copper, and must possess only an inappreciable resistance. The ends of the connections should be cleaned with emery paper before fastening them in the binding screws. The leads, which are to dip into mercury cups, or into the mercury contacts of the conductivity cell, should be cleaned by immersing in dilute nitric acid, washed, and amalgamated by immersing in mercurous nitrate solution. Wash the electrodes of the conductivity vessel with the solution which is to serve for the measurement of the resistance capacity, in this case $\frac{N}{50}$ KCl, then place a quantity of the solution in the cell, insert the electrodes, taking care not to rub off the platinum black. Place the cell in the thermostat and make all the necessary connections. When the cell and its contents have taken on the temperature of the bath, measure the resistance of the cell. To do this, remove plugs from the resistance box, so that a resistance of 500 ohms is inserted in the circuit, and set the induction coil in action. Find the position of the slide-contact on the bridge wire at which the telephone is silent. It is generally impossible to obtain absolute silence in the telephone, but there is always a position of minimum sound, *i.e.* a position at which moving the slide contact in either direction causes the sound to increase in intensity.

Should the sound minimum be indistinct, the electrodes require replatinising. The resistance in the box should be chosen so that the position of balance is near the middle of the bridge, for here the accuracy is greatest. Having found the position, note the reading, change the resistance in the box and remeasure. Make three determinations, and then empty the solution from the conductivity vessel, refill it with a fresh portion of the solution and remeasure. Should the second set of readings differ from the first set, it indicates that the electrodes were not free from absorbed substances, and that these have dissolved in the first portion of potassium chloride solution. If the two sets of readings do not agree, pour out the solution after the measurements have been made and measure a further quantity; repeat the process until two successive quantities give practically the same values. Calculate the resistance of the solution for each measurement; the mean of the whole can then be taken as the resistance of the solution. If l represents the position on the bridge in mm. at which the sound minimum occurs, and R the resistance in the box, then if R_1 is the resistance of the solution

$$R_1 : R :: 1000 - l : l,$$

$$R_1 = \frac{(1000 - l)R}{l}.$$

The conductivity, C, of the solution is then given by

$$C = \frac{1}{R_1} = \frac{l}{(1000 - l)R}.$$

If now K represents the specific conductivity of $\frac{N}{50}$ potassium chloride solution at 25°, and N the cell constant,

$$N = \frac{K}{C} = \frac{K(1000 - l)R}{l}.$$

A table of the values of $\log_{10}\frac{l}{1000-l}$ will be found in Appendix B, Table I. The cell constant, as already indicated, depends on the position of the electrodes; care should therefore be taken that they are not changed in any way. The cell constant should be redetermined if the electrodes are replatinised, and generally ought to be redetermined if the cell is out of use for any length of time.

(ii) *Determine the Conductivity of Pure Distilled Water.* For this experiment, a cell with large electrodes which are close together, should be used. Wash out the cell and electrodes several times with specially distilled and purified water, taking care not to injure the electrodes. Fill the vessel with the pure water, place in a thermostat at 25°, and allow it to attain the temperature of the bath. When this has happened measure the conductivity, as described above, using a resistance of 10,000–20,000 ohms in the resistance box. It will doubtless be found in this measurement, and in all measurements of high resistances, that the sound minimum is somewhat indistinct. It is wise therefore to redetermine the point several times and take the mean of the several readings, which should not differ by more than 2–3 mm. The vessel must now be emptied and a fresh portion of water measured. Repeat the measurement until two successive portions of the water measure the same.

If now l represents the reading on the bridge wire at which the minimum sound is observed in the telephone, and R the resistance in the box, then the specific conductivity, K, is given by

$$K=\frac{l}{1000-l}\cdot\frac{N}{R},$$

where N is the cell constant.

(iii) *Determine the Molecular Conductivity of Acetic Acid, and Calculate its Degree of Ionisation at various Concentrations.* Make a solution of exactly $\frac{N}{16}$ acetic acid, using conductivity water for the purpose. This solution cannot be made up accurately enough by directly weighing out the acid, but must be made up approximately and brought to the required strength by further dilution, after its strength has been determined by titration. Clean and dry a conductivity vessel; the most suitable for this experiment is one of the type B, Fig. 13. The electrodes must be cleaned by washing them several times with conductivity water. The excess water is removed by placing the edges of the plates against a piece of filter paper. The electrodes must then be dried, either by placing them in a steam oven for an hour, or by moving them rapidly to and fro in the hot air above a bunsen burner.

When the apparatus is cleaned and dried, introduce exactly 20 c.c. of $\frac{N}{16}$ acetic acid into the conductivity vessel, place the vessel and contents into a thermostat at 25°, and then put the electrodes in the solution, taking care that no air bubbles remain attached to the surface of the plates. Allow the conductivity vessel and its contents to take up the temperature of the bath, and then measure the conductivity as described above. When three readings for this solution have been obtained, remove exactly 10 c.c. of the solution from the conductivity vessel by means of a 10 c.c. withdrawal pipette (Chapter II., Part I.), and add 10 c.c. of conductivity water by means of a 10 c.c. delivery pipette. A quantity of conductivity water should be kept standing in a stoppered flask in the thermostat for this purpose. This will ensure that the volumes of the water added to, and the solution removed from the conductivity vessel are the same, and further, it will save the time which must otherwise have been lost waiting for the solutions to reach the temperature of the thermostat. Mix the solution and water thoroughly by slowly moving the electrodes up and down, taking care not to touch the sides of the vessel or to knock the plates in any way. Measure the conductivity of this $\frac{N}{32}$ solution, obtaining three readings as before. Dilute the solution again in exactly the same way, and measure its conductivity as before. Repeat the measurements and dilutions until the solution is 64 times as dilute as it originally was, *i.e.* until it is $\frac{N}{1024}$. Now empty the conductivity vessel, clean and dry it, and repeat the whole series of measurements, starting with a fresh quantity of acetic acid solution.

Calculate the specific conductivity for each dilution, taking the mean of the six determinations which have been obtained. The molecular conductivity μ is obtained by multiplying the specific conductivity κ by the number of cubic centimetres v of solution which contain 1 gram molecule of the dissolved substance

$$\mu = \kappa v.$$

The molecular conductivity of a substance increases with the dilution up to a certain maximum value. This value is known as the molecular conductivity at infinite dilution μ_∞, and is obtained when the substance is completely ionised. The conductivity of a solution depends upon the concentration of the ions present; hence, if the molecular conductivity of a substance at infinite dilution be known, it is possible to calculate the degree of ionisation of that substance at a given concentration, from the molecular conductivity at that concentration.

Thus if μ_v represent the molecular conductivity of a substance at dilution v, μ_∞ the molecular conductivity at infinite dilution, and a the degree of ionisation, then

$$a = \frac{\mu_v}{\mu_\infty}.$$

The value of μ_∞ may often be obtained by diluting the solution until further dilution makes no difference to the value of μ. But for weak electrolytes, like acetic acid, this is not possible, for the specific conductivity of acetic acid solution approximates to that of water before the acid is all ionised, consequently the determination is valueless. In cases of this sort the value of μ_∞ is obtained indirectly (see Chapter IV.). The value of μ_∞ for acetic acid may be taken as 389 at 25°. Hence the degree of ionisation for the solutions whose conductivities have been determined can be calculated from

$$a = \frac{\mu_v}{389}.$$

Plot the values of a as abscissae against the dilution as ordinates, and draw a curve showing the influence of dilution on ionisation.

Ostwald has shown that weak binary electrolytes obey the Law of Mass Action. Thus if an acid HA ionises into $\mathrm{H}^{\cdot}$ ions and A' ions as indicated in the equation

$$\mathrm{HA} \rightleftarrows \mathrm{H}^{\cdot} + \mathrm{A}'.$$

Then if a is the degree of ionisation and v the dilution

$$\frac{a^2}{(1-a)v} = K \text{ (constant)}.$$

This constant is termed the *ionisation* or *dissociation constant*, and in the case of acids and bases it gives a measure of the strength of the acid or base, in the sense that the larger the value of K the stronger the acid or base.

The value of K can therefore now be calculated for acetic acid from the values of a which have already been determined. A table of the values of $\log_{10}\frac{a^2}{1-a}$ is given in Table II., Appendix B. The value of K may be obtained without calculating the value of a for

$$K=\frac{a^2}{(1-a)v}=\frac{(\mu_v)^2}{\mu_\infty(\mu_\infty-\mu_v)v}.$$

A list of acids, which may be substituted for acetic acid in the above experiment, is given in the table below, along with the values of their molecular conductivity at infinite dilution at 25° and their ionisation constants at the same temperature.

Acid.	μ_∞ at 25°.	100 K.
Acetic, - - -	389	18×10^{-2}
Benzoic, - - -	381	6×10^{-3}
Succinic, - - -	381	$6{\cdot}6\times10^{-3}$
Cinnamic, - -	378·5	$3{\cdot}5\times10^{-3}$
Hippuric, - - -	372·5	$2{\cdot}2\times10^{-2}$
Salicylic, - - -	382	$10{\cdot}2\times10^{-2}$

It will be noticed in the above table that succinic acid, a dibasic acid, is included. Many of the weaker dibasic acids ionise as monobasic acids at ordinary dilutions, *i.e.* they yield only one hydrogen ion, and consequently in calculating K for them, may be treated as monobasic acids.

(iv) *Determine the Molecular Conductivity and Degree of Ionisation of Hydrochloric Acid.* In this experiment a conductivity vessel of the type illustrated in Fig. 14 must be used. Make up a semi-normal solution of hydrochloric acid and measure its conductivity by the method already described. Dilute the solution in the way described in the previous experiment, until further dilution makes no difference in the value of μ; measure the conductivity at each dilution. From the results calculate the molecular conductivity and the degree of ionisation at each dilution, taking the final measurement as the conductivity at infinite dilution. From the ionisation values calculate the value of the ionisation constant. It will be found here that the value of K is not in any sense constant. The same absence of a dissociation constant will be found for all strong electrolytes.

Basicity of Acids

Ostwald has shown that the equivalent conductivity of the sodium salts of monobasic acids increases by approximately 10 units when diluted from $\frac{N}{32}$ to $\frac{N}{1024}$; similarly the sodium salts of dibasic acids increase 20 units under the same circumstances, tribasic acids 30 units, and generally the equivalent conductivity of the sodium salts of acids increases $B \times 10$ units when they are diluted from $\frac{N}{32}$ to $\frac{N}{1024}$, where B is the basicity of the acids. This fact makes it possible, and indeed simple, to determine the basicity of an acid. The method consists in exactly neutralising a known amount of pure caustic soda solution with a solution of the acid whose basicity is to be determined, and then making up the solution with water so that the concentration shall be exactly $\frac{N}{32}$. The conductivity of the solution is then measured, the solution diluted to $\frac{N}{1024}$, and again measured. The equivalent conductivity is calculated for each dilution. If Λ_{32} is the equivalent conductivity at dilution $\frac{N}{32}$ and Λ_{1024} at $\frac{N}{1024}$, then if B is the basicity of the acid,

$$\frac{\Lambda_{1024} - \Lambda_{32}}{10} = B.$$

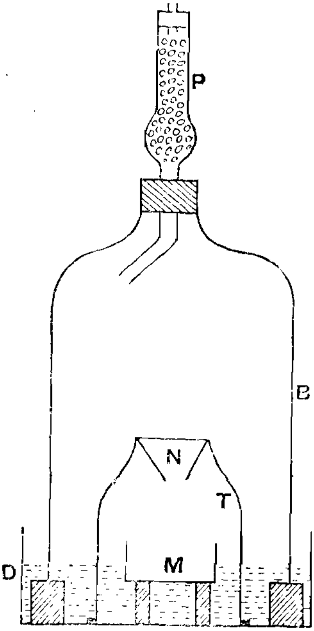

FIG. 17.

To carry out such a determination, it is absolutely essential that the caustic soda used shall be free from sodium carbonate, and consequently it must be specially prepared. This is best done in the following manner: A quantity of clean sodium, weighed roughly to correspond with the quantity of caustic soda required, is placed in a funnel of nickel gauze N (Fig. 17). The funnel is supported by a tripod T, which stands under a large glass bell-jar B. The bell-jar stands in a large glass dish D, containing water which has been made alkaline with caustic soda. The bell-jar is closed by a soda-lime tube P, bent, as indicated in the diagram, to prevent any water which may condense upon it from dropping on the sodium. In this the sodium is acted on by water vapour and converted into caustic soda solution, in an atmosphere which is entirely free from carbon-dioxide. The solution of caustic soda drips, as quickly as formed, into a nickel dish M, placed on a tripod stand beneath it. When the sodium has all reacted, the caustic soda is quickly transferred to a stoppered bottle and sufficient conductivity water added to make it about $\frac{N}{10}$.

EXPERIMENT

(i) *Determine the Basicity of Citric Acid.* Determine the exact strength of the caustic soda solution prepared by the method described above, by titration with an $\frac{N}{10}$ oxalic acid solution. Then place just so much of the caustic soda solution in a 100 c.c. graduated flask as will make an $\frac{N}{32}$ solution when the flask is filled up to the mark. Add one drop of phenol-phthalein solution, and then add a strong solution of citric acid, made up with conductivity water, to the flask from a burette, until the caustic soda is just neutralised, *i.e.* until the colour of the phenol-phthalein is discharged. It is better to have a drop too much of the acid rather than leave any of the alkali unneutralised. Add conductivity water to make up to 100 c.c. This then constitutes an $\frac{N}{32}$ solution of sodium citrate. Place 20 c.c. of this solution in a vessel of the type A (Fig. 13), measure the conductivity and then dilute to $\frac{N}{1024}$ as indicated above, using two 10 c.c. pipettes, one for withdrawal of the solution and the other for the addition of water. Measure the conductivity of the dilute solution, and calculate the equivalent conductivity of both solutions. From the data thus obtained calculate the basicity of the acid. The experiment may be repeated, using one of the following acids: tartaric, succinic, oxalic, phthalic or malic acid.

Determination of the Relative Strengths of Acids and Bases. The strength of an acid or a base depends upon its degree of ionisation; thus acids which are equally ionised are equally strong, and consequently since all acids are completely ionised at infinite dilution, all acids must be equally strong at this dilution. Ostwald has shown that for weak binary electrolytes, the product of the concentrations of the two ions, divided by the concentration of the undissociated part, gives a constant value. This constant has been termed the "affinity constant," or, as we have seen above, the dissociation or ionisation constant. The strengths of the acids are proportional to their affinity constants, hence if the affinity constants of a series of acids be determined, they will furnish a measure of the relative strengths of the acids. This, of course, only for weak acids, since the strong acids do not obey the Ostwald Law, and consequently do not yield an affinity constant in this way.

EXPERIMENTS

(i) *Determine the Relative Strengths of Acetic, Mono-chloracetic, Di-chloracetic, and Tri-chloracetic Acids.* Prepare $\frac{N}{16}$ solutions of the four acids, and determine the molecular conductivity at dilutions $\frac{N}{16}$, $\frac{N}{32}$, $\frac{N}{64}$, $\frac{N}{128}$ and

$\frac{N}{256}$. Calculate the affinity constant from the degree of ionisation at each dilution, and take the mean value of K as the value for each acid. The strengths of the acids will be directly proportional to the affinity constants. Thus calling the strength of acetic acid unity, the relative strengths of the other acids may be calculated thus:

$$\text{Relative strength} = \frac{K_1}{K},$$

where K is the affinity constant of acetic acid, and K_1 that of the other acid.

The values of μ_∞, at 25°, necessary for the calculation, may be taken as acetic acid = 389, mono-chloracetic acid = 382, di-chloracetic acid = 391, and tri-chloracetic acid = 380.

(ii) *Determine the Influence of the Substitution of various Substituents for Hydrogen on the Strength of Benzoic Acid.* This experiment is to be carried out exactly in the same way as the previous one. A series of acids must be made up with conductivity water, and their molecular conductivities determined at a series of known concentrations. From the results calculate α and K for each acid, and so obtain their relative strengths, from which the influence of the various substituting groups will be apparent. A series of acids suitable for this experiment is given in the table below, together with their conductivities at infinite dilution, and the strengths of the solutions which should be measured. It is not suggested that all these acids be measured, but a few picked out. As an example, the influence of the hydroxyl group in the ortho, meta, and para positions may be examined.

Acid.	μ_∞ at 25°.	Concentrations to be measured.
Benzoic,	381	$\frac{N}{64} \ldots\ldots\ldots \frac{N}{1024}$
o-Hydroxy-benzoic,	381	$\frac{N}{64} \ldots\ldots\ldots \frac{N}{1024}$
m-Hydroxy-benzoic,	380	$\frac{N}{32} \ldots\ldots\ldots \frac{N}{1024}$
p-Hydroxy-benzoic,	379	$\frac{N}{32} \ldots\ldots\ldots \frac{N}{1024}$
o-Toluic,	375	$\frac{N}{128} \ldots\ldots\ldots \frac{N}{1024}$
m-Toluic,	379	$\frac{N}{128} \ldots\ldots\ldots \frac{N}{1024}$
p-Toluic,	379	$\frac{N}{256} \ldots\ldots\ldots \frac{N}{1024}$
o-Nitro-benzoic,	380	$\frac{N}{128} \ldots\ldots\ldots \frac{N}{1024}$
m-Nitro-benzoic,	379	$\frac{N}{64} \ldots\ldots\ldots \frac{N}{1024}$
p-Nitro-benzoic,	376	$\frac{N}{128} \ldots\ldots\ldots \frac{N}{1024}$
o-Chloro-benzoic,	383	$\frac{N}{64} \ldots\ldots\ldots \frac{N}{1024}$
m-Chloro-benzoic,	380	$\frac{N}{256} \ldots\ldots\ldots \frac{N}{1024}$
p-Chloro-benzoic,	379	$\frac{N}{2048}$

Use of Electro-conductivity in Volumetric Analysis

Conductivity of a solution is due to the number and the velocity of the ions present in the solution (see Chapter IV.). If the conductivity of a base, such as caustic soda, be considered, it will be seen to be due to the cation and the rapidly moving hydroxyl ions. Should a small quantity of an acid be added, a number of the hydroxyl ions will combine with the hydrogen ions of the acid to form unionised water molecules, and a quantity of anions of the acid, which have a much smaller velocity than the hydroxyl ions, will take the place of the hydroxyl ions. The conductivity of the solution will therefore decrease, and if successive quantities of acid be added the conductivity will continue to decrease until all the alkali has been neutralised; a further addition of acid will now cause the conductivity to increase again, due to the introduction of a quantity of rapidly moving hydrogen ions. Hence, if the conductivity of a solution of a base be plotted after each addition of acid against the quantities of acid added, a curve will be obtained which will change its direction suddenly, *i.e.* it will have a distinct minimum. The minimum represents the point at which the alkali is exactly neutralised, and consequently serves as an indicator of the end of the titration. In this method of titration either the acid or alkali may be placed in the conductivity vessel if they are both strong, but if the acid is weak then the alkali should be placed in the conductivity vessel and the acid added to it.

EXPERIMENT

Determine the Strength of a given Solution of Caustic Soda by means of Hydrochloric Acid. Place 10 c.c. of pure caustic soda solution in a conductivity of type A (Fig. 13); insert a resistance in the resistance box so that the point of minimum sound is in the middle of the bridge wire. Now run in an $\frac{N}{10}$ solution of hydrochloric acid from a burette, adding 1 c.c. at a time; after each addition thoroughly mix the solution, and redetermine the point of balance on the bridge. It will be found at first that the sliding contact will have to be moved continuously toward the zero end of the bridge wire. After several additions have been made, the point of balance will move back toward the centre of the bridge. Make several determinations after the turning point has been reached, and plot the bridge readings as ordinates against the number of cubic centimetres of acid added as abscissae. Draw curves through the points obtained before and after the turning point. The intersection of these curves will give the quantity of $\frac{\mathrm{N}}{10}$ hydrochloric acid required to neutralise the caustic soda in the conductivity vessel. This method of titration is particularly useful in determining the amount of acid in highly coloured liquids, such as vinegars and wines.

Determination of the Solubility of Sparingly soluble Salts. The solubility of many substances, such as silver chloride, barium sulphate, etc., cannot be easily determined by the ordinary analytical methods. It may, however, be determined from the conductivity of saturated solutions of these substances in the following way. The conductivity of a saturated solution of a sparingly soluble salt is measured in the usual manner. Let R be the resistance of the solution. Then $\frac{\mathrm{N}}{\mathrm{R}}$ is the specific conductivity if N is the cell constant. If now v is the number of cubic centimetres of the solution which would contain 1 gram molecule of the dissolved substance

$$\mu_v = \frac{\mathrm{N}}{\mathrm{R}} v,$$

i.e. the product of the specific conductivity and the dilution gives the molecular conductivity at the dilution v. The solution, however, is so very dilute that the dilution v is identical with infinite dilution, *i.e.* the dissolved substance may be regarded as completely dissociated.

Hence $$\mu_\infty = \mu_v = \frac{\mathrm{N}}{\mathrm{R}} v.$$

The values of N and R are known, and the value of μ_∞ is the sum of the ionic conductivities of the ions of the salt (see Chapter IV.), hence μ_∞ is known. Hence v the volume of water in cubic centimetres which contains one gram molecule of the dissolved substance, *i.e.* the solubility, is known.

In many cases sparingly soluble salts of weak acids and bases are hydrolysed in solution, so that in these cases hydrolysis must be taken into account in calculating the solubility. Thus if a carbonate of one of the alkaline earth metals is under consideration, this substance will hydrolyse in solution, giving the hydroxide, which is much more soluble than the carbonate, and unionised carbonic acid. This may be prevented by driving the hydrolysis back by the addition of hydroxyl ions in the form of dilute caustic soda. So that the solubility is determined in a dilute solution of caustic soda, and not in pure water, and calculated from the increase in the conductivity of a dilute solution of caustic soda due to the solution of the alkaline carbonate in it.

EXPERIMENT

Determine the Solubility of Barium Sulphate in Water at 25°. This determination must be carried out in a conductivity vessel provided with fairly large electrodes which are not far apart. Determine, first of all, the specific conductivity of the water to be used in the experiment. Then grind up a quantity of barium sulphate to a very fine powder in an agate mortar. Place the powder in a 125 c.c. glass flask, which has been steamed out, and add a quantity of conductivity water, shake well and allow the solid to settle. Pour the liquid away, and repeat the operation 3 or 4 times to dissolve out any soluble impurities. Then make up the solution for measurement by adding conductivity water to the washed powder, shaking and allowing the heavier particles to settle. The whole process must be carried out at 25°. Pour a quantity of the still turbid liquid into the conductivity vessel and measure the conductivity. Repeat the measurement until two fresh portions of the solution give the same value. The solubility may now be calculated as follows.

If κ_0 represents the specific conductivity of the water used in the experiment, and κ_1 that of the solution, then $(\kappa_1 - \kappa_0) = \kappa$, the specific conductivity of the solution corrected for the conductivity of the water. The specific conductivity multiplied by v will give the equivalent conductivity, where v is the number of cubic centimetres of solution, containing 1 gram equivalent of barium sulphate

$$\Lambda_v = \kappa v.$$

In such a dilute solution only a very small error will be introduced by assuming that $\Lambda_v = \Lambda_\infty$.

The value of Λ_∞ at 25° for barium sulphate is 155·3.

Hence
$$v = \frac{155{\cdot}3}{\kappa},$$

i.e. v c.c. contain 1 gram equivalent of barium sulphate. Hence 1 litre of solution contains $\frac{500}{v}$ gram molecules of barium sulphate or $\frac{116{\cdot}5}{v} \times 1000$ grams.

Further experiment may be made with the following substances: Silver chloride ($\mu^{25}_\infty = 140{\cdot}2$), barium oxalate ($\mu^{25}_\infty = 140{\cdot}0$), silver iodide ($\mu^{25}_\infty = 140{\cdot}4$) and lead sulphate ($\mu^{25}_\infty = 151{\cdot}5$).

CHAPTER IV

TRANSPORT NUMBERS AND VELOCITY OF IONS

WHEN an electric current has been passed through an electrolyte for a time, it is generally found that the concentration of the dissolved substance differs from the original concentration, and further that the concentration at the two electrodes is not the same. Further if a current be passed through a cell divided by two porous walls *c* and *d*, as in Fig. 18, it is often found that, while the concentration in the middle compartment remains the same as it originally was, both of the electrode sections become less concentrated than they were originally, but not to the same extent. It is known that a current is carried across a solution by means of the ions, the positive ions or cations moving toward the negative electrode or cathode and the negative ions or anions toward the positive electrode or anode. It is also known that the number of anions

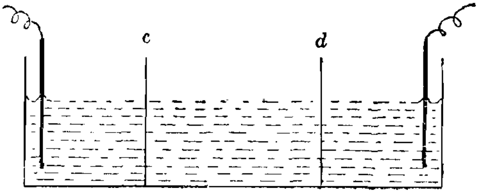

FIG. 18.

and cations discharged at the electrodes is identical. Hence an explanation of the changes in the concentration at the electrodes has been found in the hypothesis that the ions move across the solution at different rates, *i.e.* they have different velocities. From this it follows that in the passage of a current across an electrolyte, a number of cations will leave the anode portion of the cell and be discharged at the cathode in the same time that an entirely different number of anions leave the cathode portion of the cell and are discharged at the anode. These numbers, however, do not represent the whole of the ions discharged at the electrodes, for the cations travelling from the anode half of the cell leave behind them an equal number of anions, which are also discharged at the anode, and in the same way the anions, moving away from the cathode portion of the cell, leave behind them an equal number of cations which are discharged at the cathode, thus making the total number of anions discharged at the anode equal to the total number of cations discharged at the cathode. Since the ions travel or migrate at different velocities it follows that the quantity of electricity carried by the anions in one direction differs from the quantity carried by the cations in the other direction. The two quantities are indeed in the ratio of the respective velocities. Hence, if u be the migration velocity of the cation, and v that of the anion, $u+v$ is proportional to the total current carried, and $\frac{u}{u+v}$ represents the fraction of the total current carried by the cation, and $\frac{v}{u+v}$ the fraction carried by the anion.

Hittorf has termed these fractions the **Transport Numbers** n_c and n_a, where n_c is that of the cation and

n_a that of the anion. Hence

$$n_c = \frac{u}{u+v} \text{ and } n_a = 1 - n_c = \frac{v}{u+v}.$$

If one gram equivalent of a salt is dissolved in water and ionised to an amount a, then it follows that there are present in the solution a equivalents of both anion and cation. If a current is passed through such a solution under unit fall of potential the current density may be expressed by

$$96540a(u+v),$$

where u and v are the migration velocities of the cation and anion respectively, and 96540 represents the charge in coulombs on a gram equivalent of ions. This expression is the equivalent conductivity, hence

$$\Lambda = 96540a(u+v).$$

Since the total conductivity is made up of the conductivities of the two ions, it follows, if l_a and l_c represent the ionic conductivities or mobilities of the anion and cation respectively, that

$$\Lambda = l_a + l_c$$

and $$l_a = 96540av; \quad l_c = 96540au.$$

Hence $$l_a = \Lambda \frac{v}{u+v} = \Lambda n_a; \quad l_c = \Lambda \frac{u}{u+v} = \Lambda n_c,$$

so that if the transport numbers are known the ionic conductivities follow at once from the equivalent conductivity. The calculation may be taken a step further; if l_a and l_c have been determined, we have the expressions

$$av = \frac{l_a}{96540} \text{ and } au = \frac{l_c}{96540},$$

i.e. the actual velocities of the anion and cation in cms. per second can be calculated if a the degree of dissociation is known. This may be regarded in another way, if instead of a representing the degree of ionisation in the ordinary sense of the fraction of the molecules which are split up, it represents, what is really the same thing, the fraction of time during which the ions are dissociated, *i.e.* the period during which they are free. Then av and au represent the average velocities of the ions for the whole time, whether they are free or combined. Should the solution under consideration be completely dissociated, *i.e.* be at infinite dilution, then $a=1$, and the velocities of the ions in cms. per second are given by

$$v=\frac{l_a}{96540} \quad \text{and} \quad u=\frac{l_c}{96540}.$$

The values l_a and l_c for an anion or cation are always the same, no matter what the cation or anion is with which they are respectively combined. Hence it follows that the equivalent conductivity of an electrolyte at any given dilution may be calculated from the values of l_a and l_c of the two ions, furnished by the substance in question. In the case of weak organic acids, it is experimentally impossible to determine directly the equivalent conductivity at infinite dilution; this quantity may, however, always be calculated from the ionic conductivities.

Thus, let Λ_∞ represent the equivalent conductivity at infinite dilution of the weak acid HA. This is made up of the ionic conductivities of $H^{\cdot}$ and A' ions, and if these are known, the equivalent conductivity at infinite dilution is obtained by adding the two values together, thus:

$$\Lambda_\infty = l_a\ (\text{for } A') + l_c\ (\text{for } H^{\cdot}).$$

If the value l_a for A' ions is unknown, it may be obtained in the following way. The equivalent conductivities of the sodium salt of the weak acid, the sodium salt of a strong acid, *e.g.* NaCl, and the strong acid itself, are measured at infinite dilution, which, since these substances are all very much ionised, is a simple operation. Let now Λ'_∞, Λ''_∞ and Λ'''_∞ represent the equivalent conductivities of these substances respectively, then,

$$\Lambda'_\infty = l_a \text{ (for A}') + l_c \text{ (for Na}^\cdot),$$
$$\Lambda''_\infty = l_a \text{ (for Cl}') + l_c \text{ (for Na}^\cdot),$$
$$\Lambda'''_\infty = l_a \text{ (for Cl}') + l_c \text{ (for H}^\cdot).$$

Combining these three expressions, the following equation is obtained:

$$\Lambda'''_\infty - \Lambda''_\infty + \Lambda'_\infty = l_c \text{ (for H}^\cdot) + l_a \text{ (for A}'),$$

i.e. $$\Lambda'''_\infty - \Lambda''_\infty + \Lambda'_\infty = \Lambda_\infty \text{ for HA};$$

and since l_c (for $H^\cdot$) is known, l_a for A' ion follows.

1. Determination of Transport Numbers

The transport number of an ion may be determined by allowing an accurately measured quantity of electricity to pass through a solution of known concentration, and measuring the change in concentration which has occurred at one of the electrodes. The method presupposes that the change in concentration has all occurred at the electrodes, and that none of it is due to diffusion. Hence it is usual to allow the current to pass for a short time only, and to keep the apparatus cool.

EXPERIMENTS

(i) *Determine the Transport Numbers of the Silver Ion and the Nitrate Ion.* This experiment is carried out in a piece of apparatus designed as shown in Fig. 19. It consists of two tubes, A and B, of about 1·5 cms. diameter, connected by a short tube, H, of the same diameter. The tube A is about 18 cms. long, and is fitted at the bottom with a stopcock T; the tube B is about 12 cms. long. Two electrodes, C and D, are fitted into these tubes by means of corks. The electrode C consists of a stout silver wire, cemented into a glass tube so that only the projecting end *e*, which is wound into a spiral, comes in contact with the liquid. The electrode D consists of a copper wire, similarly protected from the liquid at all but its lower end. To carry out the experiment, make up a solution of silver nitrate, approximately $\frac{N}{20}$, and determine its concentration by weighing out about 20 grams of the solution and titrating with a standard solution of ammonium thiocyanate, using a saturated solution of ferric alum as indicator. Then prepare a small quantity, about 50 c.c., of a saturated solution of copper nitrate, and acidify it slightly with nitric acid. Place about 8 c.c. of the copper nitrate solution in the tube B, so that it fills the tube to a depth of about 5 cms. Then cautiously add the silver nitrate solution to both tubes, taking care that the silver and copper solutions do not mix. This is best done by filling a dry pipette with the silver nitrate solution, placing the point of the pipette against the wall of the tube B just above the surface of the copper nitrate, and allowing the solution to flow slowly from the pipette into the tube, raising the pipette continuously, as the level of the liquid rises, until the tube is full. Then fill the tube A and the cross

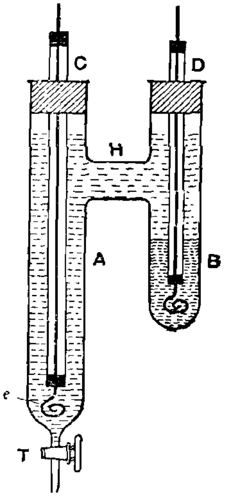

FIG. 19.

tube H with silver nitrate solution, weigh the silver electrode, and insert the electrodes as indicated in the diagram. Connect the electrodes, through a milliammeter, an adjustable resistance, a switch and a voltameter, with a battery of 25–30 accumulator cells. The current strength used in the experiment should be about 10 milliamperes; this is obtained by means of the adjustable resistance, the ammeter being used to indicate when the right current has been obtained. Should a battery of 25–30 cells be unobtainable, the lighting circuit may be used in place of it by having a correspondingly large adjustable resistance in the circuit. The voltameter is inserted in the circuit to measure the total quantity of electricity passed through the circuit. The most suitable voltameter for this purpose consists of two stout copper plates, *a*, *b* (Fig. 20), 5 cms. wide and 2·5 cms. deep, which are immersed in a dish containing a solution of copper sulphate. The plate constituting the cathode is cleaned by immersing in dilute nitric acid, washed with distilled water and alcohol, and dried by passing it through the hot air above a bunsen flame. It is weighed before the experiment, and again after the experiment, the difference in weight giving the amount of copper

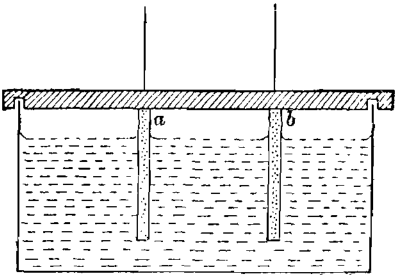

Fig. 20.

deposited, from which the quantity of current can be calculated.

The solution to be used in the voltameter should be made up by dissolving 15 grams of crystallised copper sulphate in 100 c.c. of water, and adding to it 5 c.c. of concentrated sulphuric acid and 5 c.c. of absolute alcohol. A slow current of carbon-dioxide should be bubbled through the solution in the voltameter during the experiment.

When all is fitted up, and the weighings of the silver anode of the experimental vessel and the cathode of the voltameter have been made, switch on the current, and allow it to flow for 1½–3 hours. A more prolonged passage of the current will probably cause a change in the concentration of the middle portion of the liquid, which, as has already been shown, must not take place. Stop the current, and run off the solution from **A** into two weighed flasks, about ⅔ being run into the first flask and ⅓ into the second. The latter quantity will constitute the middle portion of the liquid, and the success of the experiment depends upon its concentration being the original concentration of the solution before the experiment was begun. Remove the anode, wash it with water and alcohol, dry by passing it through the hot air above a bunsen flame, and weigh it. Treat the cathode of the voltameter similarly. Then weigh the two quantities of solution which have been run from **A**, and titrate them with a standard solution of ammonium thiocyanate. The transport numbers can now be calculated as follows:

Suppose a grams of the original solution contain b grams of silver nitrate,

i.e. $(a-b)$ grams of water contain b grams of silver nitrate, or $\frac{b}{170\cdot0}$ equivalents of silver.

After the experiment, let c grams of the solution contain d grams of silver nitrate, *i.e.* $(c-d)$ grams of water contain d grams of silver nitrate, or $\frac{d}{170{\cdot}0}$ equivalents of silver.

If the solution had remained unchanged $(c-d)$ grams of water would have contained

$$\frac{(c-d)}{(a-b)}\,\frac{b}{170}\text{ equivalents of silver.}$$

Hence the solution has changed by an amount

$$\frac{d}{170}-\frac{b}{170}\cdot\frac{(c-d)}{(a-b)}\text{ equivalents.}$$

This will be found experimentally to be an increase. If the experiment has been carried out successfully, this amount should represent the total change at the anode. If the voltameter cathode has increased by w grams, then $\frac{w}{31{\cdot}5}$ represents the number of equivalents of copper which have been deposited; this is proportional to the total current used in the experiment, and is equal to the number of equivalents of silver dissolved from the anode, as may be confirmed from the weighings of the anode before and after the experiment. Had no silver wandered from the anode, the solution round the anode should contain $\frac{w}{31{\cdot}5}$ equivalents more than it originally did; experimentally it is found to contain

$$\frac{d}{170}-\frac{b}{170}\left(\frac{c-d}{a-b}\right)$$

more than it originally did; we can call this quantity y. Hence $\frac{w}{31{\cdot}5}-y$ equivalents of silver must have wandered from the anode compartment.

This means that of the total current carried through the solution, represented by $\frac{w}{31 \cdot 5}$ equivalents, $\left(\frac{w}{31 \cdot 5} - y\right)$ was carried by the cations. Since the transport number of the cation is the fraction of the total current carried by the cations,

$$n_c = \frac{\frac{w}{31 \cdot 5} - y}{\frac{w}{31 \cdot 5}},$$

and $n_a = 1 - n_c$.

(ii) *Determine the Transport Numbers of Potassium and Chlorine Ions.* In this experiment it is impossible to use an electrode of the same material as the cation. The difficulty is surmounted by using an anode of amalgamated cadmium. Fit up the apparatus as described in the last experiment, substituting a rod of cadmium, whose surface has been amalgamated by first cleaning with dilute nitric acid, and then dipping into mercurous nitrate solution, for the silver anode. Wash and dry the cadmium electrode, which need not be weighed. Fill the apparatus as described in the last experiment, substituting an $\frac{N}{2}$ solution of potassium chloride for the silver nitrate solution. Fit up the copper voltameter and make all the connections as described above. Allow a current of about 10 milliamperes to flow for about two hours. Then analyse the liquid in the anode compartment by titration with $\frac{N}{2}$ silver nitrate solution, and calculate the number of equivalents of chlorine contained in the solution. If w be the number of equivalents of copper deposited in the voltameter, a the initial number of equivalents of chlorine contained in the potassium chloride solution, and b the number after the experiment, then b is made up of a and a quantity c which has wandered into the anode compartment,

$$i.e.\ c=b-a.$$

There has been no loss of chlorine from this part of the cell, for the chlorine ions discharged at the anode have combined with the cadmium and come back into the solution. Hence the fraction of the total current carried by the chlorine ions is given by

$$n_a=\frac{b-a}{w},$$

where n_a is the transport number of the chlorine ion, and $n_c=1-n_a$ is the transport number of the cation. Calculate the absolute velocities and ionic conductivities of the chlorine and potassium ions, being given μ_∞ at 25° for potassium chloride $=130{\cdot}2$ and $\mu_{\frac{N}{2}}=102{\cdot}3$ at 25°. For method of calculation see introduction to this chapter.

2. Direct Determination of the Absolute Velocity of Ions

Methods for the direct determination of the velocities of ions have been devised by Lodge (B.A. reports, 1886, p. 389), Whetham (*Phil. Trans. A.* clxxxiv., 337, 1893; clxxxvi., 507, 1897, *Phil. Mag.*, Oct. 1904), Orme Masson (*Phil. Trans. A.* cxcii., 311, 1899), and Steele (*Phil. Trans. A.* cxcviii., 105).

(i) *Lodge's Method.* The method due to Lodge consists in measuring the rate at which the colour of a faintly alkaline phenol-phthalein solution is discharged by hydrogen ions travelling under a measured electromotive force.

The determination is carried out in the following manner: a horizontal tube A, Fig. 21, about 40 cms. long and 1 cm. internal diameter, fitted at each end with a wider, short, right-angled piece of glass tube, B, B, as indicated in the diagram, is filled with a solution of potassium chloride in a 10 per cent. agar-agar jelly, which is rendered faintly alkaline by the addition of a few drops of 10 per cent. caustic soda solution, and coloured by one or two drops of phenol-phthalein solution. The jelly solution is poured into the straight tube while still warm and allowed to solidify. Then the vertical tubes, at the ends, are filled with dilute sulphuric acid and a current passed by means of two platinum electrodes, *a*, *b*, placed in the acid. As the hydrogen ion proceeds along the tube, in its migration toward the cathode, it discharges the colour of the jelly; the rate at which this happens gives the velocity of the hydrogen ions under the potential fall between the electrodes.

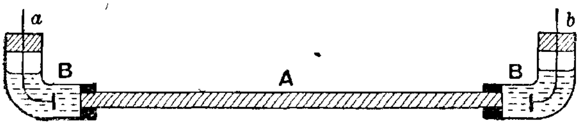

FIG. 21.

EXPERIMENT

Determine the Absolute Velocity of the Hydrogen Ions. Fit a glass tube A of uniform bore, about 60 cms. long and 1·5 cms. diameter, with small right-angled glass cups B, as indicated in Fig. 21. Place corks in the cups to carry the platinum electrodes *a* and *b*, and bore small holes in the corks to allow the escape of any gas which may be generated during the experiment. Fill the horizontal tube with a jelly solution of potassiu chloride made up in the following manner. Weig out roughly 16–17 grams of dry agar-agar, and plac it in a 5 per cent. solution of acetic acid until it ha completely swelled out; this usually requires about a hour. Then pour off the solution and wash until al the acetic acid has been removed. This is best don by shaking up with two or three quantities of wate and then allowing to stand with two separate quantitie of water for half an hour. Squeeze out all wate possible and add 250 c.c. of a solution of potassiu chloride, containing 28 grams per litre. Place in

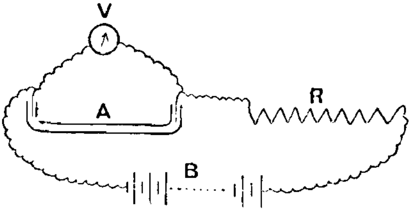

Fig. 22.

water bath and warm until an homogeneous solution ha been obtained, then add 2–3 drops of phenol-phthalei solution, and add a solution of caustic potash drop b drop until the solution shows a full red colour. Fil the tube **A** with the jelly while it is still liquid an allow to cool when the jelly will set. Place the en pieces **B** in position, and fill them with $\frac{N}{2}$ sulphuric acid Then place the electrodes in position so that the plate are as near the ends of **A** as possible. Connect th electrodes through an adjustable resistance **R** (Fig. 22 with a battery **B** of 30–40 cells. Place a voltmeter **V** across the electrodes and adjust the resistance so that th voltmeter reads just as many volts as the distance between the electrodes in centimetres. This will give a fall of potential along the tube of 1 volt per cm. Now mark the red boundary at the anode end of the tube and allow the current to flow for 60 minutes. Measure the displacement of the red boundary; this will give directly the velocity of the hydrogen ion in centimetres per hour. Calculate to centimetres per second. If the jelly tends to melt during the experiment, due to the heating effect of the current, the tube should be immersed in cold water.

2. *Whetham's Method.* The remaining methods, although much more accurate than the foregoing method, are not suitable for use in the hands of any but expert experimenters. They may, however, be described here, and sufficient detail will be given to allow of advanced students carrying out the determination should they so desire.

Whetham superposed two solutions, *a* and *b*, Fig. 23, having a common ion, in a vertical tube CD. The two solutions were of the same equivalent concentration, and of almost the same specific resistance, but of different densities, and one solution was coloured. Thus, for example, the two substances, potassium carbonate and potassium bichromate, were taken and a current passed; *the anions* wandered toward the positive electrode, and the coloured boundary slowly progressed in the same direction; the rate of movement of the coloured boundary gave

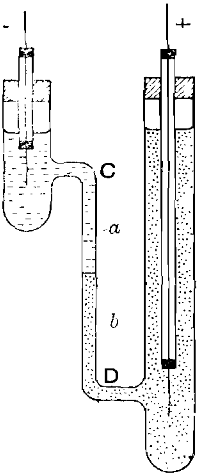

FIG. 23.

the rate of movement of the bichromate ions under the potential gradient of the experiment. The success of experiments of this type depends on the maintenance of a sharp boundary between the two solutions. Whetham has shown that a sharp boundary may always be preserved if the current flows in such a direction that of the two different ions the relatively slower ion follows the relatively faster ion, *i.e.* in the example just considered the slower carbonate ion follows the somewhat faster bichromate ion. The reason for this will be clear from the following consideration. Suppose there are superposed in a tube two solutions of salts of the same anion, but of different cations, one solution having a high conductivity and the other a low conductivity. Then on passing a current there will be a relatively low potential gradient in the solution of high conductivity, and in the solution of low conductivity there will be a relatively high potential gradient.

Assume now that the current is passing from the solution of low conductivity to that of high conductivity, then a cation which chances to get ahead of the boundary line of the two solutions will find itself in a region of low potential gradient, and its velocity will be decreased so that it will drop back to the boundary. On the other hand, a fast moving cation, which finds itself behind the boundary, will be in a region of higher potential gradient and will consequently move still faster and be pushed forward to the boundary, so that the boundary line will be kept sharp.

Suppose, now, that the current flows in the opposite direction, *i.e.* from the liquid of high conductivity to that of low conductivity, then a slow moving cation, remaining behind the boundary, will be in a region of low potential gradient, and be still further retarded, whilst a quick moving cation, finding itself ahead of the boundary, will have passed into a region of high potential gradient, and thus be hastened forward, the result being a blurring of the boundary line.

From the foregoing it follows that when a current passes from a solution of high conductivity to one of low conductivity, the potential gradient adjusts itself so that the actual velocity of the specifically slower ion under the high potential gradient is the same as that of the specifically faster ion under the lower potential gradient. Hence the rate of motion of the coloured boundary gives the velocity of both ions, but under different potential gradients.

3. *Orme Masson's Method.* Orme Masson, making use of the foregoing facts, has devised a more accurate method of determining the velocities of ions. In outline the method is as follows. A tube, AB (Fig. 24), about

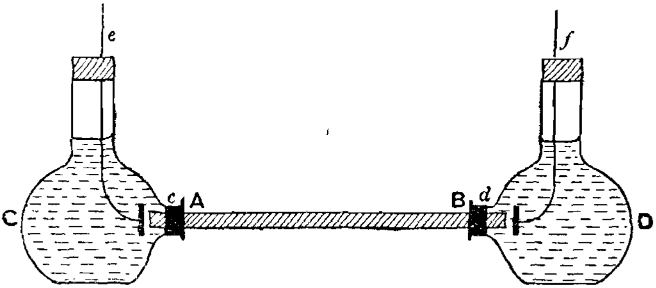

FIG. 24.

40 cms. long, was filled with a gelatine solution of the salt, the velocities of whose ions were to be measured. This tube was then inserted into the side tubes, *c*, *d*, of two flasks, C, D. A gelatine solution of a salt having a coloured cation was placed in the flask C, and a gelatine solution of a salt having a coloured anion was placed in

the flask **D.** The coloured ions must be so chosen that they are specifically slower than the corresponding ions of the solution in **AB.** Thus, in an experiment, potassium chloride was placed in **AB**, copper sulphate in **C**, and potassium bichromate in **D.** Two platinum electrodes, *e*, *f*, were then placed in the flasks and a current passed. The rates at which the coloured boundaries advanced up the tube were measured, and these gave directly the velocities of the potassium and chlorine ions under the potential gradient existent in **AB.**

4. *Steele's Method.* Steele has improved the method of Orme Masson, by showing that the boundary between two solutions can be followed without the use of coloured ions, and, further, by making the measurements in

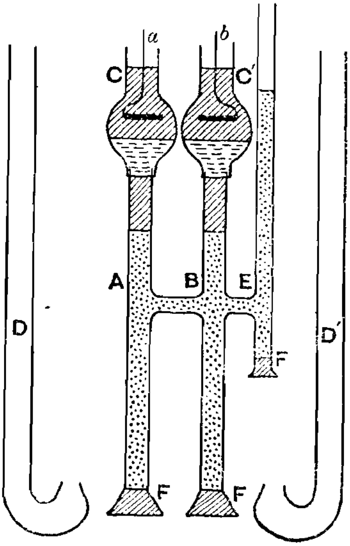

FIG. 25.

aqueous solution, thus removing the objections made to the use of jelly solutions. The apparatus used by Steele is given in Fig. 25, and consists of two tubes, A, B, of the same diameter (about 1 cm.) connected together by a cross tube of slightly larger diameter than A and B. A side tube E is fitted to the tube B. The upper and lower ends of A and B are ground to fit the tubes, C, C′ and D, D′, respectively. The method consists in half filling the bulbs, C, C′, with a gelatine solution of substances which shall serve as indicators, *i.e.* which will produce a boundary line with the solution to be measured. The rubber stoppers, F, F, are then placed in the ends of the tubes, and the solution, whose ions are to be measured, is run in through E. When the tubes are full the bulbs, C, C′, are placed firmly in position; the tube E is then filled with the solution to such a height that the pressure is atmospheric. A quantity of an aqueous solution of the salts in C and C′ is then placed above the jellies, and two electrodes, *a*, *b*, are inserted, which are made of such metal that no gas will be evolved when the current is passed. The current is then passed until the boundary line is visible in the aqueous solution. The position of the boundary line is quite visible because of the difference in the coefficient of refraction of the two liquids. The positions of the boundary lines are then noted, and the rate at which they move gives the velocity of the ions of the solution under the potential gradient existing in the solution. It will be seen that the jelly solutions have nothing to do with the measurement, and serve simply to get a definite boundary at the commencement of the experiment, and to prevent a displacement of the solution. The indicator liquids must have ions which move specifically slower than the ions of the solution which they are following up. Thus in an experiment Steele measured the velocity of the ions of potassium chloride, and used as indicators lithium chloride for the cation, and sodium acetate for the anion, the lithium and acetate ions being respectively slower than the potassium and chlorine ions. When the aqueous solutions of the indicators are specifically heavier than the solution to be measured, the jellies and the electrodes are placed in the tubes, D, D′, which are then attached to the apparatus instead of the bulbs, C, C′.

CHAPTER V

DIELECTRIC CONSTANTS

EVERY substance behaves in two different ways toward an electric stress, which are respectively defined by two constants, (i) the electric conductivity and (ii) the dielectric constant. The former, as has already been seen, is a measure of the capacity of a substance to conduct electricity, whilst the latter may be defined as the power of a substance to transmit an electrostatic force across a space. The relationships existing between the dielectric constants of liquids and their power of dissociating substances dissolved in them on the one hand, and the connection between the dielectric constant, power of absorption of electric waves, and chemical constitution on the other, justify a short description of the methods in use for the determination of the dielectric constant. J. J. Thomson and Nernst have shown that, generally, those liquids which possess a high dielectric constant furnish solutions which are good conductors of electricity, *i.e.* exercise considerable ionising power, whilst those of low dielectric constant furnish solutions which do not conduct electricity, *i.e.* do not ionise. This is, however, not an absolute rule, and, further, different solvents do not act in the same way with all electrolytes. Thus, for example, acetone (dielectric constant 20·7) dissociates potassium chloride to a moderate extent, but it hardly dissociates hydrochloric acid at all, whereas both substances are about equally dissociated by water.

Any method of determining the dielectric constant suitable for chemical purposes must be capable of dealing with substances which are not perfect insulators, *i.e.* with substances which conduct electricity to some extent. Further, the method must be capable of dealing with relatively small quantities of substances. The methods due to Nernst and Drude fulfil these conditions, and are therefore the most suitable for physico-chemical purposes.

Method of Nernst. The capacity of two condensers may be compared by using a Wheatstone bridge, with telephone and induction coil by the method of Palaz, which is as follows. Two condensers, C and C′ (Fig. 26), are connected with the ends of a Wheatstone bridge, *a*, *b*, as indicated in the diagram. A telephone T, and an induction coil I, are connected in the usual manner. To make a measurement the slide contact *s* is moved until the sound minimum is obtained. When this is the case

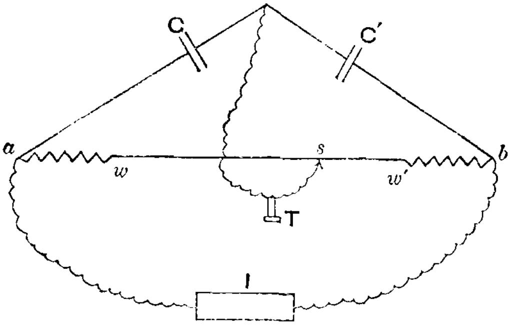

FIG. 26.

$$w' : w :: C : C',$$

where w' and w are the resistances of the two portions of the bridge, and C and C′ the capacities of the two condensers. If the capacity of one of the condensers is known then that of the other may be calculated.

If one of the condensers is made of a substance which is not a perfect insulator, it will be found impossible to obtain a sharp minimum, or indeed any minimum usable in the calculation of the capacity of the condenser made of the imperfect insulator. This difficulty may be surmounted by giving the second condenser a known conductivity of the same order as the conductivity of the imperfect insulator, by means of a parallel conducting circuit, as illustrated in Fig. 27, in which everything is the same as in the apparatus for the comparison of two perfect insulators, except the parallel circuit w'''. A point can now be obtained at which the telephone will give a good minimum, and from this not only the capacity of the cell, but also its conductivity, can be obtained. For if w'' is the resistance of the condenser C, *i.e.* the one which is not a perfect insulator, w''' the resistance of the parallel circuit to the condenser C′, w and w' the resistances of the arms of the bridge, then

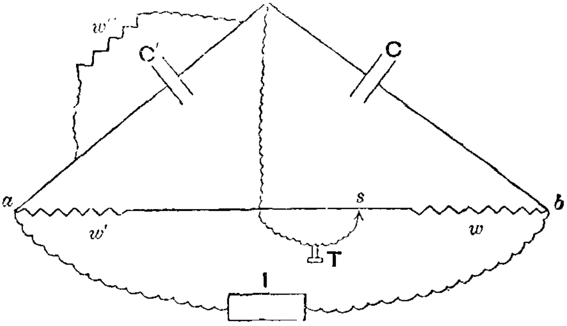

FIG. 27.

$$w : w' :: w'' : w'''$$

$$\text{and} \quad w : w' :: C' : C,$$

provided always that the resistances w, w' and w''' have a negligible capacity. It is obviously possible to obtain silence or a minimum sound in the telephone by changing the resistance w''' and the capacity C′, if the telephone leads are fixed instead of being connected to a sliding contact.

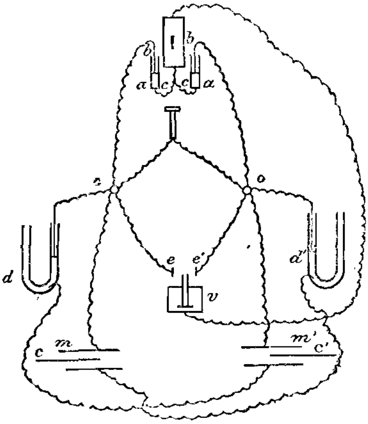

Fig. 28.

The foregoing is the principle of the Nernst method for determining the dielectric constant. The apparatus consists of two vertical glass cylinders, *a*, *a* (Fig. 28); these are fitted with platinum electrodes, *b*, *b*, furnished with binding screws. Into the base of each cylinder a platinum wire, *c*, is fused; these are connected together, and to one pole of the secondary coil of an induction coil I of the type shown in Fig. 12. The cylinders are filled with a solution containing 282 grams of mannite and 124 grams of boric acid in 1 litre of water, and constitute liquid resistances. This solution has a specific conductivity of $0{\cdot}9 \times 10^{-7}$ reciprocal ohms, and is not influenced to any great extent by changes of temperature. These resistances remain constant, and must not be changed during an experiment. The platinum electrodes, *b*, *b*, are connected to two terminals, *o*, *o*, which are mounted on glass pillars. These terminals are connected to the measuring condensers, *m*, *m′*, made of two stout brass plates, 8 cms. high and 30 cms. long, and a uniform glass plate, *c*. The glass plate may be drawn out about 20 cms. along a graduated scale to change the capacity, and so after calibration of the condenser at various positions of the glass plate, the capacity can be directly read off from the scale. The binding screws, *o*, *o*, are further connected with resistances *d*, *d′*, for compensating the conductivity of the substance under observation.

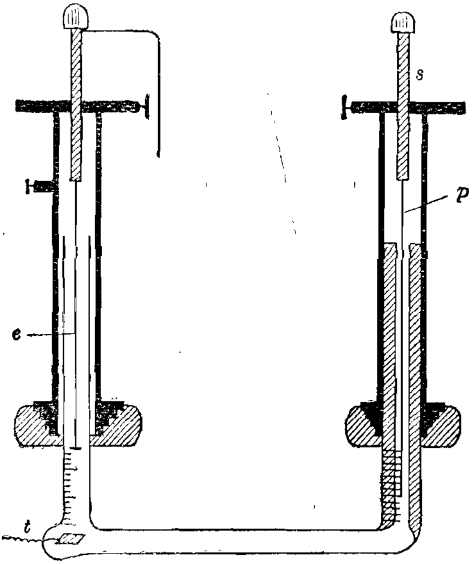

FIG. 29.

These resistances are connected at the bottom with the other plate of the opposite measuring condenser, *i.e.* *d′* with *m*, and *m′* with *d*. The compensating resistances consist of a U-tube (Fig. 29), one limb of which is a carefully graduated and calibrated capillary tube, 12 cms. long and 1 mm. diameter. This is fitted with a platinum wire, *p*, which can be raised or lowered by a definite amount by means of the micrometer screw, *s*. The other limb is 5 mm. diameter, and similarly fitted with a movable electrode, *e*. A third electrode, *t*, is fused into the bottom of the U-tube. The tube is filled with distilled water, and when a large resistance is required the capillary tube is used, whilst for smaller resistances, *i.e.* better conductivity, the wider tube is used. The vessel *v* is a small condenser in which the measurement is made; it consists of a nickel trough, A (Fig. 30), 3·6 cms. diameter and 2·7 cms. deep. It is fitted with an ebonite cover, B, through which a metal tube, C, passes; this is attached to a nickel plate, D, kept at a definite distance from the bottom of the nickel vessel by a small glass bead, E. This vessel does not require more than 2 c.c. of liquid for a measurement. The telephone, T, is attached to the two terminals, *o*, *o*, and the metal trough *v* to the free end of the induction coil. The plate of the measuring vessel may be attached to either *e* or *e'*, and in an actual measurement is connected alternately with both.

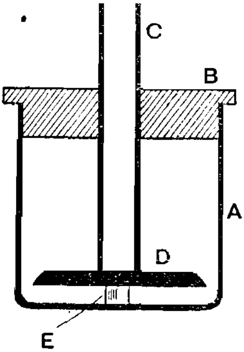

FIG. 30.

Before making a measurement the condensers *m* and *m'* must be calibrated. This is best done by placing in the empty vessel *v* a plate of glass so that its capacity is made to correspond when added to that of *m'* to the withdrawal of the plate *c'* by 1 cm. The plate *c'* is then placed at zero, and the other condenser plate *c* withdrawn until the sound minimum is observed in the telephone. Then the measuring vessel *v* is connected to

c' and c' withdrawn until the minimum is again obtained, the position is accurately measured on the scale by means of a vernier attached to c'. The measuring vessel is now disconnected and c' placed at division 1 and c again brought to the minimum position; v is then added to m' and c' again moved to the minimum position, which is carefully read. The rest of the scale is treated in exactly the same way. If the condenser plate were uniform, each addition of the measuring vessel v would demand the same movement of c' and consequently the same addition to the scale reading (approximately 1 cm.). The corrections for the scale readings follow directly from the observed readings. The calibration of the other condenser plate c is carried out by direct comparison with c'. The determination may now be carried out. The two resistances a and a' must be made equal. This is done by starting the coil and moving the electrode in one or other until the sound minimum is obtained. The resistances should be controlled by interchanging them, when the sound minimum should persist. The empty measuring vessel is then connected alternately with m and m', and the plate c' moved each time until the sound minimum is obtained. About 2–3 c.c. of a liquid of known dielectric constant is added to the vessel v, and the measurement made again in the same way. The vessel is then emptied, cleaned and dried, and the same quantity of the liquid to be measured is placed in it and the determinations repeated. Should the substance conduct slightly the regulating resistances d and d' must be changed, so that the sound minimum, which will be indistinct, becomes sharp. If D_0 is the dielectric constant of the known liquid, D that of the substance to be measured, s the number of scale divisions the condenser plate has to be moved when the empty vessel is connected, s_0 the number for the substance of known dielectric constant, and S for the unknown substance, then

$$\mathsf{D}=(\mathsf{D}_0-1)\frac{\mathsf{S}-s}{s_0-s}+1.$$

Meta-xylene, which has a dielectric constant 2·345 at 25°, is the best substance to use for comparison.

The second method, due to Drude, may be used for substances which, in its inventor's own words, conduct as well as river water. The method depends on the use of Tessla oscillations, and as apparatus for producing these is not generally available in a chemical laboratory the method will not be described here. Readers who wish to use the method will find full details in the original papers (*Zeit. f. Physik Chemie*, 23, 1897, 267, and 40, 1902, 635).

The dielectric constant is determined with reference to a standard substance, but the actual value is given in terms of dielectric constant of the vacuum, which, as will be seen from the following definition, is taken as unity: "The dielectric constant may be defined as the ratio existing between the capacity of a condenser filled with the substance under discussion and that of the same empty condenser in a vacuum. Since the dielectric constant of a vacuum is taken as unity, the ratio expresses the dielectric constant in terms of that of a vacuum."

CHAPTER VI

ELECTROMOTIVE FORCE

WHEN a chemical reaction takes place it is said to be due to chemical affinity. This quantity cannot be directly measured, but it is a function of the energy change, and since by the first law of thermodynamics a quantity of energy of one kind may be exactly converted into an equivalent quantity of energy of another kind, it is possible to obtain a measure of the chemical energy by determining other energy changes which accompany the reaction. Thus the heat of reaction or the electrical changes may be measured. In this chapter it is proposed to consider the electrical changes, and for this purpose the reactions studied must take place in a galvanic or electrolytic cell. Suppose two different reactions be taken, these may give rise to the same quantity of current, but the electrical energy changes accompanying the reactions may still be very different; for the electrical energy change is proportional to the product of the quantity and the intensity of the current, *i.e.* the electromotive force or fall of potential. Thus, if H represents the electrical energy change, C the current strength, and E the electromotive force,

$$H = KCE,$$

where K is a constant.

So that the electromotive force is directly proportional to the energy change, and if determined would give a measure of the chemical affinity, which may now be defined as the force tending to bring about a chemical reaction, and hence becomes the analogue of electromotive force. When a reaction takes place without the addition of energy from outside, the system reacting passes from a condition of higher free energy to one of lower, *i.e.* the affinities of the products of reaction are less than those of the reacting substances, or, in other words, the tendency of these substances to react is less than that of the original substances. If such a reaction takes place in an electrolytic cell, the electromotive force driving the current which accompanies the change is therefore a measure of the difference of the free energy of the two systems. Hence the measurement of the electromotive force gives a ready means of studying the energy changes accompanying various reactions, and of solving other problems connected but remotely with these changes.

Measurement of Electromotive Force

Of the many methods available for measuring electromotive force, that due to Poggendorf, and generally known as the Compensation method, is most suited to the present purpose. If a battery or cell C (Fig. 31) of constant electromotive force is connected to the ends of a uniform bridge wire AB, there will be a uniform fall of potential along its length. The amount of fall along any length AD will be proportional to the length AD, and equal to the fraction $\frac{AD}{AB}$, of the total fall of potential along the whole wire. Suppose, now, a second cell E of smaller electromotive force than **C** be connected to **A** and through a galvanometer **G** with a sliding contact **D**, in such a way that its current is opposed to that of **C**. A current will flow through the circuit **AEGD**, and will be indicated by the galvanometer at all positions of the sliding contact but one. This point will be that at which the fall of potential along the wire from **A** to **D** is equal to the electromotive force of **E**. Hence if **V** is the electromotive force of **C**, and **V′** that of **E**, then

$$V : V' :: \text{Length } AB : \text{Length } AD.$$

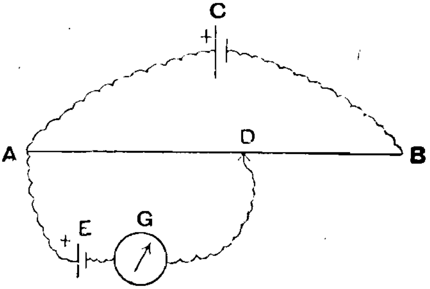

FIG. 31.

If the cell **C** were of quite constant and accurately known electromotive force the foregoing would constitute a method of measuring electromotive force. The cell **C** is generally an accumulator and as is well known possesses a variable electromotive force, and further, since considerable quantities of current are drawn from **C** it is impossible to substitute the accumulator by a cell of accurately known electromotive force. The difficulty is surmounted by comparing the accumulator with a standard cell of known and constant electromotive force, and then comparing the unknown cell with the standardised accumulator. Fig. 32 gives the arrangement; the point D′ represents the point at which the standard cell S gives no deflection in the galvanometer, and this is first determined. Then the standard cell is replaced by the unknown cell E by means of the switch K, and the point of no deflection D determined. If V_s is the electromotive force of the standard cell, V_1 that of the unknown cell, and V that of the accumulator,

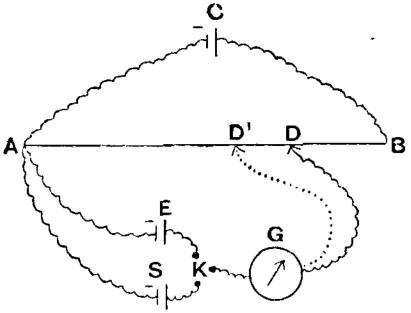

FIG. 82.

$$V : V_1 :: \text{Length AB} : \text{Length AD},$$
$$V : V_s :: \text{Length AB} : \text{Length AD}';$$

combining these expressions

$$V_1 : V_s :: \text{Length AD} : \text{Length AD}'.$$

The accuracy of electromotive force determinations, and that of the subsequent calculations based on them, depends on a careful attention to many details in the apparatus and conduct of the experiment. These will be noted along with the description of the apparatus.

1. *The Standard Cell.* A normal element or standard cell must be easily reproducible, and must change but slightly with change of temperature. These desiderata are possessed by the cadmium or Weston element, and

in a lesser degree by the Clark cell. The cadmium cell is to be preferred to the Clark cell, because its temperature coefficient is less than that of the Clark element, and the electromotive force of the Clark cell has a tendency to follow the temperature change irregularly, *i.e.* often when its temperature has changed the electromotive force persists for an indefinite period at the value characteristic of the original temperature. The Weston cell may be made by the student himself, and with ordinary care should at once give the correct electromotive force. It is made in an H-shaped glass vessel (Fig. 33).

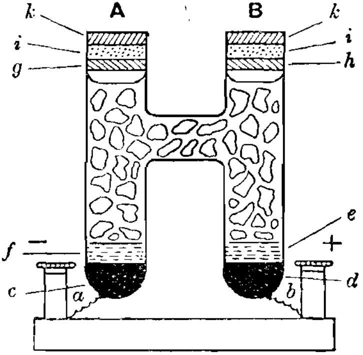

Fig. 33.

Platinum wires, *a* and *b*, are fused into the bottom of the limbs, A and B, and are connected to two terminals screwed into the base of the stand. A quantity of cadmium amalgam, *c*, constituting the negative pole, is poured into the limb A to a depth of one centimetre. The amalgam is made by warming 7·5–8·0 parts by weight of mercury on a water bath, and adding one part of pure cadmium to it. The amalgam must be poured into A whilst it is still hot, since it solidifies at about 85°, and to prevent cracking the vessel it should be placed in a water bath, and heated up to the boiling point before the amalgam is added. An approximately equal quantity of pure mercury, *d*, constituting the positive pole, is poured into B. The mercury is then covered by a layer of a paste of mercurous sulphate, *e*, 2–3 mm. thick, made by grinding in a mortar mercurous sulphate, a few cadmium sulphate crystals and a drop of mercury, together with a small quantity of a saturated solution of cadmium sulphate to form a thin cream. The excess liquid is filtered off through cotton wool, the paste again rubbed with cadmium sulphate solution, and again filtered. This process should be repeated twice more for the purpose of removing any mercuric sulphate which may be present. The amalgam in the limb A is covered by a layer, *f*, 2–3 mm. thick, of finely powdered moist cadmium sulphate crystals. Both limbs are then loosely filled with fairly large cadmium sulphate crystals, and the whole apparatus filled to within 15 mm. of the top with a saturated solution of cadmium sulphate

$$3CdSO_48H_2O.$$

In making this solution it must not be heated above 75°, for at this temperature the crystals change from

$$3CdSO_48H_2O \text{ to } CdSO_4H_2O.$$

Great care should be taken to see that neither the cadmium sulphate nor the metallic cadmium contain zinc, and that the mercury is quite pure, for nearly all the irregularities observed in Weston cells are due to one or other of these causes. For the method of purification of mercury, see Chapter IV., Part I. A layer of molten paraffin wax, *g*, 5 mm. thick, is poured on the liquid in the limb A, and when this has set the apparatus is carefully tilted, so that a bubble of air enters the closed limb through the side tube. The apparatus is then placed in its normal position, and the limb B closed by a similar layer of paraffin, *h*. Discs of cork, *i*, *i*, are then forced on to the paraffin wax, and the top of the cork covered with sealing wax, *k*. A cell prepared carefully according to the above instructions should at once give its normal electromotive force, but it ought to be compared with a cell of known electromotive force before use. The Weston cell has the electromotive force given in the table below, and for any other temperature the value may be calculated by means of the expression

$$E = 1{\cdot}0186 - 0{\cdot}000038(t-20) - 0{\cdot}00000065(t-20)^2,$$

where t is the temperature and E the electromotive force.

Temperature.	Electromotive Force.
5°	1·0189
10°	1·0189
15°	1·0188
20°	1·0186
25°	1·0184

2. *Bridge Wire.* A bridge wire similar to that described in Chapter III. may be used for the measurement of electromotive force. It must be calibrated before use, and should be at least one metre long. If the fall of potential along the whole wire is about 2 volts an accuracy of about 0·2 millivolt is obtainable, which demands that the position of the sliding contact must be read to 0·1 mm. In most measurements, however, an accuracy of 1 millivolt is all that is required.

If more accurate measurements are required a longer bridge wire or a potentiometer made up of known resistances and a wire, must be used.

3. *Source of Current.* As source of current a cell of larger electromotive force than the largest electromotive force to be measured must be used. This is found in a large lead accumulator of 40–50 ampere-hours capacity. Such a cell serves admirably to produce the necessary fall of potential along the bridge wire. It has an electromotive force of a little over 2 volts, and will not run down very quickly. The electromotive force accompanying chemical changes rarely exceeds 2 volts, and consequently the lead accumulator will meet all ordinary cases.

4. *Measuring Instrument.* The measuring instrument is only used in electromotive force determinations to indicate the point at which the electromotive force of the cell to be measured is exactly balanced by the fall of potential between the two points on the bridge wire to which it is attached, *i.e.* it serves solely as a zero instrument. A galvanometer or a capillary electrometer is generally used for this purpose. The former is more convenient and less likely to get out of order than the latter, but it is influenced by the resistance of the cell being measured. Should the resistance of the cell be very high, the galvanometer is less sensitive than the capillary electrometer. The capillary electrometer, in addition to being less expensive than the galvanometer, is very easily fitted up, and when in good working order answers the required purpose admirably. The capillary electrometer is made in many forms, but that illustrated in Fig. 34 is best suited for the present purpose. It consists of a wide tube, W, 4–5 mm. internal diameter, and a bulb tube, B; these are connected by a capillary tube, C, 0·5 mm. diameter. A quantity of pure dry mercury, sufficient to cause the meniscus to stand about two-thirds up the capillary tube, is poured into W. The bulb

of the other tube is also about half filled with mercury, and the rest of the bulb and tube filled with dilute sulphuric acid by means of a fine pipette. The dilute sulphuric acid is made by mixing six volumes of water with one volume of concentrated sulphuric acid, allowing to cool, and then shaking with a drop of pure mercury for a few minutes. A piece of rubber tubing is then attached to **W** and the mercury blown up the capillary until contact is made with the sulphuric acid. A few drops of mercury will fall into the bulb, and then the thread will run back into the capillary, drawing the sulphuric acid with it. The walls of the capillary must be thoroughly wetted with the acid by drawing the mercury up and down by alternately blowing and sucking at the rubber tube, but under no circumstances must the acid be drawn round the bend of the tube. Electrical contact is made with the mercury by means of platinum wires, *a* and *b*. The wire *a* must be insulated from the sulphuric acid. This is most conveniently done by drawing out a capillary tube from a piece of glass tubing, threading the wire through it, and then sealing the lower end, leaving about 0·5 cms. projecting for the purpose of making contact. The outside ends of both platinum wires should be fused to insulated copper leads, and these permanently attached to two fixed terminals. The principle on which the capillary electrometer depends may be briefly explained as follows: If the mercury electrodes of a capillary electrometer are raised to different potentials by attaching them to the poles of a battery,

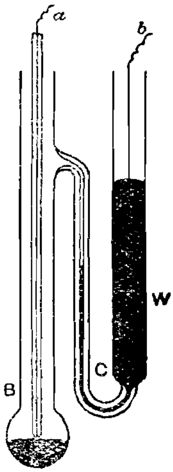

FIG. 34

the one will be charged positively and the other negatively. Helmholtz and Lippmann have shown that when a mercury surface is charged positively its surface tension decreases, but when charged negatively the surface tension increases. Hence, if the mercury in the capillary tube is charged negatively, its surface tension will increase, and consequently it will travel up the tube; in the same way, when it is charged positively, it will descend the tube, owing to a decreased surface tension. When there is no difference of potential between the two mercury surfaces, *i.e.* when the cell being measured is exactly balanced by the potential fall on the bridge wire, the mercury thread in the capillary will remain stationary. Hence it follows that such an instrument will serve excellently as a zero indicator for the comparison of small potential differences, but it is of no use whatever as an electrometer in the strict sense of the word, for the amount of movement in the capillary is not uniformly proportional to the potential applied. The electrodes of a capillary electrometer must be connected together by means of a short-circuiting tapping key when not actually employed in making a measure-

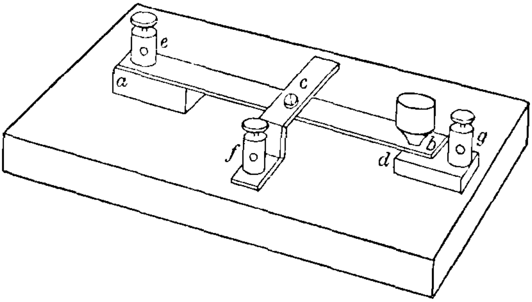

Fig. 35.

ment. Such a key is depicted in Fig. 35. It consists of a metal bar, *ab*, actuated by a spring, which is so arranged that its position of rest is against the platinum contact *c*. The electrometer is connected permanently to the terminals *e* and *f*, and consequently is always short-circuited. The terminal *g* and one of the fixed terminals of the electrometer are connected to the circuit containing the cell to be measured. The terminal *g* is connected to a platinum contact *d*, so that on pressing down the key, contact is made between the electrometer and the rest of the circuit; on releasing the key again the circuit is broken, and the electrometer short-circuited.

Although the capillary electrometer will work, no matter in which direction the current flows, yet it is advisable to connect it so that the positive current flows from the bulb to the capillary. This effectually prevents the formation of mercurous sulphate in the capillary, which inevitably occurs after short usage if the current flows in the opposite direction. The scheme for connecting a capillary electrometer to the cell circuit is given in Fig. 36.

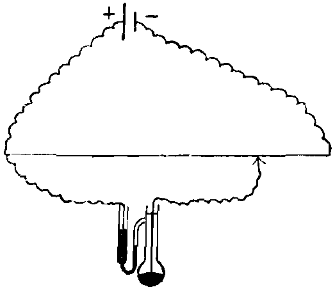

FIG. 36.

As the point of balance is approached the movements of the mercury thread become very small, and it is necessary to observe them by means of a low power microscope. Capillary electrometers may be purchased, fixed in a stand to which a suitable microscope is attached. One of these is illustrated in Fig. 37, which, as will be seen, is fitted with a small lamp *h* for illuminating the capillary. A small vertical scale is placed in the eye-piece of the microscope. This may be used to compute fractions of a millimetre on the bridge, if the electrometer is working sufficiently sharply. When an electrometer is working perfectly, the mercury thread should move sharply on pressing the key, and on releasing it the meniscus should move sharply back to its position of rest, there should not be a slow movement back to this position. A capillary electrometer in perfect working order ought to indicate a potential difference of 0·0001 volt. When an electrometer ceases to function properly it may often be made to work by blowing two or three drops of mercury from the thread over into the bulb. If this does not make it work then doubtless the walls of the capillary are dirty. It is often best when this is the case to discard the electrometer altogether, but it may be cleaned in the following manner: about 100 c.c. of a hot concentrated solution of chromic acid is drawn through it by means of a pump; this is followed by a large quantity of distilled water. The vessel is then dried by warming and drawing a current of filtered air through it. *Alkalies should never be used* to clean electrometers for they are liable to produce a slight roughness on the walls of the capillary which will effectually prevent the free movement of the mercury thread.

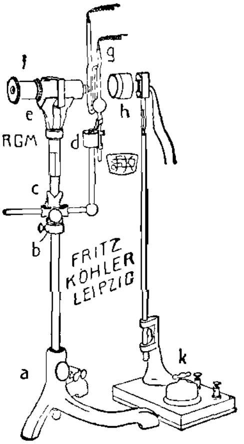

FIG. 37.

Testing a Standard Cell

The first thing to be done after the preparation of a Weston cell is to compare it with a cell of known electromotive force. This may be carried out in the following manner: The apparatus is connected up as indicated in *Fig.* 38. The accumulator A is connected to the ends of the bridge wire, *b*, *w*, through a key K. The electrometer E is connected to the end of the bridge wire *b*, to which the positive pole of the accumulator is attached, through the fixed terminal *x*, and also to the tapping key T through the terminal *y*. The tapping key is connected to the two way switch S, which is connected to the standard cell *c* and to the freshly made cell *c*′. The negative poles of these two cells are connected together and to the sliding contact N. Switches, such as are necessary in this class of work can easily be made, if not available, in the following manner. Three fairly deep holes, *a*, *b*, and *c*, are bored in a block of paraffin wax or ebonite as illustrated in Fig. 39; the holes are filled with mercury, and connection made

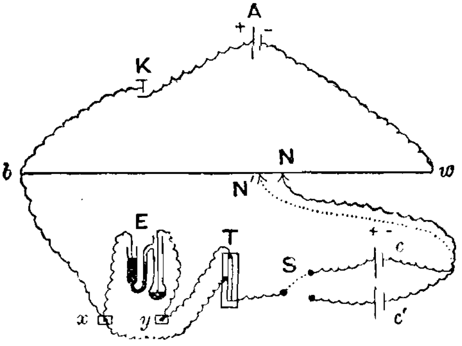

FIG. 38.

between the pairs *a*, *b* and *a*, *c* by means of a stout piece of copper wire *d*, bent twice at right angles. The wires, which are to be connected through the switch are amalgamated at the ends and placed in the several mercury cups. All wires used in electromotive force measurements should be flexible and well insulated. To compare the electromotive force of the freshly made cell with the standard cell, arrange the switch **S** so that the standard cell is placed in the circuit; then, observing the capillary thread through the microscope, depress the tapping key sharply. Notice the direction in which the meniscus moves; now move the sliding contact and depress the key again; notice whether the movement of the meniscus is greater or less than before. If it is less, continue moving the slide contact in the same direction until the meniscus moves slightly in the opposite direction; if the movement of the meniscus is greater, then move the contact in the opposite direction. When two points, about 1 cm. apart, have been obtained, at which the meniscus moves in opposite directions, place the contact on the middle point between them and note the deflection, and in this way find the point of no deflection. It may be, if the apparatus is working well, that two points one millimetre apart give deflections in opposite directions; when this is the case note the number of

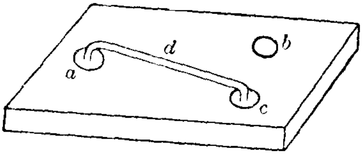

FIG. 39.

microscope scale divisions in each direction and calculate from them the position between the two points on the bridge at which there would be no deflection. Should the apparatus not be working well, or if the cell being measured has a very high resistance, the deflection may be difficult to observe when nearing the point of balance. In this case the reading is often made easier by holding the key down for a few seconds and then suddenly releasing it and observing the motion of the meniscus back to its position of rest.

Having found the position of balance for the standard cell, place the freshly-made cell in the circuit by altering the position of the switch S, and determine the position of no deflection for the newly-made cell. If the two cells have the same electromotive force, the point will be the same as in the previous measurement. If the point is not the same the electromotive force of the cell may be *calculated from the readings thus:*

$$\text{E.M.F. of standard} : \text{E.M.F. of new cell} :: b\mathrm{N} : b\mathrm{N}';$$

$$\therefore \quad \text{E.M.F. of new cell} = \frac{b\mathrm{N}'}{b\mathrm{N}} \times \text{E.M.F. of standard cell},$$

where N and N′ are the points of balance of the standard and the new cell respectively.

It is always wise in a series of electromotive force determinations to remeasure the position of no deflection for the standard cell at the end of the measurements to ascertain that the accumulator has not changed. There is, however, little danger of this happening if a freshly charged accumulator of large capacity is used, provided that the accumulator circuit has been closed for twenty minutes before the measurements are made.

Origin of the Electromotive Force of a Cell

If the electromotive force of a cell of any kind, *e.g.* a Daniell cell, is measured, the value obtained is made up of the sum of several factors. The Daniell cell, consisting of a zinc electrode immersed in a solution of zinc sulphate contained in a porous pot, and a copper electrode immersed in copper sulphate solution surrounding the porous pot, may be represented thus:

	$CuSO_4$	$ZnSO_4$	
Cu	solution	solution	**Zn.**
	i.e. $Cu^{\cdot\cdot}$ ions	*i.e.* $Zn^{\cdot\cdot}$ ions	

The electromotive force of a Daniell cell, or the difference of potential between the electrodes, actually measured is made up of the difference of potential at the surface contact of (1) the copper and copper sulphate solution, (2) zinc and zinc sulphate solution, (3) copper sulphate solution and zinc sulphate solution, and (4) the copper and zinc electrodes with the leads of the apparatus. If the temperature is kept constant the potential difference at the connection of the leads with the zinc and copper electrodes vanishes. The potential differences due to the other causes, therefore, make up the potential difference between the poles of the cell. In building up cells for the investigation of energy changes, the potential difference due to the contact of two liquids must be eliminated, since it is not due in any sense to the processes occuring at the electrodes, but, as will be seen later, to the differences in the migration velocities of the ions. In some cases the value of the liquid contact potential can be calculated, but in almost every case it can be reduced in amount to such an extent as to be negligible.

The liquid contact potential may be eliminated by adding to the two solutions an equal concentration of an indifferent electrolyte, *e.g.* potassium chloride, or by making contact between the solutions through a saturated solution of potassium chloride, potassium nitrate, or ammonium nitrate. Ammonium nitrate may not be used for alkaline solutions. The elimination of the liquid contact potential has the effect of making the electromotive force of the cell equal to the sum of the potential differences existent between the electrodes and their contiguous solutions.

When a current is being drawn from a cell, chemical changes take place at the electrodes; in the case of a Daniell cell the changes are the solution of the zinc electrode with the formation of zinc ions, and the discharge of copper ions with the accompanying deposition of copper. When zinc ions are formed by the solution of metallic zinc, the zinc electrode becomes negatively charged with reference to the solution of zinc ions, and when copper ions are discharged the copper electrode becomes positively charged with reference to the solution of copper ions. There is then a difference of potential between the zinc electrode and the solution of zinc ions contiguous to it on the one hand, and between the copper electrode and the copper ions on the other; the algebraic sum of which represents the electromotive force of the cell. The electromotive force depends on the nature of the metals forming the electrodes and the concentrations of the ions in contact with them. *The difference of potential between an electrode and its ions gives a measure of the tendency of the metal to form ions, i.e. to pass into solution.* A metal which is positive to a solution of its own ions, *i.e.* one whose ions tend to come out of solution, is said to have a positive potential, whilst a metal which is negative to a solution of its own ions is said to have a negative potential. Since the total potential difference between the poles of a cell is the sum of the potentials at the two electrodes, it follows that if the value of the potential difference at one electrode is known, the value of the potential difference at the other electrode may be calculated, *i.e.* a measure of the affinity at the electrode may be obtained. These single potential differences are generally known as "single electrode potentials," and to measure them a single electrode of known potential is employed, *viz.* a calomel electrode. The principle of the method of measuring a single potential may be illustrated thus: A cell is constructed in two parts, one consisting of the metal and solution to be measured, and the other of the calomel electrode of known potential. The two parts are connected by liquid contact through a vessel containing a saturated solution of potassium chloride to eliminate the liquid contact potential. Then the electromotive force of the composite cell is measured in the usual way. Its electromotive force, as has already been explained, is the algebraic sum of the potential of the calomel electrode and that of the electrode under investigation. The method of calculating the single potential difference will be clearer if a specific example is considered.

Suppose a cell is made up of cadmium in cadmium sulphate solution and a normal calomel electrode, and is found to have an electromotive force of 0·980 volts, with the mercury as positive pole. The signs of the poles can always be obtained by observing which way the cell is connected up when the point of balance is obtained, for it is only when the cell is opposed to the accumulator that the point of no deflection can be obtained. The cell can therefore be represented thus:

$$\overset{-}{\mathrm{Cd}} \;\Big|\; \mathrm{Cd}^{\cdot\cdot} \;\Big|\; \begin{matrix}\mathrm{Hg_2Cl_2}\\ n\mathrm{KCl}\end{matrix} \;\Big|\; \overset{+}{\mathrm{Hg}}$$
$$\xrightarrow[0{\cdot}980]{\hspace{12em}}$$

indicating that since the mercury is the positive pole, the current must flow in the cell as indicated, with an electromotive force of 0·980 volts. Now it is known that mercury is positive to a saturated solution of mercurous chloride in normal potassium chloride by 0·560 volts at 18°. So that this potential tends to produce a current in the same direction as the total current. This may be represented thus:

$$\overset{-}{\mathrm{Cd}} \;\Big|\; \mathrm{Cd}^{\cdot\cdot} \;\Big|\; \begin{matrix}\mathrm{Hg_2Cl_2}\\ n\mathrm{KCl}\end{matrix} \;\Big|\; \overset{+}{\mathrm{Hg}}$$
$$\hspace{6em}\xrightarrow[0{\cdot}560]{\hspace{5em}}$$
$$\xrightarrow[0{\cdot}980.]{\hspace{12em}}$$

Since the total potential difference is 0·980 volts, it follows that the potential difference between the cadmium and the solution of cadmium ions must be 0·420 volts and this must be in the same direction as the total current, thus:

$$\mathrm{Cd} \;\Big|\; \mathrm{Cd}^{\cdot\cdot} \;\Big|\; \begin{matrix}\mathrm{Hg_2Cl_2}\\ n\mathrm{KCl}\end{matrix} \;\Big|\; \mathrm{Hg}$$
$$\xrightarrow[0{\cdot}420]{\hspace{5em}}\;\; \xrightarrow[0{\cdot}560]{\hspace{5em}}$$
$$\xrightarrow[0{\cdot}980.]{\hspace{8em}}$$

Hence there is a tendency for a positive current to flow from the cadmium to the solution, *i.e.* there is a tendency for cadmium to pass into the solution in question, represented by 0·420 volts, and in this process the cadmium becomes negatively charged with respect to its solution. It is therefore customary to express this by saying that the potential difference between cadmium and the given solution of cadmium ions is −0·420 volts. There are many other methods of expressing these results, but if the above method is adhered to, much confusion and many errors will be avoided.

The Calomel Electrode. Since the accuracy of all single potentials will depend on the accuracy of the calomel electrode, the greatest care must be taken in making it.

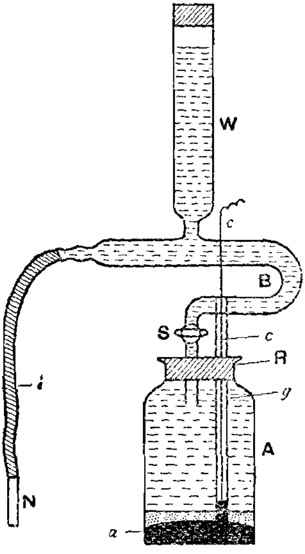

Fig. 40.

It is best made in a stout, wide-mouthed glass bottle A (Fig. 40), of about 250 c.c. capacity, the bottom of which is filled to a depth of 5–10 mm. with pure mercury *a*. Electric connection is made with the mercury by means of a short length of platinum wire fused into a glass tube *g* which passes through a rubber stopper R. A few drops of mercury are shaken down the tube on to the platinum wire, and a stout piece of copper wire *c*, amalgamated at its lower end, is placed in the mercury. The copper wire is fastened in the tube by running molten sealing wax into the top. A glass tube B, bent as in the diagram and fitted with a stopcock S, is inserted through a second hole in the rubber stopper. A length of about 30 cms. of black indiarubber tubing *i* is attached to the free end of the horizontal U-tube; this is terminated by a glass nozzle N, which is tightly packed with cotton wool, and closed by an indiarubber cap, made by inserting a short piece of glass rod into one end of a short length of rubber tubing. A tube W, 1·5 cms. diameter, is attached vertically to the upper limb of the horizontal U-tube. To fill the vessel: place about 10–15 grams of pure calomel in a bottle along with a few drops of mercury and 15 c.c. of an accurately prepared N or N/10 solution of potassium chloride, and shake the whole together until a thick grey paste has been obtained. Then add about 30 c.c. of the potassium chloride solution, shake up again, allow the calomel to settle and decant the liquid. Add two further quantities of potassium chloride, decanting each time after the calomel has settled. Then add about 50 c.c. of potassium chloride solution, transfer the whole to the bottle A, and fill to the brim with the potassium chloride solution. Now insert the rubber stopper, having previously opened the stopcock, press the stopper tightly into the neck, so that the platinum contact is completely covered by the mercury and the solution is driven up into the U-tube. Close the stopcock and wire the rubber stopper to the neck of the bottle. Pour potassium chloride into the vertical tube so that the U-tube, rubber connecting tube and the vertical tube are filled. Insert the stoppers in the vertical tube and the glass nozzle of the rubber tubing.

To use the calomel electrode, the glass nozzle is uncovered and placed in the indifferent electrolyte used to eliminate the liquid contact potential, the stopcock is opened and the mercury electrode connected to the circuit.

The form of calomel electrode described here is less likely to give inaccurate results than many other forms, for it is nearly impossible for the liquid in the cell to become contaminated with other liquids, which may diffuse back from the contact vessel, and further, the connecting tube can always be washed out by pouring potassium chloride solution through the vertical tube. The stopcock S should always be closed when the electrode is not in actual use. The electrode may be made up with either a normal or a tenth-normal solution of potassium chloride, and is known either as a normal or a tenth-normal calomel electrode. The potential difference between the mercury and solution has the following values at 18°.

Normal electrode
= +0·5600 volts.

Tenth-normal electrode
= +0·6130 volts.

The temperature coefficient of the normal calomel electrode is +0·0006 volts per degree increase of temperature, and that of the tenth-normal electrode is +0·0008 volts. This makes it necessary, in accurate measurements, to keep the calomel electrode in a thermostat.

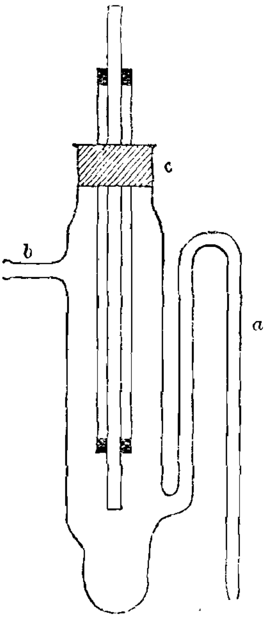

FIG. 41.

Potential Vessels. Single potential differences are measured in small glass vessels shaped as in Fig. 41; these are about 12 cms. long and 1·5 cms. wide, and are fitted with two tubes *a* and *b*. The tube *a* is about

2–3 mm. diameter and is inserted into the contact vessel containing the indifferent electrolyte. The tube *b* is fitted with a small rubber cap. The electrode is supported by a rubber stopper *c*, and consists either of a rod of the metal to be measured, cemented into a glass tube as in the diagram, in which case it must be freshly coated with an electrolytic deposit of the pure metal, or of a platinum wire, sealed into a glass tube and coated with an electrolytic deposit of the metal to be measured. Exact instructions for the preparation of the electrodes are given under the various experiments.

EXPERIMENT

Determine the Potential Difference between Copper and a Series of Copper Sulphate Solutions at 18°. Make a series of solutions of copper sulphate of the following concentrations: N, $\frac{N}{10}$, $\frac{N}{50}$, and $\frac{N}{100}$.

Place these solutions in a series of potential vessels, and place copper electrodes in the solutions. The electrodes are made by fixing lengths of copper wire in narrow glass tubes by means of sealing wax, as indicated in Fig. 41. The end of the wire which is to come into contact with the solution must be cleaned with dilute nitric acid, and then coated electrolytically with copper. This is best done by connecting a series of electrodes (4 or 5) in parallel, and making them the cathode in the electrolysis of a solution of copper sulphate in which a thin sheet of electrolytic copper serves as the anode. The solution should be made up of 150 grams of crystallised copper sulphate dissolved in 1000 c.c. of water, to which 50 c.c. of absolute alcohol and 50 c.c. of concentrated sulphuric acid have been added. The electrolysis should be carried out by means of two accumulators, and the current cut down to 1–2 milliamperes. When the electrodes are uniformly coated with copper, remove them from the solution, and wash with distilled water. To ensure the uniformity of the electrodes, reconnect them to one another, and place them in a solution of copper sulphate, which contains no acid, for about an hour. Wash each electrode with the solution with which it is to be used. Place the point of one of the potential vessels in a stout glass vessel, "middle vessel," containing saturated potassium chloride solution, and then place the glass nozzle of the calomel electrode in the same solution, as indicated in Fig. 42. In this way a cell is built up which is usually written

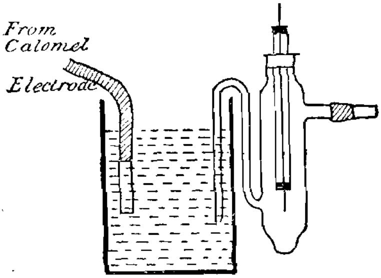

Fig. 42.

$$\mathrm{Cu}\;\Big|\;\mathrm{Cu}^{\cdot\cdot}\;\Big|\;\begin{matrix}\text{Sat}\\ \text{KCl}\end{matrix}\;\Big|\;\begin{matrix}\mathrm{Hg_2Cl_2}\\ \text{nKCl}\end{matrix}\;\Big|\;\mathrm{Hg}.$$

The middle vessel should be placed on a shelf in a thermostat at 18°, and then the vessel containing the single electrode, or half element, to be measured will hang in the water of the thermostat, and so gain the requisite temperature. Connect the cell with the measuring apparatus as indicated in Fig. 32, where E represents the cell to be measured. It is necessary to have a reversing switch for changing the direction of the current flowing in the cell should it be incorrectly connected.

To make the measurement, first find the point of balance for the Weston cell; let this be at the point D. Then find the point of balance for the composite cell; should it be impossible to obtain a point of balance the cell is connected up wrongly, but on reversing the poles by means of a reversing switch the point will readily be found, say D′.

Then

$$\begin{array}{ccccc} \text{The electromotive} & & \text{The electromotive} & & \text{Length} \quad \text{Length} \\ \text{force of the} & : & \text{force of the} & :: & \mathsf{AD} : \mathsf{AD}'; \\ \text{standard cell} & & \text{composite cell} & & \end{array}$$

$$\text{or, } \begin{array}{c}\text{The electromotive force} \\ \text{of the cell}\end{array} = \frac{\mathsf{AD}'}{\mathsf{AD}} \times 1{\cdot}0190 \text{ volts.}$$

The value of the calomel electrode is known, hence the value of the half element Cu | $CuSO_4$ may be calculated. Proceed similarly with the other solutions.

Further experiments may be made with zinc and a series of solutions of zinc sulphate, and silver with a series of solutions of silver nitrate. The zinc electrodes are made by rubbing rods of pure zinc with dilute sulphuric acid and then with pure mercury. The amalgamated rods are soldered to stout copper wires, and fastened in glass tubes by means of sealing wax. The silver electrodes should be made of lengths of silver wire fastened into glass tubes by sealing wax. The uncovered ends which come in contact with the solution should be coated electrolytically with a thin layer of pure silver from a dilute solution of silver cyanide in potassium cyanide. The solution is made by carefully adding potassium cyanide to a dilute solution $\left(\text{about } \frac{N}{50}\right)$ of silver nitrate until the precipitate at first formed has redissolved. The deposition should be made by a current of 0·2 milliamperes from two accumulators.

Effect of Concentration on Potential

It has already been stated that the electromotive force of a cell depends on the nature of the electrodes and the concentration of the solutions in contact with the electrodes. The effect of concentration will have been observed in the last experiment. Nernst has shown that the relationship between the potential of a single electrode and the concentration of the solution may be represented by the expression

$$E = EP + \frac{RT}{nF} \log_e C\alpha,$$

where E is the potential of the single electrode under consideration, C the concentration of the solution, α the degree of ionisation of the dissolved substance, R the gas constant, *i.e.* $8{\cdot}32 \times 10^7$ absolute units, T the temperature in absolute degrees, n the valency of the ion furnished by the electrode, F the charge on one gram equivalent ion, *i.e.* 96540 coulombs, and EP the normal potential (electro-affinity), *i.e.* the potential difference between an electrode and a normal solution of the ions furnished by the electrode. A list of normal potentials is given in Table III., *Appendix B.*

Putting in the constant values in the above expression, it becomes

$$E = EP + \frac{0{\cdot}058}{n} \log_{10} C\alpha \text{ at } 18°,$$

and

$$E = EP + \frac{0{\cdot}0595}{n} \log_{10} C\alpha \text{ at } 25°.$$

The values of E and EP must be put in with their proper signs, so that it follows if the electrode potential is positive it will decrease with dilution, whilst if it is negative, dilution will make it more negative.

If the value of EP is known, it is obvious that the value of αC, *i.e.* the concentration of the ions, in any solution may be determined by measuring the value of E for the given solution against the metal which furnishes those ions, and using a calomel electrode.

Calculate the potential which the solutions you have measured should have given, using the following data and compare your results with the calculated values:

		α			
	E.P.	N.	N/10.	N/50.	N/100.
$ZnSO_4$ -	−0·4930	0·23	0·39	0·55	0·63
$AgNO_3$ -	+1·0480	0·58	0·81	0·91	0·93
$CuSO_4$ -	+0·6060	0·21	0·38	0·53	0·61

Suppose we have a cell made up of two electrodes of one metal dipping into two solutions of the same salt, but of different concentrations, *e.g.* two silver electrodes dipping into two solutions of silver nitrate of different concentrations, such a combination will be found, on measurement, to have an electromotive force, *i.e.* there will be a difference of potential between the two silver electrodes. A cell of this type is known as a concentration cell, and if the two solutions are in contact with one another without any intermediate solution, it is known as a concentration cell with migration. The electromotive force is not the sum of the electrode potentials, but contains the potential difference at the surface of contact of the two solutions, and is given by

$$\mathsf{E}=\frac{v}{u+v}\times\frac{2\times0{\cdot}058}{n}\log_{10}\frac{a_1\mathsf{C}_1}{a_2\mathsf{C}_2},$$

where $\frac{v}{u+v}$ is the transport number of the anion, n the valency of the metal, C_1 and C_2 the concentration of the salt in the two solutions, and a_1 and a_2 the degree of ionisation of the salt in the two solutions. Hence if a cell is made up of two solutions of the same salt and two electrodes of the same metal, the concentration of one solution may be calculated from the measured electromotive force of the cell and the known concentration of the other solution.

EXPERIMENTS

(i) *Determine the Concentration of Silver Ions in a given Solution of Silver Nitrate.* Fit up two potential vessels with silver electrodes, prepared as described above. Place an N/50 solution of silver nitrate in one of the vessels, and in the other a solution of silver nitrate of unknown strength (say about N/500). Make contact between the two vessels by dipping them in a middle vessel, containing a normal solution of potassium nitrate, and measure the electromotive force at 18°. Calculate the concentration of the ions in the unknown solution from the expression

$$\mathsf{E}=\frac{2\times0{\cdot}058}{1}\log_{10}\frac{a_1\mathsf{C}_1}{a_2\mathsf{C}_2},$$

where $a_1=0{\cdot}91$, $\mathsf{C}_1=0{\cdot}02$, *and* $a_2\mathsf{C}_2$ *is the* concentration of the ions in the unknown solution.

Repeat the experiment, placing N/50 silver nitrate in the middle vessel and use the formula at the top of the page to calculate the ionic concentration; $\frac{v}{u+v}=0{\cdot}528$.

Confirm your result by measuring the potential of the unknown electrode against a calomel electrode, as in the last experiment, and calculate from the formula

$$\mathsf{E} = \mathsf{EP} + 0{\cdot}058 \log a_2\mathsf{C}_2.$$

Compare the results of the two experiments with the actual concentration of silver ions present, being given

$$a_2 = 0{\cdot}93.$$

(ii) *Determine the Concentration of Zinc Ions in a Solution of Zinc Chloride.* Make up a solution of zinc chloride, place it in a potential vessel and insert a zinc electrode prepared as described above. Determine its potential, using a calomel electrode as the other half of the cell. Calculate E from the result, and by means of the equation

$$\mathsf{E} = \mathsf{EP} + \frac{0{\cdot}058}{2} \log_{10} a\mathsf{C}.$$

Calculate the value of $a\mathsf{C}$, *i.e.* the concentration of the zinc ions.

Determination of the Solubility of Sparingly Soluble Salts

It is obvious that the ionic concentration of a saturated solution could be determined by the method described in the last section. If the ionic concentration of a saturated solution is known, the solubility of the dissolved substance can easily be calculated. Hence it follows that the solubility of sparingly soluble salts may be determined by means of potential measurements. Consider the case of a saturated solution of silver chloride as an example. A saturated solution of silver chloride can be readily prepared by adding a drop of silver nitrate to a quantity of a solution of potassium chloride of known concentration. If a precipitate of silver chloride is formed it follows that the solution is saturated with silver chloride. The concentration of silver ions in this solution can now be determined by the method described above. Let C be the concentration of silver ions. It is known that the product of the concentrations of the two ions of a sparingly soluble salt gives a constant value known as the **Solubility Product.**

Hence $$C \times C_2 \times \alpha_2 = L,$$

where C_2 is the concentration of the potassium chloride, α_2 the degree of ionisation, *i.e.* $C_2\alpha_2$ is the concentration of chlorine ions, and L is the solubility product.

In a saturated solution of silver chloride in water it may be assumed, since the solution is so dilute, that the salt is completely dissociated, *i.e.* the concentrations of the silver ions and the chlorine ions are alike. Let this concentration be C_1.

Hence $$C_1 \times C_1 = L,$$

i.e. $$C_1 = \sqrt{L}.$$

Now since the molecular concentration of silver chloride is the same as the ionic concentration of the silver ions it follows that $\sqrt{L}$ gives the solubility of silver chloride in gram molecules per litre, *i.e.*

$\sqrt{C \times C_2 \times \alpha_2}$ = The solubility in gram molecules per litre.

EXPERIMENT

Determine the Solubility of Silver Chloride in Water at 18°. Make up a $\frac{N}{10}$ solution of potassium chloride and fill a potential vessel with the solution; prepare a silver electrode by the method already described, and before inserting it in the solution add one drop of a 10 per cent. solution of silver nitrate to the solution. A precipitate will be formed signifying that the solution is saturated with silver chloride. Measure the potential of the solution against a calomel electrode, using a saturated solution of potassium chloride in the middle vessel. If E is the single potential of the half element, and EP the electro-affinity of silver (see Table III., Appendix B), the concentration C of the silver ions in the saturated solution may be calculated by means of the formula

$$E = EP + 0{\cdot}058 \log_{10} C.$$

Having obtained this value, the solubility product may be obtained by multiplying it by the concentration of the chlorine ions present in the solution. Tenth-normal potassium chloride is dissociated to the extent of 85 per cent., hence the concentration of chlorine ions is $0{\cdot}1 \times 0{\cdot}85$ gram ions per litre.

The solubility product therefore is

$$0{\cdot}1 \times 0{\cdot}85 \times C = L,$$

and $\sqrt{L}$ is the solubility of silver chloride in gram molecules per litre.

The concentration of silver ions in the saturated solution may also be determined by measuring the half element against a solution of silver nitrate of known concentration. Measure it against an $\frac{N}{10}$ solution of silver nitrate, and calculate the concentration of the silver ions in the saturated solution of silver chloride by means of the expression

$$E = \frac{v}{u+v} 2 \times 0{\cdot}058 \log_{10} \frac{a_1 C_1}{aC},$$

where E is the measured electromotive force, $\frac{v}{u+v}$ is the transport number of the NO'_3 ion, C_1 is the concentration of the silver nitrate solution, a its degree of ionisation.

The transport number of the nitrate ion will be found in Table IV., Appendix B; the degree of ionisation of $\frac{N}{10}$ silver nitrate is 0·81.

Having obtained the value of c, calculate the solubility as described above. Compare the results obtained in the two experiments.

Further experiments may be made to determine the solubility of silver bromide and silver iodide. The degree of ionisation of $\frac{N}{10}$ potassium bromide $= 0{\cdot}85$, and that of $\frac{N}{10}$ potassium iodide $= 0{\cdot}86$ at 18°.

Cells with Electrodes of Different Concentrations

That the electromotive force of a cell depends on the concentrations of the ions has been seen already. If a cell is made up of two electrodes of the same metal, and of one and the same solution, there will be no difference of potential between the electrodes, but if by any means the concentration of the metal can be made different in the two electrodes, then a difference of potential will be set up. Such a concentration cell may be built up by using as one electrode a dilute amalgam, *i.e.* a solution of the metal, whose ions are present in the electrolyte, in pure mercury. An amalgam of this sort will have a potential which depends on the concentration of the metal, when in contact with a solution of its own ions.

EXPERIMENT

Determine the Potential Difference between Zinc Amalgam of various concentrations and a Solution of Zinc Sulphate. This èxperiment must be carried out in a potential vessel of the type depicted in Fig. 43. It consists of an ordinary potential vessel, 20 cms. long and 2–3 cms. diameter, fitted with a side tube which has a tap, E, at the bend. The vessel is closed by a rubber stopper, which carries a glass stirrer, C, a protected platinum electrode, B, and a rod of pure zinc, A. Place about 5 c.c. of pure mercury, accurately weighed to the nearest centigram, in the vessel, and then fill with a normal solution of zinc sulphate. Insert the stopper, taking care that the platinum point is completely immersed in the mercury, and then close the tap E. The tap must be quite free from grease in this experiment, and should be wetted with the solution of zinc sulphate

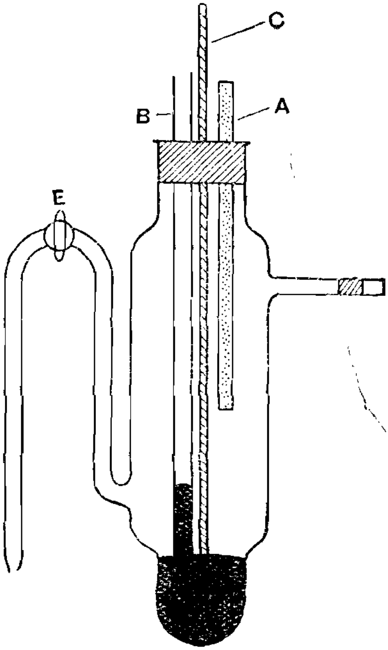

FIG. 43.

before being inserted. Connect the zinc rod, through a large variable resistance and a milliammeter, with the positive pole of a battery of two accumulators, and the platinum point with the negative pole. Allow a current of 3–10 milliamperes, accurately measured, to flow for about four minutes, also accurately measured, using a stop-watch to determine the time. Then break the circuit, stir the amalgam and measure the potential difference between the zinc rod and the amalgam. The potential difference between the amalgam and the calomel electrode should also be measured, contact between the two electrodes being made through a middle vessel containing a saturated solution of potassium chloride. Then reconnect the zinc rod to the battery circuit and allow the current to flow for 10 minutes; measure the potential differences as before. Allow the current to flow for further periods of 10, 15, 20 and 30 minutes, and measure the potential differences.

Record the results in tabular forms thus:

Current in amperes. 1	Time in seconds. 2	Total coulombs passed. 3	Total weight of Zn dissolved in Hg. 4	Concentration of Zn in amalgam mols. per litre. 5	E.M.F. of cell against zinc. 6	Difference. 7	E.M.F. of cell against calomel electrode. 8	Difference. 9	Calculated difference. 10

The weight of zinc dissolved in the mercury is obtained by Faraday's Law from the expression

$$Q = Czt,$$

where Q is the weight of zinc in grams, C the current strength in amperes, z the electrochemical equivalent, and t the time in seconds. The value of z for zinc is 0·00338, the value for Ct is the total number of coulombs, *i.e.* the number given in column 3, obtained by multiplying the current in amperes by the time in seconds. The values in column 5, *i.e.* the concentration of the zinc in gram molecules per litre are obtained from the expression

$$\text{Concentration} = \frac{\text{Q} \times 1000}{v \times 65},$$

where Q is the weight of zinc, v the volume of mercury, and 65 the molecular weight of zinc in mercury solution. The values in column 6 are those actually measured against the zinc rod, and the values in column 7 are the differences between the successive measurements. The values in column 8 are the figures obtained for the composite cell,

Zn Amalgam | $ZnSO_4$ | Calomel Electrode,

and the figures in column 8 are the differences between the successive values. The values obtained in columns 7 and 9 should be identical. The calculated differences are obtained from the expression

$$\text{E} = \frac{0{\cdot}058}{n} \log_{10} \frac{\text{C}_1}{\text{C}_2},$$

in which n is the valency of zinc, *i.e.* 2, C_1 and C_2 are the concentrations of the two amalgams, and E is the difference of potential which ought to exist between them if they were the two electrodes in a cell.

Further experiments may be carried out with copper, lead and cadmium amalgams. For details see Spencer (*Zeit f. Elektrochemie*, 1905, 41, 681).

CHAPTER VII

ELECTROMOTIVE FORCE (*Continued*)

Gas Cells and Electrodes

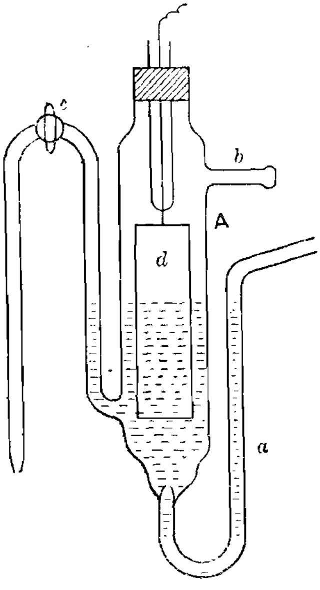

Fig. 44.

In the last chapter, cells made up of reversible soluble electrodes were considered; it is also possible to have reversible gas electrodes, *i.e.* cells in which the electrodes are gases whose ions are present in the solution. At first sight it appears improbable that a gas which has no metallic conductivity can serve as an electrode, but by a special contrivance this becomes possible. The arrangement is given in Fig. 44, and consists of a glass potential vessel, A, fitted with three side tubes, *a*, *b*, and *c*, and an electrode, *d*, made of a sheet of platinum which is coated with platinum black and half immersed in the solution. The gas under consideration is slowly bubbled into the vessel through a, and is absorbed by the platinum black to an amount which is in equilibrium with the gaseous atmosphere surrounding the electrode. The platinum then behaves as a gas electrode, *i.e.* as though it were made entirely of the gas in question. By means of such an arrangement gas electrodes of hydrogen, oxygen, and chlorine may be measured if the solutions in which they are immersed contain hydrogen, oxygen, and chlorine ions respectively. An acid solution always contains hydrogen ions, and consequently the concentration of its ions may be measured by means of a hydrogen electrode. Oxygen ions are always present in an alkaline solution, being derived from the dissociation of the hydroxyl ions thus:

$$4OH' \rightleftarrows 2O'' + 2H_2O.$$

Chlorine ions are always present in solutions of chlorides.

Gas cells obey exactly the same laws as cells with metallic electrodes, and consequently may be treated in exactly the same way as these cells.

For example, a hydrogen concentration cell may be considered thus:

$$H_2 \Bigg| \begin{array}{c}\text{Concentrated solution}\\ \text{of HCl, } i.e. \text{ H}^{\cdot} \text{ ions}\end{array} \Bigg| \begin{array}{c}\text{Dilute solution of}\\ \text{HCl, } i.e. \text{ H}^{\cdot} \text{ ions}\end{array} \Bigg| H_2.$$

The electromotive force of this cell is given by

$$E = \frac{v}{u+v} \cdot \frac{RT}{nF} \log_e \frac{a_1 C_1}{a_2 C_2},$$

where the symbols have the same significance as in the former cases.

EXPERIMENTS

(i) *Determine the Electromotive Force of a Hydrogen Concentration Cell made up of two Solutions of Hydrochloric Acid, at* 18°. The success of this experiment depends on the platinum electrode, which must be prepared with the greatest care. The electrode consists of a strip of platinum foil, 3 cm. long and 1·5 cm. wide; this is welded to a short stout piece of platinum wire, which is fused into a glass tube, electrical connection being made by a drop of mercury placed in the tube. The foil is then coated with a uniform layer of platinum black. For the method of coating with platinum black, see Chapter III. The electrode, as thus prepared, may contain a large amount of occluded chlorine. This is removed by allowing the electrodes to stand in a solution of ferrous sulphate, acidified with sulphuric acid, for half an hour. The electrodes are then thoroughly washed with distilled water, and kept in water until required. If electrodes prepared in this way are used for measuring gas potentials, a considerable time, amounting sometimes to hours, must elapse before an equilibrium between the gas and the solution is set up. Wilsmore has found, however, that if only a small quantity of solution is used in the potential vessel, the equilibrium will be set up in a quarter of an hour. An electrode, which gives the potentials very quickly, has been devised by Luther and Brislee, and is preferable in every way to the one described above. Such electrodes may be purchased very cheaply, but are quite easily made in the following way: A piece of Jena tube is drawn out to the shape indicated in A (Fig. 45). The surface of this tube from *a* to *b* is then coated with a thin uniform layer of chloroplatinic acid in oil of bergamot, and dried by carefully warming it above a bunsen flame, taking care to keep the tube constantly rotated the while. In this way a thin film is produced, which may be thickened by applying a second coating of the solution. When the film is thick enough the tube is rapidly rotated in the lower part of the bunsen flame;

this will cause the film to darken, due to the decomposition of the oil in the film. The heating should be continued in this part of the flame until the tube is uniformly black. It is essential to note at this stage that the film must not be blistered; if this has happened the whole process must be recommenced. The tube is now heated more strongly until all the organic matter has been completely burnt away. The tube will then present a greyish white appearance, but the platinum will easily peel off. To prevent this the platinum is burnt into the glass by heating to bright redness in a blowpipe flame. The tube is then drawn off at *a*, and a piece of soft tubing is placed over the end *b*, and cemented to the electrode by sealing wax. Contact is made between the thin platinum layer and the circuit by means of a drop of mercury. The electrode must finally be coated with a layer of platinum black, and when finished has the appearance depicted in B (Fig. 45). The potential vessel differs slightly from the vessels used hitherto; it is fitted with three side tubes, *a*, at the bottom, narrowed as in Fig. 44 for the admission of the gas, *b* at the top for the gas exit, and *c*, fitted with a tap, for insertion in the middle vessel. The tap in the tube *c* must not be greased, but may be wetted with the solution contained in the potential vessel.

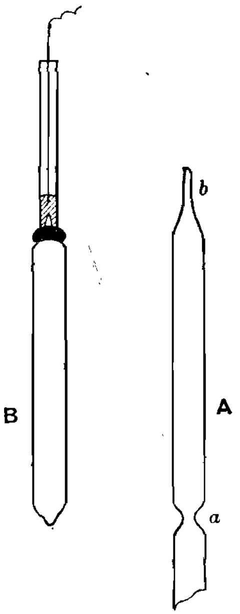

FIG. 45.

To make a determination: fill one potential vessel with a normal solution of hydrochloric acid and the other with a tenth-normal solution of hydrochloric acid, insert the electrodes, open the taps, and allow the acid to flow out until the electrode is about half immersed in the liquid. Connect the tube *a* in each case to a hydrogen generator, and the tube *b* to a small mercury trap. Place both potential vessels in a middle vessel, which stands in a thermostat at 18°, and contains a normal solution of hydrochloric acid. Allow a slow stream of hydrogen to bubble through the solutions for half an hour. The hydrogen should be purified by passing through wash bottles containing potassium permanganate and mercuric chloride respectively, and finally through a solution of hydrochloric acid of the same strength as the solution in the potential vessel. Connect up the gas cell to the measuring circuit, and determine its electromotive force, keeping the hydrogen bubbling through all the time. Allow the gas to pass for twenty minutes longer and remeasure; repeat the process until the electromotive force is constant.

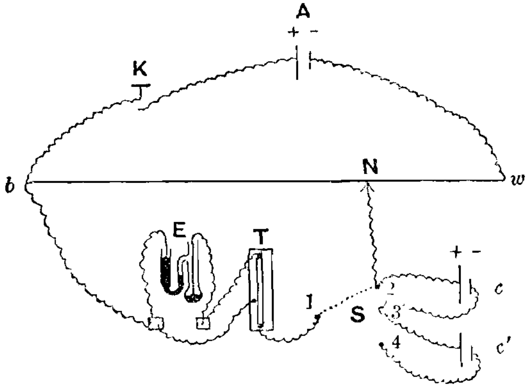

Fig. 46.

As the electromotive force of this cell is not very large the position of balance will come near the end of the bridge wire, and will be liable to considerable error. Hence it is preferable to measure the cell by connecting it in series with the standard cell. The scheme of connections for this is given in Fig. 46, in which c is the standard cell and c' gas cell. The cell c is first measured by placing the arm of the switch S in the position 1, 3, and then the two cells in series are measured by placing the switch arm in the position 1, 4. If N is the position of balance for the cadmium cell and N′ for the two cells, then we have the relationship:

$$\begin{matrix}\text{E.M.F. of}\\ \text{standard cell}\end{matrix} : \begin{matrix}\text{E.M.F. of}\\ \text{standard cell}\\ +\text{hydrogen cell}\end{matrix} :: \text{length } b\mathrm{N} : \text{length } b\mathrm{N}',$$

i.e.

$$\begin{matrix}\text{E.M.F. of}\\ \text{hydrogen cell}\end{matrix} = \left(\frac{b\mathrm{N}'}{b\mathrm{N}} \times \begin{matrix}\text{E.M.F. of}\\ \text{standard cell}\end{matrix}\right) - \begin{matrix}\text{E.M.F. of}\\ \text{standard cell,}\end{matrix}$$

and inserting the value of the standard cell at 18° we get:

$$\text{E.M.F. of hydrogen cell} = \left(\frac{b\mathrm{N}'}{b\mathrm{N}} \times 1{\cdot}019\right) - 1{\cdot}019 \text{ volts.}$$

Compare the value you obtain with the value calculated from the expression:

$$\mathrm{E} = \frac{v}{u+v} \times 2 \times 0{\cdot}058 \log_{10}\frac{a_1\mathrm{C}_1}{a_2\mathrm{C}_2},$$

where C_1 and a_1 are the concentration and degree of ionisation of the more concentrated solution, and C_2 and a_2 of the more dilute solution. The value of a_1 for N hydrochloric acid is 0·80, and that of a_2 for $\frac{\mathrm{N}}{10}$ hydrochloric acid is 0·91. The transport number of the anion is 0·172. The experimental result should be within 2–5 per cent. of the calculated value.

(ii) *Determine the Degree of Ionisation of Water at* 18°. Since water is ionised it follows from the law of mass action that in any solution containing either hydrogen or hydroxyl ions,

$$\text{Concentration of } H^{\cdot} \text{ ions} \times \text{concentration of } OH' \text{ ions} = \text{constant} \times \text{concentration of water.}$$

The concentration of undissociated water is always extremely large when compared with the concentrations of the ions, and consequently may be regarded as constant. Hence $H^{\cdot} \times OH' = K.$

From which it follows that every solution containing OH′ ions must contain H˙ ions to the extent represented by $\frac{OH'}{K}$. Prepare $\frac{N}{100}$ solutions of caustic potash and hydrochloric acid and place them in potential vessels fitted with electrodes as described in the last experiment. Pass a current of hydrogen through the solutions, and measure the electromotive force of the cell

$$H_2 \mid 0{\cdot}01\ N, HCl \mid 0{\cdot}01\ N, KCl \mid 0{\cdot}01\ N, KOH \mid H_2,$$

as described in the last experiment, using a hundredth-normal solution of potassium chloride in the middle vessel. Let E_0 be the measured value of the electromotive force of the cell; this value will be found to differ from the value calculated from the expression

$$E_1 = 0{\cdot}058 \log_{10} \frac{a_1 C_1}{C_2},$$

where C_1 and a_1 are the concentration and degree of ionisation respectively of the hydrochloric acid, and C_2 is the concentration of the hydrogen ions in the caustic potash.

The difference between the observed and calculated values of the cell is due to the large liquid contact potentials at the surfaces of contact of HCl and KCl and KCl and KOH; and since these oppose the electrode potentials the measured value will be smaller than the calculated value. In the case of completely dissociated solutions it is possible to calculate the potential difference at the liquid contacts. Thus, if there are two completely dissociated solutions of hydrochloric acid and potassium chloride in contact, the contact potential will be given by

$$\mathsf{E} = \frac{\mathsf{RT}}{\mathsf{F}} \log_e \frac{u_{\mathrm{H}} + v_{\mathrm{Cl}}}{v_{\mathrm{Cl}} + u_{\mathrm{K}}},$$

where u and v are the mobilities of the ions whose symbols are written beneath them, and the other letters have their usual meanings.

For the purpose of calculating the contact potentials, the solutions measured in this experiment may be regarded as being completely ionised, so that the potential difference at the surface of contact HCl | KCl is given by

$$\mathsf{E}_c = 0{\cdot}058 \log_{10} \frac{u_{\mathrm{H}} + v_{\mathrm{Cl}}}{v_{\mathrm{Cl}} + u_{\mathrm{K}}} \text{ at } 18^\circ,$$

and at the surface of contact KCl | KOH

$$\mathsf{E}_{c'} = 0{\cdot}058 \log_{10} \frac{v_{\mathrm{OH}} + u_{\mathrm{K}}}{v_{\mathrm{Cl}} + u_{\mathrm{K}}} \text{ at } 18^\circ,$$

where u and v are the mobilities of the ions whose symbols are written beneath them. From Table V., Appendix, the mobilities of the ions in question are found to be $\mathrm{H}^{\cdot} = 318$, $\mathrm{OH}' = 174$, $\mathrm{Cl}' = 65{\cdot}9$, and $\mathrm{K}^{\cdot} = 65{\cdot}3$.

Hence E_c and $\mathsf{E}_{c'}$ calculate out to $\mathsf{E}_c = 0{\cdot}0271$ volts and $\mathsf{E}_{c'} = 0{\cdot}0151$ volts; these two potentials act in the same direction, but in opposition to the electrode potentials; hence to get true electrode potential the sum of the contact potentials must be added to the experimentally determined value E_0,

i.e. $E_0 + 0{\cdot}0422 =$ the electrode potential difference E_1,

$$E_0 + 0{\cdot}0422 = E_1 = 0{\cdot}058 \log_{10} \frac{a_1 C_1}{C_2}.$$

Now, since the concentration of the hydrogen ions is known in the hydrochloric acid, it follows that the concentration of the hydrogen ions in the caustic potash solution may be calculated from the above expression ($a_1 = 0{\cdot}98$). Knowing the concentration of the $H^{\cdot}$ and OH' ions in the caustic potash solution, the degree of ionisation of water may be calculated:

$$H^{\cdot} \times OH' = K,$$

and since in pure water $H^{\cdot} = OH'$ it follows that $\sqrt{K}$ gives the concentration of $H^{\cdot}$ and OH' ions in water.

In the calculation the concentration of OH' ions in caustic potash may be taken as $0{\cdot}0097$, *i.e.* $0{\cdot}01 \times a_2$, where $a_2 = 0{\cdot}97$.

The degree of dissociation of water at 18° is $0{\cdot}8 \times 10^{-7}$.

(iii) *Determine the Degree of Hydrolysis of an* $\frac{N}{1000}$ *Solution of Sodium Acetate.* Sodium acetate is hydrolysed in water solution according to the equation

$$CH_3COONa + H_2O \rightleftarrows CH_3COOH + NaOH,$$

consequently there are both hydrogen and hydroxyl ions in the solution, the concentration of which may be determined by the method described in the last experiment.

Make up $\frac{N}{1000}$ solutions of hydrochloric acid and sodium acetate, and construct from them a hydrogen concentration cell according to the scheme

$$H_2 \left| \frac{N}{1000} HCl \right| \frac{N}{1000} NaCl \left| \frac{N}{1000} CH_3COONa \right| H_2.$$

Use $\frac{N}{1000}$ sodium chloride in the middle vessel, and measure the electromotive force of the cell.

Calculate the liquid contact potentials at the surfaces HCl | NaCl and NaCl | CH_3COONa, and add their values to the observed electromotive force. Then calculate the concentration of the hydrogen ion C_2 in the sodium acetate by means of the expression

$$E = 0{\cdot}058 \log_{10} \frac{a_1 C_1}{C_2},$$

where $a_1 = \mathbf{1}$.

From the relationship

$$H^{\cdot} \times OH' = K = 1{\cdot}1 \times 10^{-14}$$

the concentration of the hydroxyl ions can be obtained by substituting the value C_2 in the expression thus:

$$OH' = \frac{1{\cdot}1 \times 10^{-14}}{C_2}.$$

The percentage hydrolysis of $\frac{N}{1000}$ sodium **acetate is** then given by

$$P = \frac{\text{Concentration of } OH' \times 100}{\text{Concentration of sodium acetate}}$$

$$= \frac{1{\cdot}1 \times 10^{-14} \times 100}{C_2 \times 0{\cdot}001} = \frac{1{\cdot}1 \times 10^{-9}}{C_2}.$$

Electrodes of the Second Type

The methods adopted for the measurement of potential differences have, so far, furnished no means of considering the potentials of ions which are not directly furnished by an element, *e.g.* SO_4'', NO_3', CH_3COO', etc., *i.e.* chiefly anions of other than binary acids. These ions may be measured by electrodes of the second type. An electrode of this kind consists of a metal in contact with its *sparingly soluble salt* which contains the same anion as the solution under consideration. Thus, for example,

$$\mathrm{Ag\,.\,AgCl\,.\,KCl}$$

would constitute an electrode of the second type, for the measurement of chlorine ions, whose potential would depend entirely on the concentration of the chlorine ions furnished by the potassium chloride.

We have seen that the potential in electrodes of the first type depends on the concentration of the metal ion; in the above case, then, the potential of the electrode would depend on the concentration of the silver ions furnished by the silver chloride. The number of the silver ions is, however, determined by the number of the chlorine ions, according to the expression

$$\mathrm{Ag}^{\cdot} \times \mathrm{Cl}' = \mathbf{L},$$

where **L** is the solubility product of silver chloride, which at 18° is equal to $1{\cdot}10 \times 10^{-10}$. If potassium chloride is added to a saturated aqueous solution of silver chloride, the concentration of the chlorine ions will be very much increased, and the silver ions, according to the above equation, will be correspondingly decreased, *i.e.* the concentration of the silver ions will depend absolutely on the concentration of the chlorine ions. Consequently Ag . AgCl may be viewed as, and is in reality, an electrode for measuring chlorine ions.

The Nernst equation for such an electrode is

$$\mathbf{E} = \frac{\mathbf{RT}}{\mathbf{F}} \log_e \frac{\mathrm{Ag}^{\cdot}}{\mathbf{K}},$$

where **K** is a constant, $\mathrm{Ag}^{\cdot}$ the concentration of the silver ions, and the other symbols have the usual meaning

Now $$\mathrm{Ag}^{\cdot} = \frac{K_1}{Cl'}$$ where $K_1 = L$.

Hence $$E = \frac{RT}{F} \log_e \frac{K_1}{K \, . \, Cl'},$$

or taking out $\frac{K}{K_1}$

$$E = \frac{RT}{F} \log_e \frac{K}{K_1} - \frac{RT}{F} \log_e Cl'$$

when the concentration of the chlorine ions **is unity**

$$E = \frac{RT}{F} \log_e \frac{K}{K_1},$$

and this is designated EP, *i.e.* the potential difference between the electrode Ag . AgCl, and a normal solution of chlorine ions.

Hence $$E = EP - \frac{RT}{F} \log_e Cl'.$$

To use such an electrode it is necessary to know the value of EP and insert it in the equation. The value of EP is determined by making up such an electrode with a solution of potassium chloride containing a known concentration of chlorine ions, and measuring the single potential against a calomel electrode; then since in the equation $$E = EP - 0{\cdot}058 \log_{10} a_1 C_1$$ all the factors are known but EP this can be calculated. E is the measured single potential, C_1 is the concentration of potassium chloride, and a_1 its degree of dissociation.

EXPERIMENTS

(i) *Determine the value of* EP *for a Carbonate Electrode at* 25°. Prepare about 5 grams of pure silver carbonate by slowly adding a dilute solution of sodium bicarbonate to a concentrated solution of silver nitrate, shaking the mixture vigorously during the addition. If the silver carbonate has been correctly prepared it will have a sulphur-yellow colour. Wash the precipitated carbonate with water to remove the excess of bicarbonate, and finally wash with an $\frac{N}{10}$ solution of *pure* sodium carbonate solution. The sodium carbonate should be extracted with absolute alcohol, before being made up, to remove any free caustic soda which it may contain. Place about 2–3 grams of the moist silver carbonate in a 125 c.c. stoppered bottle, fill the bottle with $\frac{N}{10}$ sodium carbonate solution, close the bottle with a rubber cap and shake in a thermostat at 25° for 24 hours, so that the solution may become saturated with silver carbonate. Place about one gram of silver carbonate in a potential vessel; fill the vessel with the saturated silver carbonate solution, insert a freshly-silvered silver electrode, prepared as described in Chapter VI., and measure the potential against a normal calomel electrode, using saturated potassium chloride in the middle vessel. Care should be taken that the silver electrode is entirely covered by the silver carbonate.

If E is the measured single potential,

$$E = EP - \frac{0{\cdot}0595}{2} \log_{10} CO_3''.$$

The concentration of the CO_3'' is obtained in the following manner: $0{\cdot}1$ N sodium carbonate is dissociated to the extent of 63·5 per cent. and hydrolysed 4·52 per cent. Had there been no hydrolysis, then the concentration of carbonate ions would be $\frac{0{\cdot}1 \times 0{\cdot}635}{2}$, since two equivalents of sodium carbonate yield one gram ion of carbonate ions.

But of the total sodium carbonate 4·52 per cent. is hydrolysed, *i.e.* $0{\cdot}5 \times {\cdot}0452 \times 0{\cdot}1$ gram equivalents of hydroxyl ions are present.

From the equation

$$Na_2CO_3 + H_2O = NaHCO_3 + NaOH$$

it follows that of the total sodium ions there are two present due to each molecule of sodium carbonate hydrolysed, *i.e.* one for the HCO_3' and one for the OH'. So that ${\cdot}0452 \times 0{\cdot}1$ of the total sodium ions present are due to the ionisation of sodium bicarbonate and sodium hydroxide formed in the hydrolysis. The difference between this quantity and the total number of sodium ions present gives the number of sodium ions due to the dissociation of sodium carbonate, *i.e.* the quantity which is equivalent to the carbonate ions.

i.e. $$0{\cdot}1 \times 0{\cdot}635 - 0{\cdot}0452 \times 0{\cdot}1:$$

and since each carbonate ion corresponds to two sodium ions the concentration of the carbonate ions is equal to

$$\tfrac{1}{2}(0{\cdot}1 \times 0{\cdot}635 - 0{\cdot}0452 \times 0{\cdot}1) = 0{\cdot}0295.$$

Substituting this value in the above equation, EP can be calculated and should have the value 0·7457 volts.

(ii) *Determine the Solubility and Percentage Hydrolysis of a Saturated Solution of Silver Carbonate at 25°.* Prepare a quantity of pure silver carbonate by the method described above, place 5 grams of the moist salt in each of two 125 c.c. stoppered bottles, fill one bottle with carbon-dioxide free water, and the other with an approximately normal pure sodium carbonate solution. Stopper the bottles, close the stoppers with rubber caps, and shake in a thermostat at 25° for 24 hours. Measure the potentials of both solutions against a calomel electrode, using the carbonate electrode described in the last experiment. From the single potentials we can calculate the concentrations of both the silver ions and the carbonate ions in each solution.

The silver ions by means of the equation

$$\mathrm{E} = 1{\cdot}075 + 0{\cdot}0595 \log_{10} \mathrm{C}'',$$

where 1·075 is the value of EP for silver, C'' the concentration of silver ions, and E the measured single potential difference.

The carbonate ions by means of the expression

$$\mathrm{E} = 0{\cdot}7457 - 0{\cdot}029 \log_{10} \mathrm{C}',$$

where 0·7457 is the value of EP for the carbonate ion, determined in the last experiment, C' the concentration of the carbonate ions, and E the measured single potential difference.

The solubility product of silver carbonate is now given by

$$(\mathrm{C}'')^2 \times \mathrm{C}' = \mathrm{L}.$$

In pure water solution, assuming there is no hydrolysis, the concentration of the silver ions is twice that of the carbonate ions,

i.e. $$\tfrac{1}{2}\mathrm{Ag}^{\cdot} = \mathrm{CO}_3'',$$

and $$\mathrm{Ag}^{\cdot} \times \mathrm{Ag}^{\cdot} \times \mathrm{CO}_3'' = \mathrm{L} \text{ for a water solution,}$$

or $$\tfrac{1}{2}(\mathrm{Ag}^{\cdot})^3 = \mathrm{L},$$

$$\mathrm{Ag}^{\cdot} = \sqrt[3]{2\mathrm{L}}.$$

Now the concentration of $\tfrac{1}{2}\mathrm{Ag}^{\cdot}$ is the same as the molecular concentration of silver carbonate,

i.e. Solubility of silver carbonate $= \tfrac{1}{2}\sqrt[3]{2(\mathrm{C}'')^2 \times \mathrm{C}'}$.

Calculate the solubility of silver carbonate from both experiments by the above formula. The value has been found by Spencer and Le Pla to be $1{\cdot}15 \times 10^{-4}$ gram molecules per litre.

The degree of hydrolysis of silver carbonate may be calculated in the following manner:

If silver carbonate is hydrolysed, and, as we may assume, completely ionised in aqueous solution, then we shall have present the ions $Ag^{\cdot}$, OH', HCO_3', and CO_3''.

The equivalent concentration of the silver ions, as the only cations present in any quantity, must be equal to the sum of the equivalent concentrations of the CO_3'', OH', and HCO_3' ions. Hence the sum of the OH' ions and the HCO_3' ions is equal to the difference between the $Ag^{\cdot}$ ions and the CO_3'' ions. If we represent the equivalent concentrations of the ions by their symbols the above may be expressed,

$$Ag^{\cdot} = OH' + CO_3'' + HCO_3'$$
$$Ag - CO_3'' = OH' + HCO_3'.$$

Now the concentrations of the OH' ions and the HCO_3' ions are the same, as will be seen from the equations

$$Ag_2CO_3 + H_2O \rightleftarrows AgHCO_3 + AgOH,$$

which, when completely dissociated, gives the ions thus:

$$AgHCO_3 + AgOH \leftrightarrows 2Ag^{\cdot} + OH' + HCO_3'.$$

Hence the concentration of the OH' ions is given by

$$OH' = \frac{Ag^{\cdot} - CO_3''}{2},$$

or, since the concentration of the $Ag^{\cdot}$ ions and CO_3'' ions are known,

$$OH' = \frac{c'' - c'}{2}.$$

Hence the percentage hydrolysis h is given by

$$h = \frac{(c'' - c')}{2c''} 100.$$

The value of h should work out to 96·9 per cent.

Electrodes of the Third Type

The foregoing types of electrodes have not furnished a method of dealing with metals such as calcium, barium, thallium, etc., where the metal reacts with water.

The potentials of these metals may be determined by electrodes of the third type. It was shown by Luther (*Zeit f. Physik Chemie,* 27, 364, 1898) that if a chain be made up consisting of a metal, one of its insoluble salts, an insoluble salt of another metal containing the same anion, and a solution of a salt containing the same cation as the second insoluble salt, such an electrode serves to measure the concentration of the metallic ions in the solution, provided that the EP of the chain has been determined. An example will make this clearer. Suppose we have the chain

$$Hg \mid HgI . TlI . TlNO_3 \mid$$

such an electrode obeys the usual Nernst formula

$$E = \frac{RT}{nF} \log_e \frac{K_1}{Hg^{\cdot}},$$

where the symbols have their usual meanings. If such an electrode be measured the potential will depend in the first place on the concentration of the mercury ions furnished by the mercurous iodide; this is, however, controlled by the concentration of the iodine ions given by the thallous iodide, which are in their turn determined by the thallous ions furnished by the thallous nitrate. Hence the concentration of the thallous ions determines the potential measured.

This is expressed in the following equations, in which the symbols represent concentrations:

$$Hg^{\cdot} \times I' = K_2,$$
$$Tl^{\cdot} \times I' = K_3,$$

since the concentration of the iodine ions in both expressions is the same for a solution saturated with both.

$$\frac{Hg^{\cdot}}{Tl^{\cdot}}=\frac{K_2}{K_3}.$$

Substituting the value of $Hg^{\cdot}$ in the original equation we get

$$E=\frac{RT}{nF}\log_e\frac{\frac{K_3}{K_2}\cdot K_1}{Tl^{\cdot}}=\frac{RT}{nF}\log_e\frac{K_4}{Tl^{\cdot}}$$

$$=\frac{RT}{nF}\log_e K_4-\frac{RT}{nF}\log_e Tl^{\cdot}.$$

When $Tl^{\cdot}=1$, $E=\frac{RT}{nF}\log_e K=EP$,

where EP is the potential difference between the electrode HgHgITlI and a normal solution of thallium ions.

The expression resolves itself into

$$E=EP-0{\cdot}0595\log_{10}Tl^{\cdot} \text{ at } 25^{\circ}.$$

The thallous ions are not entirely due to the thallous salt, a portion of them, i, coming from the thallous iodide, hence the equation must be written

$$E=EP-0{\cdot}0595\log_{10}(C+i),$$

where C is the concentration of the thallous ions from the solution. For the method of obtaining i see Spencer (*Zeit f. Physik Chemie*, 76, 3, 360).

In making up an electrode of the third type several conditions must be observed. First the depolarisers, *i.e.* the insoluble salts, must be sparingly soluble, and must not react with one another nor with the solution. The depolariser containing the same cation as the solution must be more soluble than the other depolariser. In the example considered above thallous iodide is more soluble than mercurous iodide.

EXPERIMENTS

(i) *Determine the value of* EP *for the Electrode* $Hg, HgI, TlI, nTlNO_3$. Place 5 c.c. of pure mercury, 2–3 grams of mercuric iodide, and 2–3 grams of thallous iodide in a well-stoppered 250 c.c. bottle, fill up with an $\frac{N}{10}$ solution of thallous nitrate, and shake for 24 hours in a thermostat at 25°. Place 1 c.c. of pure mercury in a potential vessel, and fill up with the saturated solution, taking care that a considerable quantity of the solid in the bottle enters the potential vessel. Make electric contact with the mercury by means of a platinum wire fused into a glass tube. Measure the potential against a calomel electrode, using a saturated solution of potassium chloride in the middle vessel. Calculate the value of EP by means of the expression given above, using the value of $i = 0{\cdot}00471$.

(ii) *Determine the Concentration of Thallous Ions in a* 0·01 N *Solution of Thallous Chloride.* Make up a 0·01 N solution of thallous chloride, place it in a well-stoppered 250 c.c. bottle, add 5 c.c. of pure mercury, 2–3 grams of mercuric iodide, and 2–3 grams of thallous iodide. Close the bottle with a rubber cap, and shake for 24 hours in a thermostat at 25°. Measure the potential, as described in the last experiment, and calculate the concentration of the thallous ions by means of the formula given above. Taking the value of EP as $+0{\cdot}5355$ and $i = 0{\cdot}00471$. From the concentration of the thallous ions, calculate the degree of dissociation of 0·01 N thallous chloride.

Oxidation and Reduction Potentials

When a substance in solution passes from a lower to a higher state of oxidation, the change in the positive ion can be represented as due to an increase in the number of ionic changes; thus, if a ferrous salt is oxidised to a ferric salt, the change may be represented by the equation

$$\mathrm{Fe}^{\cdot\cdot} + \oplus = \mathrm{Fe}^{\cdot\cdot\cdot}.$$

In the same way the oxidation of metallic zinc to a salt in solution may be represented by

$$\mathrm{Zn} + 2\oplus = \mathrm{Zn}^{\cdot\cdot}.$$

The reversal of the above equations will naturally represent reduction.

Considering a substance which gives rise to negative ions, the change from the free element to ions must therefore be described as a reduction, and represented thus:

$$\mathrm{I}_2 + 2\ominus = 2\mathrm{I}',$$

and in the same way the increase of the number of negative charges on an anion will represent a reduction.

As an example of this, the passage of potassium ferricyanide to potassium ferrocyanide may be taken

$$\mathrm{Fe(CN)}_6''' + \ominus = \mathrm{Fe(CN)}''''.$$

If these considerations be granted, oxidation may be defined as the taking up of positive charges or the removal of negative charges, and *vice versa* reduction is the taking up of negative charges or the removal of positive charges.

The measurement of the potential difference between a metal and a solution gives, as has already been seen, the tendency of the metal to form ions, or in other words gives the tendency towards oxidation

It is possible by means of electromotive force measurements to determine the tendency of an ion in a lower state of oxidation to pass over into a higher state of oxidation,

e.g. $$\mathrm{Fe}^{\cdot\cdot} \rightleftarrows \mathrm{Fe}^{\cdot\cdot\cdot}.$$

Such measurements are made possible by the use of platinum electrodes. Suppose a cell is built up as the scheme below indicates,

$$\mathrm{Pt} \mid \mathrm{Fe}^{\cdot\cdot} \mid \mathrm{Fe}^{\cdot\cdot\cdot} \mid \mathrm{Pt},$$

then if the platinum electrodes are connected to an accumulator and a current passed through the solution as indicated by the arrow,

$$\overset{+}{\mathrm{Pt}} \mid \underrightarrow{\mathrm{Fe}^{\cdot\cdot} \mid \mathrm{Fe}^{\cdot\cdot\cdot} \mid} \overset{-}{\mathrm{Pt}},$$

the ferrous ions in the one half of the cell will all be oxidised to ferric ions, and the ferric ions in the other half will all be reduced to ferrous ions, thus:

$$\overset{+}{\mathrm{Pt}} \mid \mathrm{Fe}^{\cdot\cdot\cdot} \mid \mathrm{Fe}^{\cdot\cdot} \mid \overset{-}{\mathrm{Pt}}.$$

If, now, instead of connecting the platinum electrodes to a battery we short-circuit the cell by connecting the two platinum electrodes with a wire, thus:

$$\overgroup{\mathrm{Pt} \mid \mathrm{Fe}^{\cdot\cdot} \mid \mathrm{Fe}^{\cdot\cdot\cdot} \mid \mathrm{Pt}},$$

then the same process will be set up of itself, the ferric ions will give up electrons to the platinum and become ferrous ions, the electrons will pass through the wire to the other platinum electrode, and there convert some of the ferrous ions into ferric ions. The process will go on until an equilibrium is set up, at which the ratio $\frac{\mathrm{Fe}^{\cdot\cdot}}{\mathrm{Fe}^{\cdot\cdot\cdot}}$ will be the same in both solutions. The electromotive force with which this change takes place gives a measure of the tendency of the ions to oxidation, and is proportional to the concentration of the ions.

The expression giving the relationship between the electromotive force and the concentrations of the ions is a modified form of the Nernst equation

$$E_{(M^o \rightarrow M^i)} = P + \frac{RT}{nF} \log_e \frac{M^o}{M^i},$$

where $E_{(M^o \rightarrow M^i)}$ is the electromotive force occasioned by the passage of the lower state of oxidation to the higher, *i.e.* the tendency to oxidation, P is the potential representing this tendency when the two stages are present in equal concentration, M^o and M^i are the ionic concentrations of the lower and higher stages of oxidation respectively, n is the difference in valency of the ions in question, and the other symbols have the usual meanings.

Method of Measurement. In making a measurement, a solution is made up of salts of the same anion, but in different states of oxidation. Thus, taking a specific case, a solution of ferrous and ferric chlorides is made up and placed in two potential vessels of the usual type, and electrodes of platinised platinum are inserted. These are made by fusing short lengths of platinum wire into glass tubes and making electric contact by means of a drop of mercury. The electrodes are then coated with platinum black and freed from occluded chlorine as described above. The potential of each half element is measured against a calomel electrode, and they ought both to give the same value. It will be found, however, that usually the value is not the same, but that after a period, more or less prolonged, they become the same. Abegg and Spencer have shown that if the electrodes are polarised, either anodically or cathodically, before insertion in the liquids, constant results are at once obtained.

It is therefore usual to make all measurements in duplicate, using in one cell an anodically polarised electrode, and in the other a cathodically polarised electrode. Both cells should give the same value. The electrodes are polarised by using them as electrodes in the electrolysis of a dilute solution of sulphuric acid. The cell measured is thus

$$\mathrm{Pt} \left| \begin{array}{l} \mathrm{Fe}^{\cdot\cdot} \\ \mathrm{Fe}^{\cdot\cdot\cdot} \end{array} \right| \text{Calomel Electrode.}$$

Let the value of this combination be ϵ volts; all oxidation potentials are expressed on the basis that the tendency of hydrogen to pass into the ionic condition, when in contact with a normal solution of its ions, is zero. Hence the value of ϵ must be converted to this *standard. The calomel electrode and the normal* hydrogen electrode, when connected, have an electromotive force of $+0{\cdot}283$ volts.

Hence $$\epsilon_h = \epsilon_c + 0{\cdot}283 \text{ volts,}$$

where ϵ_h is the potential of the normal hydrogen electrode, ϵ_c the potential of the calomel electrode. Hence the values obtained when oxidation cells are measured against a calomel electrode must be increased by $-0{\cdot}283$ volts.

From the value of $\mathsf{E}_{(o \rightarrow i)}$ thus obtained, P may be calculated, if the concentrations of the two ions are known, from the equation

$$\mathsf{E}_{(o \rightarrow i)} = \mathsf{P} + \frac{0{\cdot}0595}{n} \log_{10} \frac{\mathsf{C}^o}{\mathsf{C}^i},$$

where C^o and C^i are the concentrations of the ions of the lower and higher stages of oxidation, and n is the difference in the valency between the two stages of oxidation.

The value of P for the various pairs of oxidation stages gives a series of the tendencies of these substances to undergo oxidation. The table below contains the values which have been accurately determined.

Electrode.	$H_2 \rightarrow H^{\cdot} = 0.$	$H_2 \rightarrow H^{\cdot} = 0{\cdot}283.$
$Fe^{\cdots} : Fe^{\cdot\cdot}$	+0·743	+0·460
$Cu^{\cdot\cdot} : Cu^{\cdot}$	+0·413	+0·130
$Fe(CN)_6'''' : Fe(CN)_6'''$	+0·436	+0·153
$Tl^{\cdots} : Tl^{\cdot}$	+1·191	+0·908

EXPERIMENT

Determine the Oxidation Potential of a Solution containing Equivalent quantities of Ferrous and Ferric Ions. Make up a litre of a solution of ferrous and ferric nitrates containing sufficient free nitric acid to prevent the hydrolysis of ferric nitrate; analyse the solution to determine the concentrations of the ferrous and ferric salts. The concentration should be about 0·01 in each case, but it is of no importance what the concentration is, so long as it is dilute, and accurately known. Fill two potential vessels with the solution, insert electrodes, prepared and polarised as described above. Care must be taken that the solutions are not oxidised by the air. Measure the potential difference between the electrode and the electrolyte by means of a calomel electrode. From the value obtained deduce the hydrogen value and calculate the value of P, remembering that the concentrations C^o and C^i are the ionic concentrations. The nitrates are the most strongly ionised of ferric salts, hence when in concentrations of 0·01, no great error will be introduced by assuming that they are completely ionised.

CHAPTER VIII

THERMOCHEMISTRY

As was indicated in Chapter VI. the thermal changes accompanying chemical reactions furnish a measure of the energy changes in the substances undergoing reaction. The study of these heat changes constitutes thermochemistry.

Most chemical reactions are accompanied by a heat change, either an evolution of heat, in which case they are known as "exothermic reactions," or an absorption of heat, when they are described as "endothermic reactions."

The amount of the heat change depends on (1) the nature of the reacting substances, (2) the physical condition of the substances, and (3) the quantities of the substances entering into the reaction. Consequently if the substances reacting are always in the same physical condition, *i.e.* gas, liquid, or solid, and in the same quantities, the heat change in a given reaction is constant and characteristic of the reaction.

Thermochemical quantities may be classified under the following headings:

1. Heat of neutralisation.
2. Heat of solution, dilution and hydration.
3. Heat of formation.
4. Heat of combustion.

The nature of these various heat quantities is amply specified by their names.

Units and Method of Expressing Thermochemical Results

Heat changes are almost always expressed with respect to one gram equivalent, or one gram molecule of the reacting substances; thus, for example, the heat of neutralisation of caustic soda by hydrochloric acid is generally denoted as 13·7 large calories. This must be taken to mean that the neutralisation of one gram molecule of hydrochloric acid by one gram molecule of caustic soda gives rise to a heat evolution of 13·7 large calories.

Quantities of heat are usually expressed in calories. The calorie is defined as the quantity of heat required to raise one *gram* of water from 18° to 19°, and designated by the symbol cal. For thermochemical purposes the calorie is too small, since in most cases the heat change would involve the use of very large numbers in which the last two figures are of doubtful accuracy. Hence it is usual to adopt a unit which is approximately one hundred times as large as the calorie, symbolised K. This unit is the quantity of heat required to raise one gram of water from 0° to 100°. A still larger unit, introduced by Berthelot, and known as the large calorie, is often used. This unit is equal to 1000 small calories, and designated Cal.

A thermochemical result is expressed by writing the chemical formulae of the reacting substances side by side, but separated by commas or colons, together with the amount of heat change which has accompanied it. The chemical symbols are always taken to represent the relative weights in grams which they indicate in a chemical equation; and the substances they represent, unless otherwise stated, are assumed to be in the physical condition usual to them at the temperature of the experiment. The method of expressing thermochemical results will be clearer if a few examples are considered.

Thus $$(\mathrm{K}, \mathrm{Cl}, 3\mathrm{O}) = 959\mathsf{K}$$

represents that 959K are evolved when one gram molecule of potassium chlorate is formed from its elements.

$$(\mathrm{KCl}, 3\mathrm{O}) = -97{\cdot}5\mathsf{K}$$

indicates that 97·5 centuple calories are absorbed when a gram molecule of potassium chlorate is formed by the oxidation of dry potassium chloride.

$$(\mathrm{KClO_3}, \mathrm{Aq}) = -100{\cdot}4\mathsf{K}$$

expresses that the heat of solution of one gram molecule of potassium chlorate in an excess of water is −100·4 centuple calories, *i.e.* an absorption of 100·4K takes place.

$$(\mathrm{KClAq}, 3\mathrm{O}) = -153{\cdot}7\mathsf{K}$$

states that an absorption of heat amounting to 153·7K occurs when one gram molecule of potassium chloride in aqueous solution is oxidised to potassium chlorate.

$$(2\mathrm{NaOHAq}, \mathrm{H_2SO_4Aq},) = 313{\cdot}8\mathsf{K}$$

indicates that when two gram molecules of caustic soda in dilute solution are exactly neutralised by a dilute sulphuric acid solution 313·8 centuple calories are evolved.

$$(\mathrm{Br_2}, \mathrm{Aq}) = 10{\cdot}8\mathsf{K}$$

is the heat of solution of one gram molecule of bromine, under ordinary conditions, in excess of water, whilst

$$(\mathrm{Br_2\,gas}, \mathrm{Aq}) = 76{\cdot}4\mathsf{K}$$

is the heat of solution of the same weight of gaseous bromine.

$$(\mathrm{CuSO_4Aq} : \mathrm{Fe}) = 372\mathsf{K}$$

indicates that 372 centuple calories are evolved when 56 grams of iron react with a solution containing one gram molecule of copper sulphate.

A comma is used to separate the formulae of the reacting substances when they combine directly and a colon when they react, but there is no direct combination.

Thus $(HgO:Cl_2)$ indicates that the chlorine reacts with the mercuric oxide to form mercuric chloride and oxygen, whilst (HgO, Cl_2) indicates that the two substances react together to form mercury oxychloride.

Apparatus and Method

All thermochemical operations are carried out in a calorimeter. For the present purpose the calorimeter described below is most suitable. It consists of a double-walled outer vessel, A (Fig. 47), made of polished copper, which is fitted with movable cover, C, made in two halves. The space between the walls of this vessel is filled with water. Standing inside A, supported on three pointed corks, *d*, is a cylindrical vessel, D, of about 1½ litres capacity, made of silver or silvered copper.

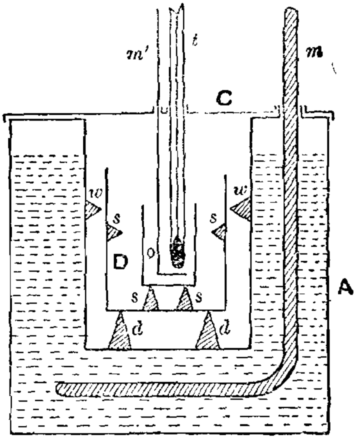

Fig. 47.

This vessel is prevented from touching the sides of the outer vessel, A, by three cork wedges, *w*, which are cemented to the walls of the outer vessel. A third vessel, *o*, of about 750 c.c. capacity, made of silver or platinum, stands inside D, and is isolated from it by cork supports, *s*. The vessel *o* is the calorimeter proper, *i.e.* the vessel in which the actual measurement takes place; the other vessels are to prevent the access of heat to *o* from the outside and the loss of heat from *o* by radiation during the experiment. The vessel *o* is provided with a stirrer, *m′*, made of the same metal as the vessel itself. The outside vessel is surrounded with a thick layer of felt, and is provided with a stirrer, *m*. Beckmann thermometers (see Chapter VII., Part I.) must be used for measuring the temperature changes occurring in the various reactions. The calorimeter fitted up for an experiment is shown in Fig. 48. The method of carrying *out a thermochemical measurement is the same in principle* as that adopted for all kinds of thermal determinations. It consists in measuring the heat change which takes place in a liquid, generally water, in the inside vessel of a calorimeter when a given process occurs in it. The details of the operations naturally vary considerably for the different processes; they will therefore be described under the various headings. See also in this connection Chapter XIII., Part I.

1. Heat of Neutralisation

The heat of neutralisation is the quantity of heat evolved when one gram molecule of an acid is neutralised by an equivalent quantity of a base. When strong acids in dilute solution, *i.e.* 1 gram molecule in 200–400 gram molecules of water, are neutralised by strong bases

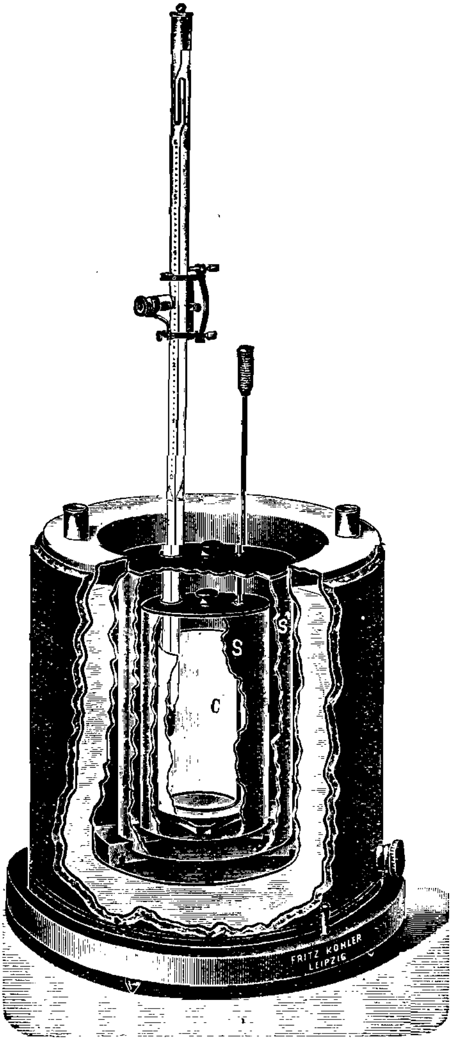

Fig. 43.

in solutions of about the same concentration, it is found that the heat evolved is practically a constant quantity, *viz.* 13·7 Cal. If one considers the changes occurring when such solutions are mixed, the reason for this constant figure becomes apparent. Strong acids and bases in dilute solution are practically completely ionised; the same may be said of the salt formed by their reaction, so that the only real change is the formation of water by the union of the hydrogen and the hydroxyl ions, thus:

$$Na^{\cdot}+OH'+H^{\cdot}+Cl'=H_2O+Na^{\cdot}+Cl'.$$

Hence 13·7 Cal., the heat of neutralisation of strong acids by strong bases, represents nothing more than the heat of combination of hydrogen ions and hydroxyl ions to form water. The heat of neutralisation of weak acids with strong bases may be either greater or less than 13·7 Cal. The reason for this being that the incompletely ionised weak acid has to become ionised before the hydrogen ion can combine with the hydroxyl ion; the ionisation of the weak acid may take place with either the evolution or the absorption of heat, and this quantity of heat is added algebraically to 13·7 Cal., the heat of combination of the hydrogen and hydroxyl ions. A further quantity of heat may be introduced due to the condition of ionisation or hydrolysis of the product of the reaction. The same remarks apply equally to the neutralisation of a strong acid by a weak base.

EXPERIMENTS

(i) *Determine the Heat of Neutralisation of Caustic Soda by Hydrochloric Acid.* Fill the outer walls of the calorimeter with water at least 24 hours before the experiment is to be commenced, and allow it to stand in the room where the experiment is to be carried out. It is important, for good work, that the temperature of the laboratory should not fluctuate. Set two Beckmann thermometers (see Chapter VII., Part I.) so that the mercury stands at the bottom of the scale at atmospheric temperature, compare the readings of the two thermometers so that the relative value of their readings is known. Prepare a quantity of $\frac{N}{2}$ caustic soda, free from carbonate (see page 67), and $\frac{N}{2}$ hydrochloric acid solution. Place the various calorimeter vessels in position, and add 250 c.c. of the caustic soda solution to the inmost vessel. Place one of the Beckmann thermometers in the caustic soda solution, so that its bulb reaches about half way down the liquid. Wash out a wide-necked flask with a little of the $\frac{N}{2}$ hydrochloric acid solution, pour the acid away, and leaving the flask still moist add 250 c.c. of the acid to it. Place this flask in a vessel similar to inmost vessel of the calorimeter, surrounded by a felt covered outer jacket (Fig. 49), and insert the other Beckmann thermometer in the hydrochloric acid.

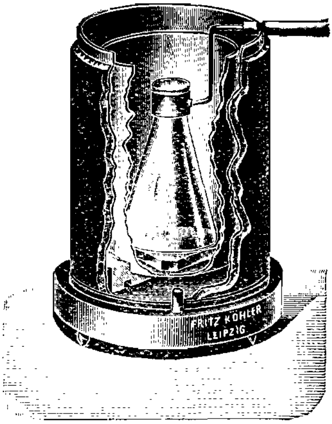

FIG. 49.

It will be noticed that the temperatures of the acid and alkali are either rising or falling in a perfectly regular slow manner, due to radiation. Record the temperatures of the acid and alkali every minute for 8 or 9 minutes, and then pour the acid into the alkali, taking care to avoid splashing. Note the exact time of the mixing, and stir slowly, reading the temperature every minute. It will be found that at first the temperature rises irregularly and then commences to fall at first irregularly, but finally in a perfectly regular manner. To obtain the actual temperatures of the acid and alkali at the moment of mixing, plot the temperature readings of each solution as ordinates against the times as abscissae. This will give two curves, representing the rate at which the temperature of the acid and the alkali is changing, and on producing the curves to the time at which the mixing took place, the temperature of the two solutions will be obtained. As the two Beckmann thermometers will in all probability not give the same reading, one or other must be taken as the standard, and the readings of the other adjusted to it, by adding or subtracting the difference of their readings. The thermometer in the alkali should be taken as the standard, for more readings are taken with it than with the other. Plot the readings after the solutions have been mixed, and draw a line through the points *after* the temperature begins to fall regularly; this gives a curve of the loss by radiation, and on producing this backward to the time at which the solutions were mixed, the point at which it cuts the ordinate through that time, gives the temperature of the end of the reaction. The method will doubtless be clearer from the diagram (Fig. 50). Suppose the points represent the temperatures at the 1st, 2nd, 3rd, 4th, 5th, 6th and 7th minutes in each case, and that the addition of the acid to the alkali took place at the 8th minute, then by producing the curves through the points 1–7 to the 8th minute the true temperatures t_1 and t_2 of the alkali and acid respectively at the moment of mixing will be obtained. Further, suppose the points on the other side of the axis drawn at the 8th minute, represent the temperatures at the 9th, 10th, 11th, 12th, 13th, 14th and 15th minutes, then the line drawn through the points at the 11th, 12th, 13th, 14th and 15th minutes, produced back to the 8th minute, will give the true final temperature t_3.

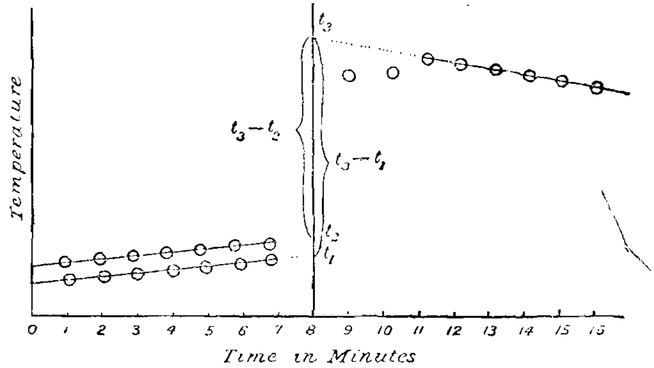

FIG. 50.

The total heat change is calculated as follows:

The reaction has given out a quantity of heat, H Cal., which has raised 250 c.c. of sodium chloride solution from t_2° to t_3°, and 250 c.c. of sodium chloride solution, the calorimeter, stirrer, and thermometer, from t_1° to t_3°. If s_1 is the specific heat of the solution of sodium chloride, and W the water value of the calorimeter, stirrer and thermometer (see Chapter XIII., Part I.), then the quantity of heat used up in effecting this change is

$$s_1 \times 250 \times d(t_3-t_2)+s_1 \times 250 \times d(t_3-t_1)+\mathrm{W}(t_3-t_1),$$

where d is the density of the sodium chloride solution.

An $\frac{N}{4}$ solution of sodium chloride has a density at 18°–20° of 1·043, and a specific heat of 0·978.

The expression therefore becomes

$$H = \frac{1}{1000}\left\{0{\cdot}978 \times 250 \times 1{\cdot}043[(t_3 - t_2) + (t_3 - t_1)] + W(t_3 - t_1)\right\}$$

where H is the heat evolved in large calories.

The quantity H is evolved by the neutralisation of 250 c.c. of an $\frac{N}{2}$ solution of hydrochloric acid, *i.e.* $\frac{1}{8}$ gram molecule, by an equal quantity of caustic soda. Hence the heat of neutralisation $= 8H$ large calories.

The result should be 13·78 Cal.; an error of 0·2 Cal. is permissible in this experiment.

As a further exercise the heat of neutralisation of sulphuric acid by caustic potash may be determined.

(ii) *Determine the Heat of Ionisation of Acetic Acid.* Determine the heat of neutralisation of $\frac{N}{2}$ acetic acid by $\frac{N}{2}$ caustic soda, using the method described in the last experiment. Let H Cal. be the value obtained. Had acetic acid been completely ionised, the amount of heat evolved would have been 13·70 Cal. Hence $(H - 13{\cdot}70)$ Cal. represents the heat change due to the ionisation of the unionised fraction of the acetic acid. Let δ be the degree of ionisation of acetic acid at the dilution and temperature of the experiment, then $(1 - \delta)$ represents the unionised portion. The heat change $(H - 13{\cdot}70)$ Cal. is therefore due to the ionisation of $(1 - \delta)$ gram molecules of acetic acid. Hence, if I is the heat of ionisation,

$$I = \frac{H - 13{\cdot}70}{(1 - \delta)}.$$

The value of δ for acetic acid in $\frac{N}{2}$ solution is 0·6 per cent. and in this experiment acetic acid may be assumed, therefore, to be completely unionised. To determine the value of the degree of ionisation see Chapter III. and Table VI., Appendix B.

Repeat this experiment with barium hydrate; use $\frac{N}{10}$ solutions of hydrochloric acid and baryta. In the calculation use the value of $\delta = 0{\cdot}8$ at 18°–20° for tenth normal baryta.

Avidity of Acids

The heat of neutralisation of acids by alkalies has been made use of to determine the avidity or relative strength of acids. When solutions of two acids are brought into contact with a quantity of a base insufficient to completely neutralise them, the base will be shared between them in the proportion of their strengths if the salts formed remain in solution. This reaction will give rise to a thermal change which will be proportional to the amounts of the two salts formed. The same effect will be produced if the salt of one of the acids is treated with the other acid. Thus, the same final condition will be arrived at if one gram molecular weight of sodium sulphate is treated with two gram molecular weights of nitric acid, or if two gram molecular weights of caustic soda are treated with a mixture of two gram molecular weights of nitric acid and one gram molecular weight of sulphuric acid. If x is the fraction of the caustic soda neutralised by the nitric acid, then $(1-x)$ will represent the fraction neutralised by the sulphuric acid, and the condition of the substances will be represented by the equations

$$2NaOH + H_2SO_4 + 2HNO_3 = (1-x)Na_2SO_4 + 2xNaNO_3 \\ + 2(1-x)HNO_3 + xH_2SO_4.$$

$$Na_2SO_4 + 2HNO_3 = (1-x)Na_2SO_4 + 2xNaNO_3 \\ + 2(1-x)HNO_3 + xH_2SO_4.$$

The fraction $\frac{x}{1-x}$ will give the ratio of the strengths of the two acids.

Avidity determinations are usually carried out by adding one acid to the sodium salt of the other acid, measuring the heat change, and calculating the value of x from the thermal result.

Suppose equivalent quantities of sodium sulphate and nitric acid, represented by Na_2SO_4 and $2HNO_3$, react in dilute solution, and that in the reaction x molecules of sodium sulphate are decomposed to form $2x$ molecules of sodium nitrate. The change will be represented by

$$Na_2SO_4 + 2HNO_3 = (1-x)Na_2SO_4 \\ + 2xNaNO_3 + 2(1-x)HNO_3 + xH_2SO_4,$$

and will give rise to a heat change, say H Cal.

The total heat change H is made up of several factors, *viz.* those due to.

(i) The decomposition of x molecules of Na_2SO_4.

(ii) The formation of $2x$ molecules of $NaNO_3$.

(iii) The interaction of x molecules of H_2SO_4 with $(1-x)$ molecules of Na_2SO_4.

(iv) The interaction of $2(1-x)$ molecules of HNO_3 with $2x$ molecules of $NaNO_3$.

(v) The interaction of $2(1-x)$ molecules of HNO_3 with x molecules of H_2SO_4.

Thomsen has shown that the factor (v) produces no heat change whatever, and that the heat change occasioned by (iv) is of such small dimensions that it can be ignored.

The heat change ($Na_2SO_4Aq, 2HNO_3Aq$), *i.e.* H becomes, therefore, equal to the heat of neutralisation of $2x$ molecules of caustic soda by $2x$ molecules of nitric acid, minus the heat of neutralisation of x molecules of sulphuric acid by $2x$ molecules of caustic soda, plus the heat of reaction of x molecules of sulphuric acid on $(1-x)$ molecules of sodium sulphate, *i.e.*

$$\mathrm{H} = \{x(2NaOHAq, 2HNO_3Aq) - x(2NaOHAq, H_2SO_4Aq) \\ + (1-x)Na_2SO_4Aq, xH_2SO_4Aq\}.$$

If, now, we have $2NaOH$, H_2SO_4 and $2HNO_3$ together the reaction can be represented thus

$$(2NaOHAq, 2HNO_3Aq, H_2SO_4Aq) \\ = (2HNO_3Aq, 2NaOHAq) + (2NaNO_3Aq, H_2SO_4Aq) \\ \text{or } = (H_2SO_4Aq, 2NaOHAq) + (Na_2SO_4Aq, 2HNO_3Aq),$$

the final state being the same in both cases.

Hence

$$(2NaNO_3Aq, H_2SO_4Aq) - (Na_2SO_4Aq, 2HNO_3Aq) \\ = (H_2SO_4Aq, 2NaOHAq) - (2HNO_3Aq, 2NaOHAq).$$

Substituting this in the above equation it becomes

$$\mathrm{H} = x\{(Na_2SO_4Aq, 2HNO_3Aq) - (2NaNO_3Aq, H_2SO_4Aq)\} \\ + (1-x)Na_2SO_4Aq, xH_2SO_4Aq.$$

Hence, if we determine the heat evolved when one molecule of sodium sulphate is acted on by two molecules of nitric acid, two molecules of sodium nitrate by one molecule of sulphuric acid, and sulphuric acid on sodium sulphate, the value of x and the relative strengths of the acids may be calculated.

The heat changes due to the action of sulphuric acid on sodium sulphate have been worked out by Thomsen and found to be

$$(Na_2SO_4\,Aq, nH_2SO_4Aq) = -\frac{n}{n+0{\cdot}8} \times 3300 \text{ Cal.}$$

where n is the number of molecules of H_2SO_4 reacting with 1 molecule of Na_2SO_4.

EXPERIMENT

Determine the Relative Strengths of Sulphuric and Nitric Acids. Prepare molecular solutions of nitric acid, sulphuric acid, sodium sulphate, and sodium nitrate. Determine the heat change when 500 c.c. of nitric acid solution reacts with 250 c.c. of the sodium sulphate solution, and when 250 c.c. of the sulphuric acid solution reacts with 500 c.c. of the sodium nitrate solution. These determinations are effected in the same way that the heat of neutralisation was carried out in the last experiment. Let H Cal. be the *actual* heat evolved in the reaction of sodium sulphate and nitric acid, and H' the heat evolved in the reaction of sodium nitrate and sulphuric acid.

Then

$$\mathsf{H} = \frac{1}{1000}\{250 \times s \times d(t_3 - t_2) + 500 \times sd \times (t_3 - t_1) + \mathsf{W}(t_3 - t_1)\},$$

where s and d represent the density and specific heat of the reaction mixture, t_3 the final temperature, t_1 the initial temperature of the liquid in the calorimeter, *i.e.* nitric acid, and t_2 the initial temperature of the sodium sulphate solution. Since $s = 0{\cdot}969$ and $d = 1{\cdot}019$, the expression becomes

$$\mathsf{H} = \frac{1}{1000}\{1{\cdot}019 \times 0{\cdot}969 \times 250[(t_3 - t_2) + 2(t_3 - t_1)] + \mathsf{W}(t_3 - t_1)\};$$

similarly

$$H' = \frac{1}{1000}\{1{\cdot}019 \times 0{\cdot}969 \times 250[(t_3' - t_2') + 2(t_3' - t_1')] + W(t_3' - t_1'),$$

where t_3' is the final temperature, t_2' the initial temperature of the sulphuric acid solution, and t_1' the initial temperature of the sodium nitrate solution in the calorimeter.

Using the values of H and H′ the value of x can be calculated from

$$4H = 4x(H - H') - \frac{3{\cdot}3x}{0{\cdot}2x + 0{\cdot}8}.$$

2. Heat of Solution, Dilution, and Hydration

The **heat of solution** is the quantity of heat absorbed or evolved when one gram molecule of a substance is dissolved in a definite number of gram molecules, which must be stated, of water or some other solvent. The determination of the heat of solution is carried out in a calorimeter in the same way as the heat changes measured in the foregoing experiments. It is important in expressing heats of solution to state the exact condition of the solid substance, *i.e.* whether it contains water of crystallisation or not, for the heats of solution are very different in the two cases.

The **heat of dilution** is the quantity of heat evolved or absorbed when a solution of one gram molecule of a substance dissolved in a known amount of water, or other solvent, is diluted by a further known quantity of that solvent. The experimental results are expressed thus:

$$(\mathrm{NaCl10Aq}, 400\mathrm{Aq}) = -0{\cdot}71 \text{ Cal.},$$

which means that one gram molecule of sodium chloride, dissolved in ten gram molecules of water, absorbs 0·71 large calories when diluted with 400 gram molecules of water.

The **heat of hydration** is the quantity of heat evolved or absorbed when a gram molecule of an anhydrous salt combines with sufficient water to form its crystalline hydrate; it is expressed thus:

$$(SrCl_2, 6H_2O) = 32{\cdot}97 \text{ Cal.}$$

Obviously when a given salt forms several crystalline hydrates, there will be just so many heats of hydration as there are hydrates. These are distinguished by the method of expressing them; thus we have in the case of sodium hydrogen phosphate the following six heats of hydration:

$$6{\cdot}03 \text{ Cal.} = (Na_2HPO_4, 2H_2O).$$
$$17{\cdot}28 \text{ Cal.} = (Na_2HPO_4, 7H_2O).$$
$$28{\cdot}47 \text{ Cal.} = (Na_2HPO_4, 12H_2O).$$
$$11{\cdot}25 \text{ Cal.} = (Na_2HPO_42H_2O, 5H_2O).$$
$$11{\cdot}19 \text{ Cal.} = (Na_2HPO_47H_2O, 5H_2O).$$
$$22{\cdot}44 \text{ Cal.} = (Na_2HPO_42H_2O, 10H_2O).$$

It will be clear from the above figures that the heat evolved in the addition of each molecule of water is not the same. The method of determining the heat of hydration is to determine the heat of solution of the anhydrous and the hydrated salt, when the difference between the two values is the heat of hydration, thus:

$$(Na_2HPO_4, Aq - Na_2HPO_412H_2O, Aq)$$
$$= (Na_2HPO_4, 12H_2O).$$

EXPERIMENTS

(i) *Determine the Heat of Solution of Potassium Nitrate in Water.* Place 540 c.c. of distilled water in the calorimeter; this volume corresponds relatively with 200 gram molecules of water. Weigh out 15·15 grams of finely-powdered potassium nitrate in a thin-walled previously weighed glass tube, seal up the tube, and weigh the piece of glass drawn off, so that the weight of the glass enclosing the salt is known. Place the tube containing the salt in the calorimeter. When the tube has taken on the temperature of the water in the calorimeter, *i.e.* in about ten minutes, begin to record the temperature, as described in the earlier experiments. Then break the glass bulb, stir rapidly to dissolve the nitre, and record the temperature again. The success of this experiment depends upon the rapid solution of the nitre. Let t_1 be the corrected initial temperature, t_2 the final temperature, W the water equivalent of the calorimeter, stirrer and thermometer, w the weight of the glass bulb, w' the weight of the potassium nitrate, m its molecular weight, s the specific heat of the solution, and d its density. Then H, the heat of solution of a molecular weight, is given by

$$\mathsf{H}=\frac{1}{1000}\left\{\frac{m}{w'}(t_2-t_1)(540\,ds+\mathsf{W}+ws_2)\right\},$$

$d=1·016$, $s=0·966$, and s_2, the specific heat of glass, may be taken as 0·16. The value of H then gives (KNO_3, Aq).

This experiment may be repeated, using potassium chloride, anhydrous calcium chloride or potassium iodide.

(ii) *Determine the Heat of Dilution of Ammonium Nitrate Solution of various strengths.* Make a solution of ammonium nitrate by dissolving 160 grams of the anhydrous salt in 180 grams of water. 141·1 c.c. of this solution will contain one gram molecule of ammonium nitrate. Place a known volume of this solution, say 141·1 c.c., in a flask which has been previously moistened with the solution. Place 360 grams of water, *i.e.* 20

gram molecules, in the calorimeter, record the temperatures of both solution and water, and then mix and record the final temperature.

If t_1 is the initial temperature of the ammonium nitrate solution, t_2 that of the water, t_3 the temperature after mixing, W the water value of the calorimeter, d the density of the diluted ammonium nitrate solution, and s its specific heat, then

$$H = \frac{1}{1000}[141{\cdot}1 \times d \times s(t_3 - t_1) + 360 \times d \times s(t_3 - t_2) + W(t_3 - t_2)]$$

Repeat the experiment for the addition of 50, 100, and 200 molecules of water, starting in each case with a suitable quantity of the solution made up above, which is $NH_4NO_35H_2O$. The values of s and d for the various dilutions are given in the table.

Dilution.	*s*.	*d*.
$NH_4NO_35H_2O + 20H_2O$,	0·865	1·074
$NH_4NO_35H_2O + 50H_2O$,	0·932	1·033
$NH_4NO_35H_2O + 100H_2O$,	0·962	1·018
$NH_4NO_35H_2O + 200H_2O$,	0·981	1·009

Further experiments may be carried out with caustic potash, for which the following values of s and d may be used:

Dilution.	*s*.	*d*.
$KOH + 30H_2O$,	0·876	1·088
$KOH + 50H_2O$,	0·916	1·055
$KOH + 100H_2O$,	0·954	1·028
$KOH + 200H_2O$,	0·975	1·014

(iii) *Determine the Heat of Hydration of Copper Sulphate.* Weigh out 15·9 grams of anhydrous copper sulphate, seal it in a thin-walled tube, and determine the heat of solution in 200 molecules of water as in the last experiment, Then weigh out 24·9 grams of finely-powdered crystallised copper sulphate, $CuSO_45H_2O$, and determine the heat of solution in 195 molecules of water. The difference between these two heat quantities will give the value of $(CuSO_4, 5H_2O)$. The value of

$$(CuSO_4, H_2O) \quad \text{and} \quad (CuSO_4H_2O, 4H_2O)$$

may also be obtained by determining the heat of solution of 17·7 grams of the monohydrated salt. If the various thermal changes are expressed thus:

$$(CuSO_4, Aq) = H'; \ (CuSO_4H_2O, Aq) = H''; \ (CuSO_45H_2O, Aq) = H'''.$$

Then

$$(H' - H''') = (CuSO_4, 5H_2O); \ (H' - H'') = (CuSO_4, H_2O),$$

and $$(H'' - H''') = (CuSO_4H_2O, 4H_2O).$$

The hydrate $CuSO_4H_2O$ may be obtained by weighing out a quantity of finely-powdered $CuSO_45H_2O$, and heating it at 100° until it has lost the requisite amount of water.

3. Heat of Formation

The **heat of formation** is the quantity of heat, evolved or absorbed, when one gram molecule of a substance is formed from its elements. This can rarely be determined directly, but since the total heat change is the same in any reaction, whether it is carried out in one stage or a series of stages, the heat of formation may always be calculated. As an example of this, we may take the heat of formation of cupric chloride as determined by Thomsen. Since copper does not dissolve in hydrochloric acid, the obvious method of dissolving the metal in hydrochloric acid is not possible. Thomsen decomposed copper sulphate solution with iron thus:

$$CuSO_4Aq + Fe = FeSO_4Aq + Cu + 37{\cdot}24 \text{ Cal.},$$

which of course means that

$$(Fe, O, SO_3Aq) - (Cu, O, SO_3Aq) = 37{\cdot}24 \text{ Cal.}$$

The heat of formation of ferrous sulphate in water, *i.e.* (Fe, O, SO_3Aq), had been previously determined and found to be 93·2 Cal.

Hence

$$(Cu, O, SO_3Aq) = 93{\cdot}2 - 37{\cdot}24 = 55{\cdot}96 \text{ Cal.}$$

The heat of solution of copper oxide in dilute sulphuric acid, *i.e.* $(CuO, SO_3Aq) = 18{\cdot}8$ Cal.

Hence

$$(Cu, O, SO_3Aq) - (CuO, SO_3Aq) = (Cu, O),$$

i.e. $$55{\cdot}96 - 18{\cdot}8 = 37{\cdot}16 \text{ Cal.}$$

If, now, cupric oxide is dissolved in dilute hydrochloric acid we have

$$CuO + 2HClAq = CuCl_2Aq + H_2O + 15{\cdot}27 \text{ Cal.}$$

Writing this as a thermal equation we have

$$(Cu, O) + 2(H, Cl, Aq) + 15{\cdot}27 - (H_2, O) = Cu, Cl_2, Aq),$$

and substituting the known values we get

$$37{\cdot}16 + 76{\cdot}64 + 15{\cdot}27 - 68{\cdot}36 = (Cu, Cl_2, Aq),$$

i.e. $$(Cu, Cl_2, Aq) = 62{\cdot}71 \text{ Cal.}$$

The heat of solution of cupric chloride is

$$(CuCl_2, Aq) = 11{\cdot}08.$$

Hence $$(Cu, Cl_2) = (Cu, Cl_2, Aq) - (CuCl_2, Aq)$$
$$= 62{\cdot}71 - 11{\cdot}08 = \mathbf{51{\cdot}63}.$$

EXPERIMENT

Determine the Heat of Formation of Sodium Chloride from its Elements. The following data are necessary for the calculation of the heat of formation of sodium chloride:

(i) Heat of formation of a solution of caustic soda, *i.e.*

$$(Na, O, H, Aq).$$

(ii) Heat of neutralisation of a solution of caustic soda by a solution of hydrochloric acid, *i.e.*

$$(NaOHAq, HClAq).$$

(iii) The heat of solution of sodium chloride, *i.e.*

$$(NaCl, Aq).$$

(iv) The heat of formation of water, *i.e.* (H_2, O).

(v) The heat of formation of hydrochloric acid solution, *i.e.* (H, Cl, Aq).

Of these five quantities we must take those under headings (i), (iv), and (v) as known.

Determine the heat of neutralisation of hydrochloric acid by caustic soda, and the heat of solution of sodium chloride as described in the previous experiments. Calculate the values of these quantities by the methods already indicated.

Let $h = (NaOHAq, HClAq)$ and $h' = (NaCl, Aq)$.

Then $HClAq + NaOHAq = NaClAq + H_2O + h$,

or

$$(Na, O, H, Aq) + (H, Cl, Aq) + h = (Na, Cl, Aq) + (H_2, O),$$

putting in the known values, *i.e.* $(Na, O, H, Aq) = 111{\cdot}81$, $(H, Cl, Aq) = 39{\cdot}315$, and $(H_2, O) = 68{\cdot}3$,

we get $111{\cdot}81 + 39{\cdot}315 + h = (Na, Cl, Aq) + 68{\cdot}3$.

Hence $(\mathrm{Na, Cl, Aq}) = h + 82{\cdot}825.$

Further,

$$(\mathrm{Na, Cl, Aq}) - (\mathrm{NaCl, Aq}) = (\mathrm{Na, Cl}),$$

i.e. $$h + 82{\cdot}825 - h', = (\mathrm{Na, Cl}).$$

4. Heat of Combustion

Reactions with organic substances proceed so slowly as a rule, and are complicated by so many side reactions, that it is impossible to determine the heat of formation or, indeed, the heat change of any organic reaction, directly. There is, however, one change which always goes directly and quickly, *viz.* the combustion of an organic substance in excess of oxygen. The heat generated by the complete combustion of one gram molecule of an organic substance is termed the **heat of combustion**, and since the heats of formation of the products of combustion, *viz.* water and carbon-dioxide, are known, it follows that the heats of formation of organic substances can be calculated from their heats of combustion. Thus, for example, the heat of combustion of alcohol is 340·53 Cal.,

i.e. $$C_2H_6O + 3O_2 = 2CO_2 + 3H_2O + 340{\cdot}53 \text{ Cal.};$$

expressing this as a thermochemical equation

$$(C_2, H_6, O) + (C_2H_6O : 6O) = 2(C, O_2) + 3(H_2, O),$$

i.e. $$(C_2, H_6, O) + 340{\cdot}53 = 2 \times 96{\cdot}96 + 3 \times 68{\cdot}36,$$

or, putting this into words, the sum of the heat of formation of alcohol from its elements and the heat of its combustion is equal to the sum of the heats of formation of the products from their elements. Hence the heat of formation of alcohol from its elements is

$$(C_2, H_6, O) = 58{\cdot}47 \text{ Cal.}$$

This value is for constant pressure, but frequently the gaseous volume of the compound is less than that of the elements from which it is formed. Thus the gram molecule of alcohol has a gaseous volume, when calculated to normal conditions, of 22·4 litres, but the hydrogen and oxygen from which it is formed occupy 3·5 × 22·4 litres at 0° and 760 mm. Hence in the formation there is a diminution in volume of 2·5 × 22·4 litres, or 2·5 molecular volumes. Now, for each molecular volume decrease there is an evolution of 0·543 Cal. at 0°, *i.e.* 0·580 Cal. at 18°. Hence, if 0·580 × 2·5 Cal. be subtracted from the heat of formation at constant pressure we shall get the heat of formation at constant volume, *i.e.*

$$58{\cdot}47 - 1{\cdot}45 = 57{\cdot}02 \text{ Cal.}$$

Method of Determination of Heat Combustion

The heat of combustion is determined in a calorimetric bomb. This consists of a strong steel vessel, **A** (Fig. 51), fitted with a lid, **B**, which screws on and is lined with platinum. The vessel itself is lined either with platinum or enamel. The lid of the bomb is pierced by two right-angled holes, *a* and *b*. Through *a* the bomb is filled with oxygen, and *b* is used for releasing

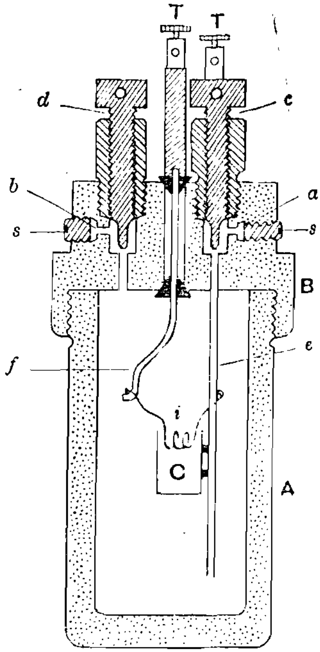

FIG. 51.

the pressure after the experiment. These holes are closed by screw-valves, *c* and *d*. The opening *a* is continued by a fine platinum tube *e*, which supports a platinum crucible, C, where the combustion takes place. Two terminals, T, T, are connected with a thin piece of iron wire, *i*, by means of the platinum tube *e* and a platinum wire *f*. The iron wire can be raised to a red heat by an electric current, and thus ignites the substance in the crucible C. Two screws, *s*, *s*, fit into the side channels in the lid; they are inserted to keep water out of the holes when the bomb is immersed in the calorimeter. The calorimeter in which the determinations are made is essentially the same as that already described; it has, however, only one inner vessel, surrounded by a double-walled vessel filled with water. *It is advisable in these determinations to* work the stirrers by means of a small electric motor The bomb is placed in the inside vessel of the calorimeter and immersed in water up to the screws, *s*, *s*. The temperature changes are recorded by means of Beckmann thermometers.

The water value of the calorimeter, bomb, stirrers, and thermometer must be determined before an experiment is made. This may be effected by the method described in Chapter XIII., Part I., but it is preferable and more accurate to determine it by burning a known weight of a substance of known heat of combustion in the apparatus, and calculating from the observed temperature change.

The following description applies equally to the determination of the water equivalent of the calorimeter and accessories, and the heat of combustion of an organic substance. In the former case the heat of combustion of the substance used must be known, and in the latter case the water value must be known.

To determine the water equivalent, weigh out about 0·7 gram of a substance of known heat of combustion, *e.g.* naphthalene. Compress it into a tablet, and place it in the crucible, C. Attach a piece of thin iron wire, 6–7 cm. long and 0·1 mm. diameter, wound in a spiral, to the tube, *e*, and the wire, *f*. Depress the wire until it touches the substance in the crucible. Smear the screw of the lid and its leaden washer with vaseline, and screw the top tightly into position. Connect an oxygen cylinder, with pressure gauge attached, to the opening, *a*, close the valve, *d*, and open *c* and allow the bomb to fill with oxygen until the pressure is 20–25 atmospheres. Then close *c*, remove the cylinder, and replace the screw, *s*. Examine the joints of the bomb for leakage; if there is none the bomb may be placed in the calorimeter, which contains a weighed quantity of water. "Set" a Beckmann thermometer so that it reads about 2° when placed inside the calorimeter. The great source of error in the determination of the heat of combustion lies in the loss of heat by radiation. This can be minimised by arranging that the temperature of the water in the calorimeter shall be just as much below the temperature of the air space before the experiment as it will be above it after the experiment. This should be about 1·5° if a correct amount of substance has been taken. Connect the terminals, T, T, with a battery of 5–6 accumulators with a key in circuit, attach the stirrers to the mechanical apparatus for working them, put on the calorimeter covers, and insert the thermometer. Start the stirrers working at the rate of about forty strokes per minute, and after about ten minutes commence reading the temperature every minute for about ten minutes. Close the electric circuit, noting the time exactly. The iron wire will thereby be raised to incandescence, and will ignite the substance in the crucible. The temperature of the water in the calorimeter will now commence to rise rapidly; take readings every minute, and note especially the highest temperature recorded; then take readings every minute for about ten minutes to obtain the rate of cooling due to radiation. The bomb must now be removed from the calorimeter and emptied; this is done by removing the screw, *s*, and opening the valve, *d*, when all the gas escapes. The top may now be removed, and the bomb washed out. Any iron which has remained unburnt must be removed and weighed, and its weight subtracted from the weight of iron taken. The corrected temperatures are obtained by the method already described. The initial temperature is always obtained in this way, but the final temperature may be obtained in another manner. If T be the end temperature, T_h the highest temperature reached during the experiment, δ the average change in temperature per minute in the measured period preceding the experiment, δ' in the measured period *after* the highest temperature has been reached, and n the time, in minutes, which elapses between the closing of the circuit and the reaching of the highest temperature, then

$$T = T_h + n\delta' + \frac{\delta' + \delta}{2}.$$

Method of Calculation

(a) *The water equivalent of the calorimeter and other apparatus.* Let W be the water equivalent of the apparatus, w the weight of water in the calorimeter, w' the weight of naphthalene burnt, w_2 the weight of iron wire actually burnt, T_1 the corrected initial temperature, and T the corrected final temperature. Then the apparatus and w grams of water have been raised

$(T-T_1)^0$ by the combustion of w' grams of naphthalene and w_2 grams of iron wire. The heat of combustion of naphthalene is 9693 small calories per gram, and that of iron is 1600 small calories per gram. Hence the total heat evolved during the experiment is

$$w' \times 9693 + w_2 \times 1600 \text{ cal.},$$

and this has raised the apparatus and w grams of water $(T-T')^0$. Now $9693w' + 1600w_2$ calories would raise

$$\frac{1600w_2 + 9693w'}{(T-T')} \text{ grams of water } (T-T')^0.$$

This factor contains the weight of water and the water to which the apparatus is equivalent, *i.e.* the water value.

$$\text{Hence} \qquad \frac{1600w_2 + 9693w'}{T-T'} - w = W.$$

(b) *The heat of combustion.* w grams of water and the apparatus have been raised $(T-T')^0$ by the burning of w' grams of the substance and w_2 grams of iron. The quantity of heat necessary to raise the apparatus and the water $(T-T')^0$ is given by

$$(w+W)(T-T') \text{ calories};$$

of this quantity 1600 w_2 has been furnished by the burning of the iron wire. Hence

$$(w+W)(T-T') - 1600w_2$$

represents the heat produced by the burning of w' grams of the substance. If M is the molecular weight, then

$$\frac{1}{1000}\left\{\frac{M}{w'}[(w+W)(T-T') - 1600w_2]\right\} = H \text{ Cal.},$$

where H is the heat of combustion.

Experiment

Determine the Heat of Combustion and the Heat of Formation of Benzoic Acid. Weigh out about 1 gram of benzoic acid for this experiment; carry out the experiment exactly as described in the foregoing. After the experiment has been completed a precautionary observation ought to be made to ascertain that the combustion has been complete. Incomplete combustion would entail either the formation of free carbon or carbon-monoxide. The presence of the minutest trace of carbon-monoxide can be detected by allowing the escaping gases to pass slowly through a solution of palladous chloride, which will be reduced with the formation of a black precipitate of metallic palladium by carbon-monoxide. The presence of unburnt carbon will be obvious when the apparatus is opened. The oxygen supplied to laboratories always contains nitrogen, and during the combustion some of this will be converted into nitric acid, which, of course, gives rise to a certain amount of heat. In very accurate determinations the quantity of nitric acid is estimated by washing out the bomb with water, boiling the solution to expel carbon-dioxide, and titrating. One gram molecular weight of aqueous nitric acid gives rise to 14·3 Cal. when it is formed. Hence the amount of heat due to this cause can be calculated and deducted from the total quantity of heat. If H be the number of large calories evolved by the combustion of w grams of benzoic acid, and M the molecular weight of benzoic acid, then

$$\frac{\mathsf{M}}{w}\,.\,\mathsf{H} \text{ gives the heat of combustion.}$$

The heat of formation is found thus:

$$C_6H_5COOH + 15O = 7CO_2 + 3H_2O.$$

$$(C_7, H_6, O_2) + \frac{\mathsf{M}}{w}H = 7 \times 96{\cdot}96 + 3 \times 68{\cdot}36,$$

$$(C_7, H_6, O_2) = 7 \times 96{\cdot}96 + 3 \times 68{\cdot}36 - \frac{\mathsf{M}}{w}H.$$

CHAPTER IX

TRANSITION TEMPERATURES

PURE substances undergo physical changes at certain definite temperatures which are characteristic of the substance and change in question. Thus, for example, we have boiling and freezing points, the temperatures at which a liquid changes to the gaseous and solid conditions. In addition to the boiling point and freezing point there are other equally definite temperatures at which definite physical changes take place, *e.g.* the temperature at which rhombic sulphur changes to monoclinic sulphur, and the temperature at which the red variety of mercuric iodide changes to the yellow variety. These temperatures are known as the **transition points** or **transition temperatures.** Just as at the freezing point of a substance solid and liquid are in stable equilibrium with one another, so at the transition temperature the two forms are in stable equilibrium. Not only are there transition temperatures in the case of polymorphous substances, but they are also found in the case of all hydrated salts. Thus it is found that a given hydrate is stable only between definite limits of temperature; above the higher limit the anhydrous salt, or maybe a lower hydrate, is stable, whilst below the lower limit a higher hydrate is stable, the hydrate in question being stable between the limits. The temperature at which one hydrate passes into another or into the anhydrous salt constitutes a transition temperature which is equally definite, and as has been shown in Chapter II., Part I., may be used as a known fixed temperature in calibrating thermometers. The physical properties of the two substances, in equilibrium at the transition point, differ from one another, and use is made of this difference to determine the exact temperature of the change.

The methods for determining the transition point may be classified under the following headings: (1) Dilatometric, (2) Tensimetric, (3) Solubility, (4) Thermometric, (5) Electro-conductivity, (6) Electromotive force, (7) Viscosity, and (8) Optical methods. These will now be considered in the above order.

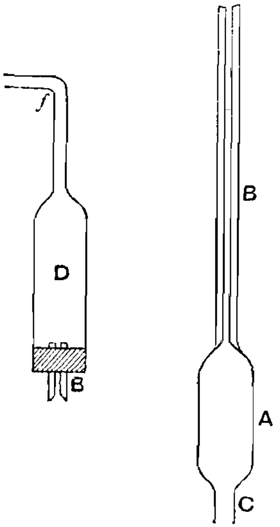

FIG. 52.

1. *Dilatometric Method.* Many substances undergo a change of volume when passing from one form to another: hence if the temperature at which the volume change occurs is determined it will constitute a determination of the transition temperature. The apparatus employed for the determination of the transition temperature by this method is known as a dilatometer. It consists of an elongated bulb A (Fig. 52), of about 30–40 c.c. capacity. A long capillary tube B, about 0·5 mm. diameter, is attached to the bulb and the other end of the bulb is open. The bulb is almost filled with the

substance whose transition point is to be determined and the open end C sealed off. The air is removed from the bulb, and the interstices between the particles of the substance filled with some liquid which does not dissolve in the substance under investigation, but which may dissolve a little of it, since this will accelerate the change at the transition point. Sufficient liquid must be present to just enter the bottom of the capillary tube. The dilatometer, when filled, constitutes a large thermometer. An opal millimetre scale is fastened to the back of the capillary and the bulb immersed in a bath at constant temperature. After the bulb has taken on the temperature of the bath, the height of the liquid in the capillary and the temperature are noted. The temperature of the bath is then slowly raised one degree and the height of the liquid in the capillary again noted. This operation is repeated degree by degree for several degrees until the transition has taken place. So long as the transition of one form into the other has not taken place the liquid will rise regularly in the capillary tube for equal increments of temperature, but at the moment transition takes place, a very much larger rise will be observed if the original substance is denser than the substance into which it is changing. If the original substance is less dense then a decreased rise will be observed. After the transition has taken place the rate of rise in the capillary will again become regular for equal increments of temperature. On allowing the dilatometer to cool down again the same changes will take place in the reverse order. If now the heights of the liquid in the capillary are plotted as ordinates against the temperatures as abscissae a curve system as depicted in Fig. 53 will be obtained. The two curves ABCDE and ABFDE should theoretically be coincident;

the reason, that they are not, is, that a lag occurs in the transition, *i.e.* it does not take place instantaneously at the transition temperature, but at a temperature slightly above the true transition point in the heating curve, and at a temperature slightly below in the cooling curve. The mean, therefore, of the points C and F will give the transition temperature. The points C and F may be brought nearer together by raising the temperature very slowly in the neighbourhood of the transition point. The dilatometer may be used in another manner.

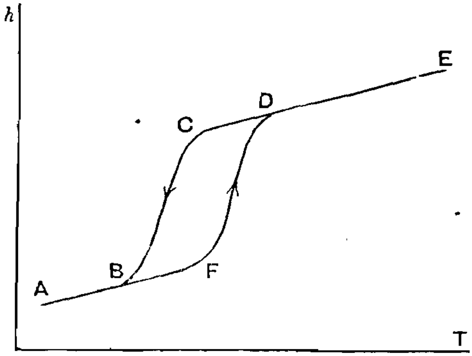

Fig. 53.

If a mixture of the two forms of a substance is placed in a dilatometer at the transition temperature, the height of the liquid in the capillary will remain constant no matter how long the bulb is kept at that temperature. If, however, the temperature is lowered or raised ever so little, one of the forms will pass over into the other and a change of volume will take place. The method, therefore, is to find approximately the transition temperature, and then to place a dilatometer containing both forms of the substance under investigation in a bath somewhere about that temperature. After about 15 minutes the height of the liquid is noted, and then after 15 minutes more it is again noted to see whether it is rising or falling. If a contraction takes place, the temperature is changed until an expansion takes place. Two temperatures are thus obtained between which the transition temperature lies. Then by careful regulation of the temperature of the thermostat these two points are brought closer together until finally a temperature is reached at which neither expansion nor contraction occurs. This is the transition temperature.

EXPERIMENTS

(i) *Determine the Transition Temperature for Anhydrous Sodium Sulphate and the Decahydrate.* Fill a dilatometer with powdered Glauber's salt. This is done by inverting the dilatometer and placing a glass bead at the joint of the capillary tube and the bulb, to prevent the capillary being filled with the powdered salt. Then add sufficient of the salt to three-quarters fill the bulb. Fuse off the end C, and, when the glass is cold, shake down the salt. Attach a glass adapter, D (Fig. 52), to the dilatometer by means of a rubber stopper. Fill the adapter with petroleum, attach the tube *f* to a water pump, and exhaust the dilatometer. After all the air possible has been extracted from the bulb remove the pump connection from *f*, when the petroleum will be forced into the bulb. Repeat the process as long as any air bubbles remain in the dilatometer. Then withdraw the petroleum from the capillary by inserting a fine capillary tube and connecting it to the pump. If the dilatometer is correctly filled the petroleum should stand at the bottom of the scale. Place the bulb of the dilatometer in a thermostat at 28°. A large beaker of water heated by a small flame will serve as a thermostat in this experiment. When the bulb has taken on the temperature of the bath, *i.e.* in about ten minutes, note the height of the meniscus and the temperature of the bath. Raise the temperature one degree; this should be done slowly, about ten minutes being taken for the change; keep the temperature constant for about five minutes, and then read both temperature and the height of the meniscus. Proceed in the same way degree by degree to 35° or 36°. It will be noticed that at about 33° the meniscus will rise much more for one degree increase of temperature than at the other temperatures. Let the bath cool slowly, and make measurements every degree as before down to 28°. Plot the measurements as described above, and deduce the transition temperature from them.

(ii) *Determine the Transition Temperature of Astrakanite and a Mixture of Glauber's Salt and Heptahydrated Magnesium Sulphate.* Astrakanite is a double sulphate of magnesium and sodium which is only stable above 21°. Below this temperature it splits up in the presence of water into Glauber's salt and hydrated magnesium sulphate thus,

$$Na_2SO_410H_2O + MgSO_47H_2O \rightleftarrows MgSO_4Na_2SO_44H_2O + 13H_2O.$$

Make a mixture of equimolecular quantities of Glauber's salt and crystallised magnesium sulphate; powder the salts separately, and then mix them by stirring with a glass rod. Place the mixture in a dilatometer, fill with petroleum as before, and place in a thermostat at 16°; slowly raise the temperature degree by degree to 25°, noting the temperature and height of the meniscus at each point. At 21°–22° the mixture will partially liquefy, and here an increased rise of the meniscus in the capillary tube will be observed. Now cool the thermostat slowly back to 16°, taking readings as before. Plot the values, and from the curves deduce the transition point.

As a further experiment the change of sodium ammonium racemate into a mixture of the dextro and laevo tartrates may be determined. The point lies about 28°.

2. *Tensimetric Method.* Two substances which change into one another by raising or lowering the temperature are in equilibrium in all respects at the transition temperature. If the substances possess a measurable vapour pressure this property may be used to determine the transition point. Measurements of this kind are carried out in a tensimeter or differential pressure gauge. The instrument generally adopted is the Bremer-Frowein tensimeter. This consists of a U-tube A (Fig. 54), the limbs of which are about 30 cms. long, and are bent together as indicated in the diagram. The limbs of the U-tube are bent apart at the top, and two bulbs, *a* and *b*, are blown in them; above the bulbs two small flasks, *f*, *f*, are attached. The substances whose vapour pressures are to be compared or measured are placed one in each of these flasks and the necks sealed

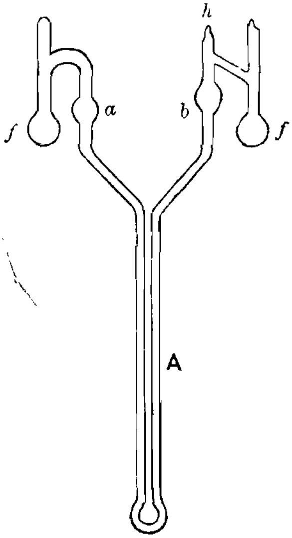

FIG. 54.

off. Then the manometer is filled with a suitable non-volatile liquid, *e.g.* α-bromnaphthalene serves excellently, and the apparatus laid horizontally so that the manometer liquid runs into the bulbs *a* and *b*. The open end, *h*, is then attached to a mercury pump, the apparatus exhausted, and the end *h* sealed. The apparatus is then placed in a vertical position, and after standing at constant temperature for some time the difference in height of the meniscus in the two limbs of the manometer gives the difference in pressure between the two substances in millimetres of α-bromnaphthalene. It will be obvious that by placing concentrated sulphuric acid in one of the flasks the vapour pressure of the substance in the other flask can be determined directly.

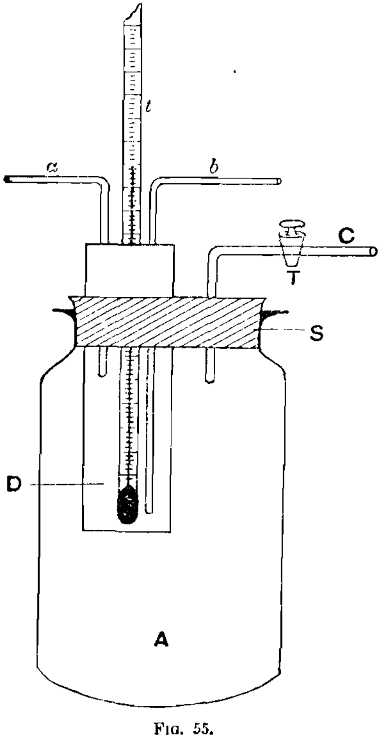

FIG. 55.

Another method, due to Cumming (*J.C.S.*, 1909, 95, 1772), may be used to determine the transition point of hydrates by measurement of vapour pressure. The apparatus consists of a strong wide-necked glass bottle, A (Fig. 55), about 750 c.c. capacity, closed with a well fitting stopper, S, which carries a highly polished silver cylinder, D, 10 cm. long and 2 cm. diameter, and a glass tube, C, fitted with a stopcock, T. The silver cylinder is closed by a cork which carries two tubes, *a* and *b*, and a thermometer, *t*, graduated in tenth-degrees. The method consists in placing a solution or hydrate in the bottle, and evacuating as completely as possible by means of a water pump. The apparatus is then placed in a thermostat, and allowed to remain there for several hours. The vapour pressure is then determined by measuring the dew point. This is done by placing a quantity of ether in the silver tube and slowly blowing a current of air through it until condensation of water takes place on the silver tube. The temperature at which this occurs is noted by the thermometer, *t*. The air current is then either stopped or reduced very much, when the temperature of the silver tube slowly rises and the film of moisture disappears from the silver tube. The temperature at which this last trace vanishes is read, and the mean of the two temperatures, which should not differ by more than 0·2°, gives the dew point. The dew point is the temperature at which the air is just saturated with aqueous vapour; the vapour pressure of water at this temperature can be found from tables (Table VII., Appendix B), and is obviously the vapour tension of the solution or hydrate at the temperature of the thermostat.

EXPERIMENTS

(i) *Determine the Transition Temperature of Glauber's Salt and Anhydrous Sodium Sulphate.* Fill one of the flasks of a tensimeter with dry powdered Glauber's salt crystals and the other with the crystals and a few drops of a saturated solution of the salt. Then exhaust the instrument and seal it up. Stand it vertically in a thermostat at 29°, and when the position of the liquid in the *manometer has become constant* read off the difference of the levels of the two limbs of the manometer and the temperature. Change the temperature of the bath by slightly altering the thermo-regulator, and when the temperature and height of the manometer liquid have again become constant take the readings. This process may take from 2–3 hours. Repeat the process, taking care not to increase the temperature by more than 1° at a time. The difference in level will become less and less until finally it is zero. The temperature at which this occurs is the transition temperature.

(ii) *Repeat the above Experiment, using the Cumming Method.* Determine the vapour pressure of solid Glauber's salt at a series of temperatures from 25° to 35°, and also for a saturated solution of Glauber's salt in the presence of some crystals. Plot the values of the vapour pressure as ordinates against the temperature as abscissae. The curves will intersect at the transition temperature, for at the transition temperature Glauber's salt crystals must be in equilibrium with a saturated solution which contains both anhydrous salt and deca-hydrate.

3. *Solubility Method.* At the transition temperature two substances which are in equilibrium with one another, and pass into one another on changing the temperature, have the same solubility. Hence if the solubility of the two substances be determined at a series of temperatures and solubility curves drawn, it will be found that they will cut when produced. The temperature at which the curves cut will be that of equal solubility, *i.e.* the transition temperature.

EXPERIMENT

Determine the Transition Temperature of Glauber's Salt and Anhydrous Sodium Sulphate by the Solubility Method. Place about 200 c.c. of water and 100 grams of finely-powdered Glauber's salt in a 250 c.c. stoppered bottle, cover the stopper and the neck of the bottle with a rubber cap, and shake in a thermostat at 25° for one hour. Allow the solid to settle, remove about 10 c.c. of the solution, transfer to a tared, stoppered, weighing bottle, and weigh to the nearest milligram. Transfer the solution to a weighed platinum dish and carefully evaporate off the water, dry at 120° till of constant weight, and weigh the anhydrous sodium sulphate. Shake again for half an hour, and redetermine the solubility. Repeat the process, if necessary, until the solution is saturated. Calculate the solubility in grams anhydrous salt per 100 c.c. of water. Now raise the temperature of the thermostat to 28° and redetermine the solubility; add more water or Glauber's salt if necessary. Make further determinations at 30°, 32°, 34°, 40°, and 45°. Plot the solubilities as ordinates and the temperatures as abscissae, and draw a curve. It will be found that the curve breaks about 32°. To find the exact transition temperature, produce the curve made by joining the points below the break and also that made by joining the points above the break. The point of intersection will give the transition temperature. Notice the solid at the bottom of the bottle at each temperature; it will be found that below 32° the decahydrate is the compound present, and that at 34° and above the anhydrous salt is the solid in equilibrium with the solution. This may be verified by filtering off the solid at 30° and 34°, drying between filter papers, and estimating the water of crystallisation in the usual way.

4. *Thermometric Method.* When a solid substance is heated the temperature will, in general, increase in a perfectly regular manner until the melting point is reached. At this point the temperature will remain constant until the whole of the solid has melted, and then it will increase in temperature again in a perfectly regular manner. The heat added to the substance while melting is used up as latent heat to effect the melting. The same process is made use of to determine the transition temperature. If a substance is slowly heated its temperature rises in a perfectly regular manner until the transition point is reached, here the temperature stops rising until the change is complete and then it commences to rise again, or if a substance has been heated above its transition temperature and is allowed to cool slowly, its temperature will fall at a definite rate until the transition temperature is reached, when it ceases falling until all the substance has been transformed and then it commences to fall again in a perfectly regular manner. By plotting the rate of heating or cooling, *i.e.* the number of degrees per minute as ordinates against the temperatures as abscissae, a cooling or heating curve will be obtained which will exhibit a break at the transition point.

EXPERIMENT

Determine the Transition Point of Glauber's Salt by the Thermometric Method. Place about 50 grams of powdered Glauber's salt in a thin-walled test tube T, (Fig. 56), insert a stirrer p and a thermometer t, graduated in tenth degrees, into the salt. Support the tube T in a large beaker B of water, provided with a stirrer *s* and a thermometer *t′*. Raise the temperature of the bath to 30°, keep it there for about 30 minutes and then read the temperature of the Glauber's salt. Slowly raise the temperature of the bath to 36°, at the rate of about 1° in 10 minutes. Read the temperature of the Glauber's salt every minute and keep it well stirred. Then allow the beaker of water to slowly cool, reading the temperature of the Glauber's salt every minute until it reaches 28°. It will be noticed that at about 32° the rate of heating and cooling of the Glauber's salt will be slower than at other temperatures. Plot the temperatures as ordinates and the times as abscissae, draw the curves, which will be of the same nature as those in Fig. 53, and deduce the transition temperature.

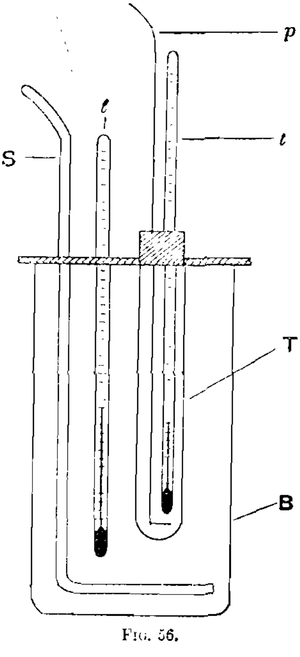

FIG. 56.

This experiment may be repeated with the double chloride of potassium and copper, which changes at about 92°, thus:

$$2KClCuCl_22H_2O \rightleftarrows KClCuCl_2 + KCl + 2H_2O.$$

Here the heating should be commenced at 85° and continued to 95°.

5. *Electro-conductivity Method.* It has already been shown that substances at their transition temperature

have the same solubility, consequently a saturated solution of a salt, which crystallises in two different forms, or with two different numbers of molecules of water of crystallisation, will have the same electro-conductivity at the transition temperature irrespective of the form of the salt used in the preparation of the solution. The method of determination of the transition point, therefore, consists simply in measuring the electro-conductivity of saturated solutions made from each of the forms of the substance, or from each hydrate, at a series of temperatures, and plotting the conductivities as ordinates against the temperatures as abscissae. The point of intersection of the two curves will be the transition temperature.

EXPERIMENT

Determine the Transition Temperature of the Hexahydrate and Heptahydrate of Zinc Sulphate. For this experiment use conductivity vessels as illustrated in Fig. 14B. Remove the electrodes and place a small quantity, 10–15 grams, of finely powdered $ZnSO_47H_2O$ and 20 c.c. of water in the vessel. Close the tube with a rubber stopper, and shake for half an hour in a thermostat at 25°. Measure the conductivity of the solution (see Chaper III.). Then raise the temperature of the thermostat to 30° and shake again for half an hour and remeasure the conductivity. Repeat at 35°, 40°, and 45°. Now make a saturated solution of the hexahydrate and measure its conductivity at 45°, 40°, and 35°. Plot the results and deduce the transition temperature as indicated above.

Instead of using the electrode vessel, as advised above, to make the saturated solutions in, a wide-mouthed bottle may be used, and the conductivities determined by means of a dipping electrode (see Fig. 15). The temperatures mentioned above indicate that the conductivity of both hydrates may be measured in regions where they are unstable. This is possible because of the extreme slowness with which the change of one into the other takes place.

6. *Electromotive Force Method.* It was shown in Chapter VI. that the electromotive force of a cell, made up of two electrodes of the same metal and two contiguous solutions of the same salt but of different concentrations, depends upon the concentration of the metal ions in the two solutions. Consequently when the concentration of the metal ions in both solutions becomes the same the cell will have no electromotive force. Two solutions of zinc sulphate, saturated at the same temperature, would therefore possess the same number of zinc ions. So also would a saturated solution of the heptahydrate of zinc sulphate and the hexahydrate of zinc sulphate at the transition temperature, for at this temperature their solubilities are the same. Hence if a cell is made up of a saturated solution of $ZnSO_4 7H_2O$, and a saturated solution of $ZnSO_4 6H_2O$ with two zinc electrodes, thus,

Zn	Sat. solution $ZnSO_4 7H_2O$	Sat. solution $ZnSO_4 6H_2O$	Zn

it will have no electromotive force at the transition temperature, but at every other temperature there will be an electromotive force. Below the transition temperature the current will flow from the part of the cell containing the heptahydrate to the part containing the hexahydrate, and above the transition temperature it will flow in the opposite direction. Hence to determine the transition temperature it is only necessary to determine the electromotive force of such a cell at a series of temperatures and deduce the point at which the electromotive force is zero from these values.

Experiment

Determine the Transition Temperature of the Hexahydrate and the Heptahydrate of Zinc Sulphate. This experiment is best carried out in a cell shaped as in Fig. 57. It consists of an H-shaped tube, the vertical limbs, *a*, *b*, of which are about 8 cms. long and 1·5 cms. diameter, and are joined by a narrower tube, *c*, about 0·4 cm. diameter, fitted with a tap, *d*. The electrodes consist of rods of amalgamated zinc. Place a solution of $ZnSO_{4}7H_{2}O$, saturated at 25°, in *a*, together with a small quantity, 3–5 grams, of the finely powdered crystals; allow the solution to fill the side tube up to the tap. Fill the other tube, *b*, with a saturated solution, at 25°, of $ZnSO_{4}6H_{2}O$ and 2–4 grams of the finely powdered crystals in exactly the same way as before. Insert the electrodes and take care that the bore of the tap is filled with solution. Close the tap, and place the apparatus in a thermostat at 25°. After half an hour measure the electromotive force of the cell to the nearest milli-volt (see Chapter VI.). The measurement may be done either with the tap open or shut. After measuring, close the tap and raise the temperature to 30°; the cell may be shaken from time to time to aid the formation of saturated solutions. After half an hour measure the electromotive force to the nearest milli-volt; to ensure

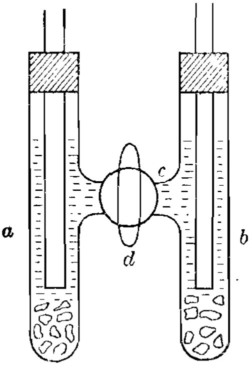

Fig. 57.

that the solutions are saturated allow the cell to remain fifteen minutes longer at this temperature and measure again; if the solutions were saturated the electromotive force will have remained constant. Repeat the process at 35°, 40°, and 45°. Call the values of the electromotive force obtained at the lower temperatures positive, and those obtained after the zero value has been passed negative. Plot the temperatures as abscissae and the electromotive force as ordinates, placing the positive values above the temperature axis and the negative values below the axis. Join the points on either side of the horizontal axis, and produce the curves thus formed until they cut the axis, which they will both do at the same point. This point is the transition temperature.

7. *Viscosity Method.* Dunstan and Thole (*J.C.S.* 1908, 93, 1815 and 1910, 97, 1249) have shown that viscosity determinations may be used to fix the transition point of a racemate into a mixture of the dextro and laevo tartrates. The change may be represented thus:

$$(C_4H_8O_6NH_4Na)_2 2H_2O + 6H_2O =$$
$$\circlearrowright C_4H_8O_6NH_4Na, 4H_2O + \circlearrowleft C_4H_8O_6NH_4Na, 4H_2O.$$

The method consists in determining the viscosity of a concentrated solution of sodium ammonium racemate below and above the transition temperature, *i.e.* between 25° and 32°, and plotting the viscosities as ordinates against the temperature as abscissae. In this way two curves are obtained which, produced, will intersect at the transition temperature.

EXPERIMENT

Determine the Transition Temperature of Sodium Ammonium Racemate. Dissolve 25 grams of sodium ammonium racemate in water and make up to 100 c.c., measure its viscosity at 25°, 26°, 27° and 28° and plot a curve; then measure the viscosity at 29°, 30°, 31°, 32° and 33° and plot a second curve. Produce the curves and deduce the transition point as indicated above. For the method of determining viscosity, see Chapter IX., Part I. Use a viscosimeter which has a large time of outflow, about 5–6 minutes. This may be obtained by lengthening the capillary and taking it of fairly fine bore, 15 cms. × 0·5 mm. is a good size. The bulb should have a capacity of 20–25 c.c. Make several determinations at each temperature and use the mean value. Plot the results on a large scale. In this experiment very careful work is necessary since the amount of change is not very strongly marked.

8. *Optical Methods.* Under this heading are included those changes which take place with a change of crystalline form, colour, or refractive index. Thus mercuric iodide changes from vermillion to yellow, a change whose temperature can easily be determined; the blue double acetate of copper and calcium, crystallising in the quadratic system, changes into green hexagonal crystals of copper acetate and white needles of calcium acetate. Further, a mixture of ferric chloride and potassium chloride in water solution is yellow in colour but on warming passes into a double potassium ferric chloride thus,

$$2KCl + FeCl_3 + 2H_2O \rightleftarrows 2KClFeCl_32H_2O,$$

the colour changing to red. The first two examples may be investigated under a microscope fitted with a stage which can be heated to any desired temperature.

CHAPTER X

RADIOACTIVITY

RADIOACTIVE substances emit rays, which possess the power of acting on a photographic plate and of discharging an electrically charged conductor. It is by means of these properties that radioactive substances are detected, and their changes investigated. The photographic method is, however, nothing like so sensitive as the other, and consequently not much used in the exact study of radioactive relationships. The electrical method is extremely sensitive, and has been used to detect substances which are present in quantities far smaller than could be detected by the most sensitive balance, and which in some cases are of so evanescent a character that they exist only for a few seconds. Further, it is the method adopted for studying changes in radioactive substances which proceed so slowly that millions of years are required before an appreciable weight has changed, and also changes which proceed so quickly that a few seconds only are required for the substance undergoing transformation to entirely disappear.

Method of Measurement

Two instruments are employed for making radioactive measurements, *viz.* the electroscope and the electrometer. The electrometer is by far the more accurate measuring instrument, and, where practicable, will be used in the following experiments. Hence a description of this instrument, together with the precautions necessary in its use, will not be out of place. The most convenient form of electrometer for the present purpose is that due to Dolezalek. It consists of four hollow metal quadrants, *a* (Fig. 58), 5–6 cm. diameter, supported on amber pillars *b*. The quadrants diagonally opposite are connected, as indicated in the diagram. The needle, *c*, is made of silver paper, and, supported by a phosphor-bronze suspension, *d*, swings inside the quadrants. The needle suspension carries a small concave mirror, by means of which its movements can be observed. The instrument is enclosed in a well-fitting metal case, provided with a window through which the movements of the mirror can be observed. The quadrant pairs are connected to two insulated terminals placed outside the metal case. The movements of the mirror are best observed by using it to reflect the image of a straight filament lamp on to a millimetre scale placed about 2 metres away. The electrometer must be set up on a rigid slate slab, which is not subject to vibrations, and adjusted by the levelling screws at the base, so that the quadrants are horizontal.

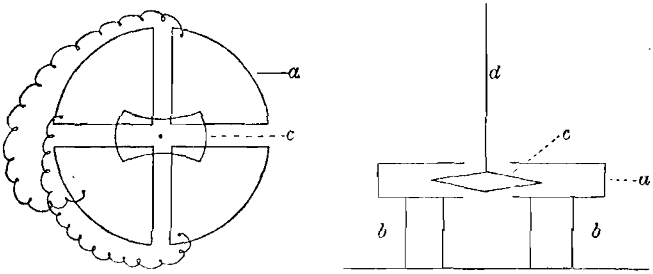

FIG. 58.

Then the needle is adjusted, so that it lies symmetrically between the quadrants, and permanently connected to one pole of a battery of 100 volts, the other being earthed. To test the symmetry of the needle, adjust the scale so that the spot of light is at the zero division, connect one pair of quadrants to earth, and the other to the positive pole of an earthed Weston cell, and note the deflection. Then connect the same pair of quadrants with the negative pole of the same cell, and earth the positive pole. The deflection in this case should be the same as before, but on the other side of the zero if the needle is hung symmetrically. If this is not so, then the position of the needle must be changed until the two deflections are alike. The insulation of the electrometer should next be tested; this is done by earthing one pair of quadrants, and charging the other pair by connecting them for an instant with one pole of a battery, whilst the other pole is earthed. The needle will be deflected to a given position, which it will maintain for a very long time if the insulation is perfect, but if any part of the insulation is bad the needle will slowly swing back to the zero position. The electrometer is so sensitive that it is often seriously affected by electrostatic charges produced in its neighbourhood. To protect it from these it is surrounded by a cage of wire gauze inside of which all keys are placed. The cage is earthed by connecting it to a water pipe. The front of the cage is perforated by an opening opposite the electrometer window, and should be removable as a whole, to allow of adjustments being made to the electrometer. The connecting wires, in all work in which an electrometer is used, should be surrounded by metal tubes; this is best done by attaching a wire to a piece of sealing-wax or sulphur, drawing the wire through the metal tube and pulling it tight. A second piece of sealing-wax or sulphur is then attached to the free end of the wire and tube, so that the wire is held centrally in the tube. The tube must then be earthed.

A suitable key for alternately connecting the electrometer to earth and to the various testing vessels is depicted in Fig. 59. It consists of a metal rod, A, which slides in a brass tube, T, supported by an earth-connected metal stand, C. The brass rod, A, is sufficiently long to make contact with the mercury cup, M; this is made of brass and stands on a rod of sealing-wax, S. The electrometer quadrants and the apparatus containing the substance to be tested are connected to M, so that when the key, which is operated by a string working over a pulley, is dropped into the mercury cup, the quadrants and the measuring vessel are earthed. The rod A carries two stops, *t*, which prevent it moving too far in either direction. All connections between the measuring vessels and

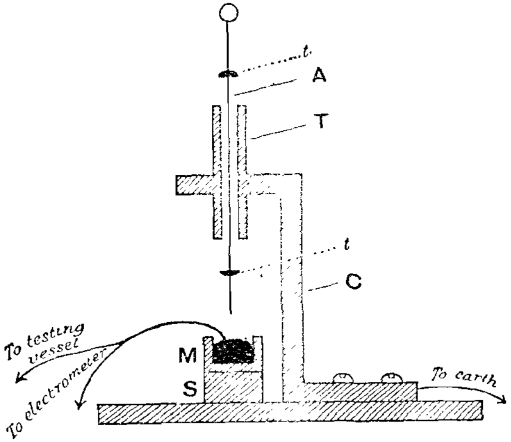

FIG. 59.

the electrometer must be protected from electrostatic disturbances in the manner already indicated. Radioactive measurements by the electrical method consist in either a direct or relative measurement of the saturation current produced by a given radioactive substance.

The meaning of the term **Saturation Current** may be illustrated in the following way. Suppose we have a pair of insulated metal plates, A, B, (Fig. 60), of which A is connected to one pair of quadrants of an electrometer and the other, B, is connected to one pole of a battery, the other pole being earthed. If now a radioactive substance is placed on B, the air between the two plates will be ionised; this will mean that a current will pass from B to A, which will charge the electrometer quadrants and cause a deflection of the needle. If now the potential on B is increased by increasing the electromotive force of the battery more current will cross the space between A, B, consequently the electrometer quadrants will charge up more quickly and the needle will move more rapidly. On further increasing the electromotive force of the battery the needle will move with increasing rapidity, but only up to a certain point, after which, no matter how much the potential on B is increased, the needle will move at practically a definite rate. The current then flowing is known as the saturation current, and this must always be the current measured. The potential difference required to furnish

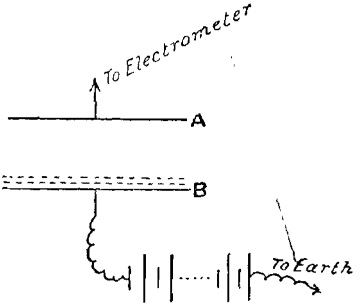

FIG. 60.

this current is known as the saturation potential difference. For all substances, except very active preparations of radium, a saturation potential difference of 300 volts is sufficient. This is best obtained from a battery of small accumulators, or from a series of lead cells (Fig. 61), made by dipping strips of lead in test tubes containing dilute sulphuric acid. Before attempting to measure radioactivity, *i.e.* the saturation current produced by a radioactive substance, the sensitiveness and capacity of the electrometer and its connections must be determined. This is not necessary for relative measurements, but for absolute measurements it is essential.

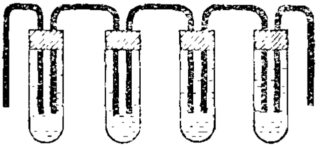

FIG. 61.

Sensitiveness and Capacity of the Electrometer

The sensitiveness of an electrometer is the number of scale divisions over which the needle moves when there is a potential difference of one volt between the two pairs of quadrants. To determine this, earth one pair of quadrants, and connect the other pair to one pole of a Weston cell, the other pole of which is earthed. Determine the number of scale divisions which the needle moves over, and since the deflection is proportional to the potential difference the number for one volt can be calculated. The electromotive force of the Weston cell may be taken as 1·019 volts. The capacity of the electrometer and its connections can be determined by charging up the electrometer to a potential P as already described, when it will give a deflection of d scale divisions; then connecting it to a condenser of known capacity C′, when the potential will fall to P′ indicated by a deflection d'. Then if C is the capacity of the electrometer and its connections

$$\mathrm{CP} = \mathrm{P}'(\mathrm{C} + \mathrm{C}'),$$

$$\textit{i.e.}\quad \frac{\mathrm{P}}{\mathrm{P}'} = \frac{\mathrm{C}}{\mathrm{C} + \mathrm{C}'} = \frac{d}{d'}.$$

Hence

$$\mathrm{C} = \mathrm{C}'\frac{d'}{d - d'}.$$

Calculation of the Saturation Current

If the sensitiveness and the capacity of the electrometer are both known the saturation current can be calculated from the deflection.

Thus, if S is the sensitiveness of the electrometer, C the capacity in electrostatic units, i the saturation current, and n the number of scale divisions through which the needle moves in one second when the quadrants are being charged by the current i, then

$$i = \frac{\mathrm{C}n}{9 \times 10^{11} \times \mathrm{S}} \text{ amperes.}$$

Measurement of Radioactivity

The activity of a solid radioactive substance can be conveniently measured by means of the apparatus depicted in Fig. 62. This consists of an insulated metal plate A, connected to one pole of an earthed battery, and a second plate B, 2 cms. distant from A and connected through a mercury cup M with one pair of the electrometer quadrants. The plates are enclosed in an earth connected metal box C. To make a determination the active substance is placed in a small metal tray on the plate A, and the earth connection between the mercury cup broken, so that the measuring vessel is directly connected with the electrometer (Fig. 63). The needle of the electrometer begins to move as soon as the connection is made and the time required for it to swing over 100 scale divisions is carefully noted by means of a stop-watch. When comparative measurements only are required the radioactivity is known directly, since it is inversely proportional to the time required for the needle to swing 100 scale divisions. Absolute measurements of the saturation current, which is also proportional to the activity, can be calculated from the time required for

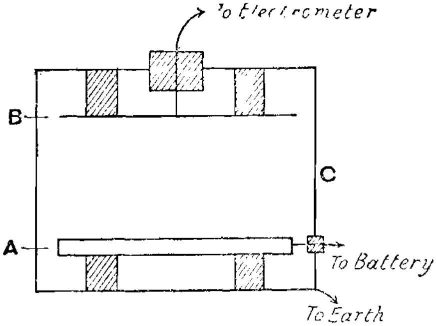

FIG. 62.

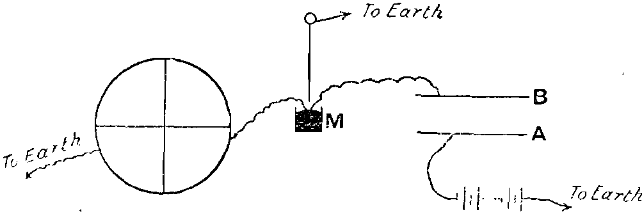

FIG. 63.

the needle to swing 100 scale divisions by the method given above.

It is essential in comparative measurements that the electrometer should not change in any way; this can be tested by measuring the rate at which the needle moves, from time to time, when a substance of constant activity is placed between the plates A, B. Such a standard is furnished by uranium oxide, U_3O_8; a small quantity, 1–2 grams, is placed uniformly on the bottom of a shallow metal receptacle and placed in the measuring vessel. The time required for the needle to swing over 100 scale divisions is noted. This value may then be termed the normal swing of the electrometer and, since the activity of uranium oxide is constant, will always be reproduced if the electrometer has not changed. Should the electrometer have changed, results obtained before and after the change can still be compared by using a correcting factor obtained from the swings recorded with the standard. Thus if t is the time required for the needle to swing 100 scale divisions with uranium oxide originally, and t' after it has changed, then a time T required for a 100 division swing after the change would have required $\frac{t}{t'}$T before the electrometer changed.

Measurement of Radioactivity by the Electroscope

Radioactive measurements may be made by means of an electroscope, often better than with an electrometer, for it is possible to measure smaller currents with it than with an electrometer. The principle is exactly the same as that on which measurements by an electrometer are based, except that instead of the rate of charging the insulated system, the rate of discharging it is measured.

The method and principle involved in the use of the electroscope may be described as follows.

It is essential that the electroscope for use in radioactive work should have as small a capacity as possible; it generally consists of a light aluminium leaf *a* (Fig. 64), attached to a narrow flat brass rod *b*, which is insulated by a sulphur bead *s*, inside a metal case M, of about 1 litre capacity. The vessel M is provided with two mica windows, through which the movements of the leaf can be observed and measured. The leaf system is charged by means of the bent rod *r*, which passes through an ebonite stopper E. To charge the electroscope the rod *r* is twisted so that it touches the top of the insulated system, and the outside end of *r* is touched with a charged stick of sealing-wax; the end of *r* is then twisted away from *b*. The motions of the leaf are observed through a reading microscope which carries a graduated scale.

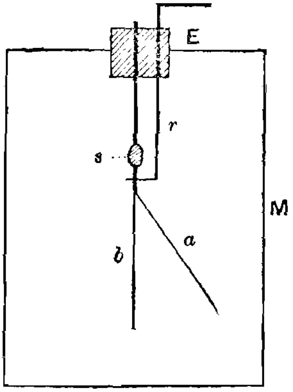

Fig. 64.

To make a measurement, the substance, if not very active, is introduced on a metal tray into the electroscope through the bottom, which is movable. The case and the charging rod are earthed, and the time required for the leaf to pass over a given number of scale divisions is noted. As the rate of the leaf passing over the scale is not uniform the same divisions must be used in each measurement. If the substance to be measured is very active it is placed at some distance *below* the electroscope and the measurement made as before.

The electroscope is not usually employed to determine the saturation current produced by a radioactive substance, but this may be obtained in the following way:

The scale divisions must be calibrated to read potentials in volts. This is done by connecting a battery of 300–400 volts across the ends of a potentiometer wire of high resistance. The leaf system is then connected to a series of points on the wire of known potential, and the scale deflections of the leaf noted. The deflections are then plotted as abscissae against the potentials as ordinates and a calibration curve drawn, from which the drop of potential between two given scale divisions can be obtained. The capacity of an electroscope may be determined in the same way as the electrometer. The electroscope is charged to a known potential, P, known from the number of scale divisions the leaf is deflected. Then it is connected to a condenser of known capacity, C', and the new position of the leaf read which corresponds to a potential, P'. Then, if C is the capacity of the electroscope,

$$\mathsf{C}=\mathsf{C}'\frac{\mathsf{P}'}{\mathsf{P}-\mathsf{P}'}.$$

If, now, i is the saturation current produced by a given radioactive substance and p the fall of potential in t seconds,

$$i=\frac{\mathsf{C}p}{t},$$

i.e.

$$i=\frac{\mathsf{C}p}{t\times 9}\times 10^{-11} \text{ amperes.}$$

EXPERIMENTS

(i) *Compare the Radioactivity of Uranium Acetate with that of Uranium Nitrate.* This experiment may be carried out by means of an electrometer or an electroscope.

(a) *By means of an electrometer.* Fit up an electrometer as described on page 210; connect the mercury key with a testing vessel as described above. The scheme of the connections is indicated in Fig. 63. In this experiment a battery of about 200 cells should be connected to the measuring vessel. Weigh out about 5 grams of uranium acetate and 5 grams of uranium nitrate to the nearest centigram, and spread them, finely powdered in thin layers on small shallow copper trays. Place one of the trays, *e.g.* that containing the acetate, on the lower plate of the measuring vessel, having previously earthed the mercury cup. Then break the earth connection and, by means of a stop-watch, note the time required for the electrometer to swing over 100 scale divisions. Make a series of determinations, earthing the mercury cup between each, and take the mean of the values obtained. Replace the tray containing the acetate by that containing the nitrate and repeat the measurements.

If t_a represents the time required for the needle to swing 100 scale divisions when the acetate is the ionising substance, and t_n that when the nitrate is in the testing vessel, then

The activity of acetate : activity of nitrate $:: t_n : t_a$.

The radioactivity is proportional to the amount of active substance present, *i.e.* in this case uranium. Hence the ratio $t_a : t_n$ should be inversely as the ratio of the weights of uranium in the two compounds. Compare your result with the ratio of the weights of uranium present. Any other uranium compound may be used instead of the salts mentioned in this experiment.

(b) *By means of an electroscope.* Fit up the electroscope as described above, illuminate the leaf system by a lamp placed behind the instrument, and focus the telescope so that both leaves are visible on the scale. Charge the electroscope, and note the time required for the leaf to pass from division 20 to division 10. This constitutes the natural leak of the instrument. Now remove the bottom of the electroscope and place the tray containing one of the uranium salts underneath the leaf system. Charge, and note the time required for the leaf to pass over the same scale divisions as were used in determining the natural leak. Repeat the measurement with the other salt. The recorded times must now be corrected for the natural leak of the electroscope, and then they will be inversely proportional to the radioactivity of the salts.

If t_0 be the time of the natural leak for the measured 10 divisions, t_1 that for the acetate, and t_2 for the nitrate, then, since the drop of potential, V, corresponding to the movement of the leaf from 20 to 10, is the same in each experiment, the times t_1 and t_2 may be corrected as follows. The leaf of itself loses a potential of V volts in t_0 seconds, hence in t_1 seconds it will lose $\frac{t_1}{t_0}.\mathrm{V}$, *i.e.* the drop of potential due to the uranium acetate is $\mathrm{V}-\frac{t_1}{t_0}\mathrm{V}$ in t_1 seconds, or V in $\dfrac{t_1\mathrm{V}}{\mathrm{V}\left(1-\frac{t_1}{t_0}\right)}$ seconds, *i.e.* $\dfrac{t_1t_0}{t_0-t_1}$; similarly, the uranium nitrate will cause the drop of potential V in $\dfrac{t_2t_0}{t_0-t_2}$ seconds.

Hence

The activity of the acetate : the activity of the nitrate

$$:: \frac{t_2t_0}{t_0-t_2} : \frac{t_1t_0}{t_0-t_1}.$$

This experiment may be repeated with thorium salts.

(ii) *Compare the Radioactivity of Thorium Nitrate and Uranium Nitrate.* Proceed in this experiment exactly as in the last. Weigh out about 1 gram of thorium nitrate and 5 grams of uranium nitrate and measure the times required for the electrometer needle to swing over 100 scale divisions, or for the electroscope leaf to pass over 10 scale divisions. Calculate the weight of uranium and thorium in the salts used, and from them the times required for the needle to swing 100 scale divisions per gram of metal, assuming strict proportionality. The inverse ratio of these times will give the ratio of the radioactivities. Thus, if with w grams of thorium nitrate the needle required t seconds to swing 100 divisions, and with w' grams of uranium nitrate t' seconds were required, then if R represents the radioactivity per gram of metallic thorium and R′ that per gram of metallic uranium,

$$\mathrm{R}' : \mathrm{R} :: \frac{t}{w} \cdot \frac{695 \cdot 5}{232 \cdot 5} : \frac{t'}{w'} \cdot \frac{502 \cdot 5}{238 \cdot 5},$$

where 696·5 is the molecular weight of $Th(NO_3)_4 12H_2O$, 502·5 that of $(UO_2)(NO_3)_2 6H_2O$, and 232·5 and 238·5 the atomic weights of thorium and uranium respectively.

(iii) *Determine the Rate of Decay of Thorium X and also the Rate of Production of Thorium X from Thorium.* It is known that the activity of thorium is accompanied by the formation of thorium X, a substance which, weight for weight, is several thousand times as active as thorium itself. Thorium X can be separated from thorium, and when separated, being strongly active, commences to disintegrate into other less active products. Its activity therefore decreases. At the same time more thorium X is produced in the thorium which has been separated; consequently, since the activity of the thorium X is added to that of the thorium, its activity is increased. Measurement will show that the rate of increase of the activity of the thorium is the same as the rate of decrease of the activity of thorium X, *i.e.* the rate of formation of thorium X is the same as the rate of its decay.

Prepare a dilute solution of thorium nitrate in water, and add ammonia to it until no further precipitation occurs. Filter and wash the precipitate. Evaporate the filtrate to dryness in a shallow platinum dish, and drive off all the ammonium salts by ignition. The platinum dish now contains thorium X and the impurities of the original salt. Dry the precipitated thorium hydrate. Measure the activity of the thorium oxide and the thorium X every day for 16 days. The activity of the thorium X will slowly decrease and finally vanish, whilst that of the oxide will slowly increase to a maximum. Call the initial value of the thorium X and the final value of the oxide 100, and plot the activities of both as ordinates against the time in days as abscissae. Draw curves for the decay of thorium X and the recovery of the activity of thorium. The curves will be found to be irregular for the first two days, but afterwards will be quite smooth.

If $\mathbf{I}_0$ is the activity of thorium X immediately after separation, and $\mathbf{I}_t$ after a time t, then

$$\mathbf{I}_0 = \mathbf{I}_t \epsilon^{-\lambda t},$$

where λ is a constant, ϵ the base of natural logarithms, and t the time.

Calculate the value of λ from your experimental results, and use the mean value of λ to calculate the value of t when $\mathbf{I}_t$ is equal to $\frac{1}{2}\mathbf{I}_0$, *i.e.* when one half of the thorium X has decayed. This will give the half life of thorium X. The value of λ may also be calculated from the rate of recovery of the thorium. If I_0 represents the increased activity of the separated thorium when it has become constant, I_t the activity recovered in time t, then

$$I_t = I_0(1 - \epsilon^{-\lambda t}).$$

Calculating now the value of t when $I_t = \frac{1}{2}I_0$, *i.e.* the time required for the formation of one half of the equilibrium amount of thorium X, the value obtained ought to be the same as the half life of thorium X.

(iv) *Determine the Relative Ionising Power of the α, β, and γ Rays of Radium.* The radiations of radium are made up of three different kinds of rays, which have been named respectively α, β, and γ rays. These rays have widely different properties, which may be briefly summarised thus:

α rays, which are positively charged particles moving with a high velocity, are very easily absorbed by gases, liquids, and solids. They ionise air more strongly than either of the other rays, and are not very active photographically.

β rays are negatively charged particles moving with a high velocity. They are more penetrating than α rays, and produce a smaller ionisation of the air. They are more strongly active toward a photographic plate than either of the other rays.

γ rays are uncharged and extremely penetrating. To measure the relative ionising power of the rays cut a small rectangular hole in a block of lead, 3 cms. long, 2 cms. wide, and 2 cms. deep. Spread a small quantity of radium bromide uniformly over the bottom of this hole. Place the lead and its contents on the lower plate of the testing apparatus (Fig. 62), and arrange so that a current of air may be blown across the plates to remove any radium emanation which may be liberated. Measure the saturation current, charging the lower plate to a high potential, about 800 volts. Now cover the lead capsule with an aluminium leaf, about 0·1 mm. thick, and remeasure the saturation current. This will cut off all the α rays and allow the β and γ rays to pass through. The difference between the two measurements will give a value proportional to the ionisation produced by the α rays. Now cover the capsule with a sheet of lead, 2–3 mm. thick; this will cut off both the α and β rays. Measure the saturation current, which will be proportional to the ionisation produced by the γ rays. The difference between the last two measurements will give a value proportional to the ionisation produced by the β rays.

If t_1 is the time occupied by the needle in swinging 100 divisions with the uncovered radium bromide, t_2 when covered by aluminium foil, and t_3 when covered by the lead plate, then if $\mathbf{I}_\alpha$, $\mathbf{I}_\beta$ and $\mathbf{I}_\gamma$ respectively represent the ionisation due to the α, β and γ rays,

$$\mathbf{I}_{\beta+\gamma} : \mathbf{I}_\gamma :: t_3 : t_2 \quad \text{and} \quad \mathbf{I}_{\alpha+\beta+\gamma} : \mathbf{I}_{\beta+\gamma} :: t_2 : t_1.$$

Should a battery of 800 volts not be available the experiment may be carried out with a thorium or a uranium salt, in which case a potential of 300 volts will be sufficient.

(v) *Determine the Absorption of γ Rays by various thicknesses of Metals.* This experiment should be carried out with an electroscope of the type described on page 218. Place a small quantity of radium bromide in a shallow thick-walled leaden dish; this is best made by cutting a shallow hole 2 cms. long, 2 cms. wide and 3 mm. deep in a block of lead 4 cms. square and 2 cms. thick. Spread the radium bromide as thinly and as uniformly as possible over the bottom of the hole, cover it with a thin sheet of mica, about 0·1 mm. thick and fasten the mica to the lead with sealing-wax, taking care that the whole of the joint shall be covered with wax. This is for the purpose of preventing the escape of the emanation. Place the electroscope on a tripod stand and measure the natural leak. Cover the radium bromide with a sheet of lead 3 mm. thick, charge the electroscope and determine the time required for the leaf to pass over the measured 10 divisions. The discharge will be due entirely to the γ rays, for the α and β rays have been cut off by the lead sheet. Add a second sheet of lead, 5 mm. thick, to the first and measure the time of discharge. Add further sheets of lead, 5 mm. thick, as long as there is an effect on the electroscope larger than that due to the natural leak. Correct the time observed in the various measurements for the natural leak and plot the corrected values as ordinates against the thickness of lead as abscissae and draw an absorption curve for the γ rays by lead.

Repeat the experiment with sheets of iron, aluminium and copper, and note that the absorption is approximately proportional to the density of the absorbing medium for equal thickness of metal.

(vi) *Determine the Rate of Decay of Radium Emanation.* Radium, simultaneously with the emission of α, β and γ rays, gives rise to a radioactive gas, known as radium emanation. This gas, being radioactive, is constantly changing into other products, just as in the case of thorium X, and is also similarly regenerated from radium. Radium emanation, therefore, has a definite period of existence which may be determined by measuring the saturation current produced by it at stated intervals of time. To measure the rate of decay of radium emanation it must be removed from the radium which has produced it. To do this dissolve 5 milligrams of radium bromide in water and place the solution in a small wash-bottle A (Fig. 65), connect this through a sulphuric acid bubbler B to a gas-holder C filled with mercury. Warm the solution of radium bromide by placing the wash-bottle in a water bath, and draw a current of air through the solution so that the air and emanation which it contains pass into the gas-holder. Transfer exactly 5 c.c. of the mixed gases to a gas burette, convey this to a measuring vessel and determine the time of swing of the electrometer needle.

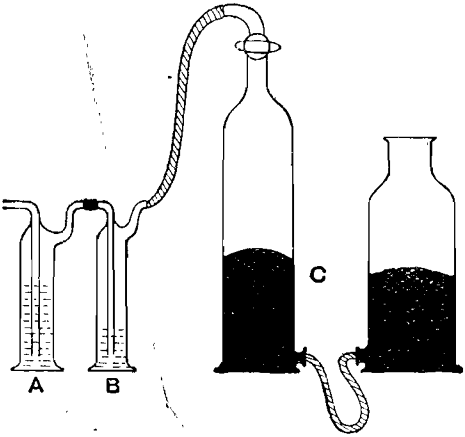

Fig. 65.

The measuring vessel in this case consists of a brass cylinder A (Fig. 66), 25 cms. long and 6 cms. diameter, fitted with an ebonite stopper B, which carries a brass rod R protected by a guard ring D. Two well-fitting taps, *s*, *t*, are attached to the side of the vessel. To transfer the emanation from the gas burette to the measuring vessel attach it to a small sulphuric acid bubbler and this to the tap *s*. Then evacuate the measuring vessel through the tap *t*. When the cylinder is evacuated close *t* and cautiously open *s*. This will draw all the gas from the burette into the bubbler; when the mercury in the gas burette has filled the bore of the tap slip off the connecting rubber and allow air to be drawn through the tube into the bubbler and so sweep all the emanation into the measuring vessel. Connect the rod R to the electrometer, the outside of the cylinder to one pole of an earthed battery of 600 volts, and the guard ring to earth.

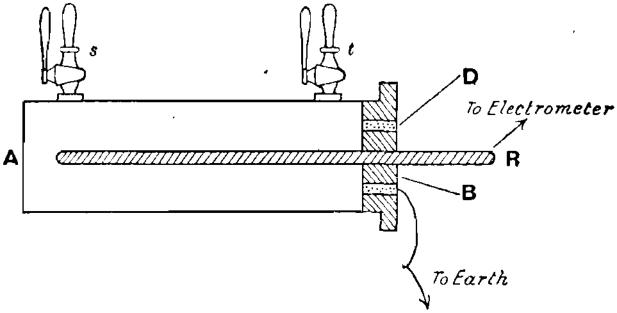

FIG. 66.

Measure the time required for the needle to swing 100 divisions as described above.

When the measurement has been completed, draw a rapid current of air through the measuring cylinder to sweep out all the emanation. This should not be done in the room containing the electrometer. Repeat the measurements with further quantities of emanation at intervals of 12, 12, 12, 24, and 24 hours, and then every two days for about a month. The saturation current will be found to gradually diminish until it finally vanishes. Plot the times required by the needle to swing over 100 scale divisions as ordinates against the time in days as abscissae, and draw a decay curve for radium emanation.

If $\mathbf{I}_0$ represents the initial activity of the emanation and $\mathbf{I}_t$ the activity after a time t,

$$\mathbf{I}_0 = \mathbf{I}_t \epsilon^{-\lambda t},$$

where λ is the decay constant of the emanation. Calculate λ for the various measurements, and then using the mean value of λ calculate the value of t when $\mathbf{I}_t = \frac{1}{2}\mathbf{I}_0$. This will give the half life of radium emanation.

Estimation of the Radium Content of Minerals

The radium content of minerals is deduced from the activity of the emanation formed in a given time by a known weight of the mineral. This is compared with the activity of the emanation produced by a standard whose radium content is known. Since uranium is disintegrating and forming radium, and the radium itself is disintegrating but much faster than the uranium, it follows that after a time the amount of radium present in a given uranium mineral will become constant and proportional to the amount of uranium present in the mineral. Further, the amount of emanation present in the mineral, assuming none escapes, is also proportional to the quantity of radium present. The amount of radium present in a uranium mineral has been found to be $3{\cdot}15 \times 10^{-7}$ grams per gram of uranium, if the mineral is of sufficient age for the equilibrium conditions to have been set up.

If, then, such a mineral be taken and analysed to find its uranium content, the amount of radium it contains will be known from the above relationship, *viz.* $3{\cdot}15 \times 10^{-7}x$ grams per gram of mineral, where x is the weight of uranium per gram of mineral. Such a mineral may now be used as the standard with which other minerals may be compared and from which their radium content may be deduced.

The method of procedure is as follows: About 50 milligrams of pitchblende, of known uranium, and consequently known radium content, is taken and ground up finely in an agate mortar. A carefully weighed quantity of this, about 30–40 milligrams, is placed in a platinum crucible and fused with a mixture of sodium and potassium carbonates and a small quantity of potassium nitrate. The melt is dissolved in hydrochloric acid and placed in a 250 c.c. flask, which is about four-fifths filled with water. The solution is boiled for about an hour to expel all the emanation, the flask is then securely closed with rubber stopper and placed on one side for four days, the time being accurately measured. In this time it will produce a quantity of emanation proportional to the amount of radium it contains. The effect produced by this emanation on an electroscope is now measured. To do this the emanation has first to be expelled from the solution. This is done in the apparatus depicted in Fig. 67, which consists of a short tube *a*, about 5 mm. diameter and 20 cms. long, fitted, by means of a rubber stopper, into the widened end *b* of the tube C. This tube is about 120 cms. long and 8 mm. diameter, and is connected at its upper end, by means of a rubber stopper *r*, with an adapter A, closed by a tap *t*. The widened part *b* is fitted with a side tube which is connected by a length of rubber tubing with a levelling bottle L. The apparatus is inverted and filled with water, then the rubber tube is closed by a pinchcock, and the apparatus turned into its right position. The flask F containing the radioactive standard is attached to *b*, and placed over a burner and boiled for an hour. This expels all the emanation, which, together with the air in the flask, rises into the *adapter* A. The tap *t* is then connected with a piece of rubber tubing through a sulphuric acid bubbler

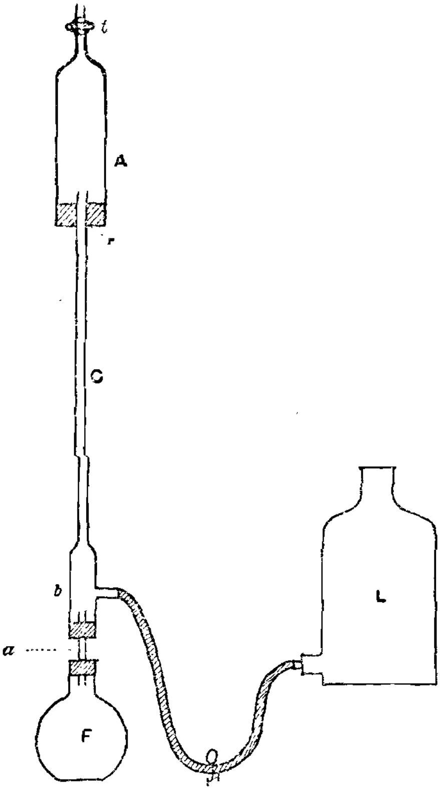

Fig. 67.

and a small tube filled with cotton wool, to remove spray, with an evacuated *electroscope*. The tap of the electroscope is opened, and the tap *t*, is also cautiously opened, and the *emanation* drawn from A into the bubbler. When all the gas has been removed from A, which is ensured by allowing the water to rise up to the rubber tubing, the tubing is slipped off the tap and air allowed to enter. This sweeps all the emanation into the electroscope, where it is allowed to stand for two hours, and then its activity is measured. The measurement is repeated half an hour later, and if the value is constant this is accepted as the value of the standard. If the value is not constant half-hourly measurements must be made until two are alike, but constant results ought to be obtained in 3–4 hours. The mineral to be examined is treated exactly in the same way as the standard, and the activity of the emanation, produced by about 50 milligrams in the *same* time, measured. Should the mineral contain sulphur, the method is varied a little. The fusion is carried out in the same way, and, since the sulphur will give a sulphate, insoluble radium sulphate will be formed if the melt is treated with acid. It is therefore boiled out with water and filtered from the insoluble carbonates, which are well washed. The filtrate and washings are rendered acid with hydrochloric acid, and placed in a 250 c.c. flask as before. The insoluble carbonates are then dissolved in dilute hydrochloric acid, and placed in another 250 c.c. flask. The measurement is then carried out as before, but in two parts, the activity of the emanation from the mineral being the sum of the activities of the two parts.

The electroscope[1] to be used in this determination is depicted in Fig. 68. It consists, as will be seen, of a well made rectangular box A, fitted with plate-glass sides which are either cemented on or attached by

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[1] This instrument was designed by the late Mr. J. Holding, engineer to the Radium Institute, Riding-House Street, London, W.

clamps. The leaf system consists of a brass rod *a*, which supports the fixed leaf *b* made of a thin narrow strip of brass, and a narrow aluminium leaf *c*. The whole is supported by the brass rod *f*, which is insulated from the case by a sulphur plug *e*. The leaf system is insulated from *f* by a rod of amber or sulphur *g*. The glass tube *w* is secured to the case and rendered air-tight by the flanges and screw caps *k*, *l*, *m*, and the leaden washers *n*. Two taps, *s* and *t*, are screwed into the sides of the case for the purpose of evacuation and admission of the emanation. An iron wire *v* swings

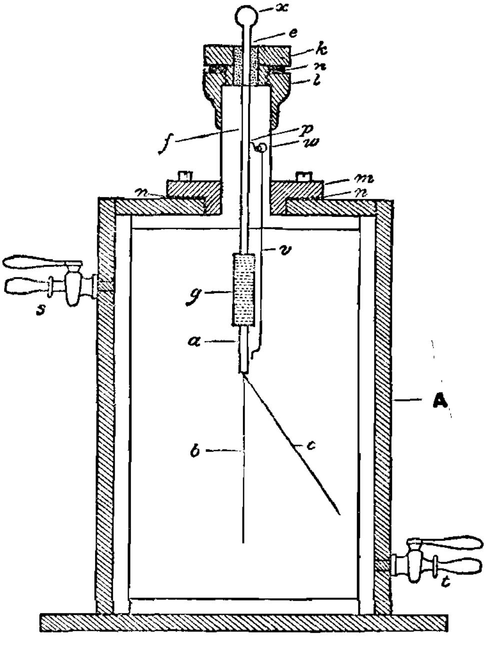

Fig. 68.

freely from a hook *p* attached to *f* and serves to charge the leaf system. This is done by drawing *v* with a magnet so that it is in contact with *a*.

The knob *x* is then raised to the required potential either by making contact with one pole of a battery or by means of a rod of sealing-wax.

EXPERIMENT

Determine the Radium Content of a given Uranium Mineral. Analyse and prepare a standard, *e.g.* pitchblende. Measure the activity of the emanation produced by it in four days. Then determine the activity of the emanation produced by the same weight of the unknown mineral in the same time. It is especially important to blow the emanation out of the electroscope as soon as the measurement is completed, or otherwise an active deposit will be formed on the walls and this will render the electroscope useless. As it is the natural leak will gradually increase and must, therefore, always be determined before an experiment. When the natural leak becomes too large take the instrument to pieces, sandpaper the metal surfaces and wash the glass to remove the active deposit. Renew all the insulators and then the normal natural leak will be reestablished.

Suppose 50 milligrams of the standard give emanation, which produces a motion of the leaf of 10 scale divisions in t seconds (corrected) and the same weight of the mineral produces emanation which gives the same motion in t' seconds (corrected). Then if w milligrams of uranium are present per gram of the standard, the weight of radium present in 50 milligrams of the standard is $3{\cdot}15 \times 10^{-7} \times \frac{w}{20}$ milligrams.

The activity of the emanation is inversely proportional to the time required by the leaf to pass over ten scale divisions, *i.e.*

$$\text{Activity of emanation from standard} : \text{Activity of emanation from specimen} :: t' : t.$$

The quantities of radium present in the two substances are proportional to the activities of the emanation, since the experiments have been carried out under identical conditions, hence

$$\text{Amount of radium in standard} : \text{Amount of radium in specimen} :: t' : t,$$

i.e. Number of milligrams of radium in 50 milligrams of specimen $= \frac{t}{t'} \times 3{\cdot}15 \times 10^{-7} \times \frac{w}{20}$ milligrams

$$\text{or} \quad \frac{t}{t'} \times 3{\cdot}15 \times 10^{-7} w \text{ mg. per gram.}$$

Suitable minerals for this experiment are pitchblende, autunite, and orangeite.

CHAPTER XI

DECOMPOSITION VOLTAGE, OVERVOLTAGE AND DISCHARGE POTENTIAL

WHEN a dilute solution of sulphuric acid is electrolysed between platinum electrodes the ions $H^{\cdot}$ and SO_4'' are discharged in accordance with the equations $H^{\cdot} = H + \oplus$; $SO_4'' + 2\oplus = SO_4$. This action is followed by the reactions $2H = H_2$; $SO_4 + H_2O = H_2SO_4 + O$; $2O = O_2$. The electrodes, therefore, become charged respectively with hydrogen and oxygen, so that a gas cell of the type

$$O_2(Pt) \mid \text{solution} \mid H_2(Pt)$$

is produced. This cell possesses an electromotive force, due to the tendency of the hydrogen and oxygen to pass into the ionic condition. The electromotive force of the cell thus produced opposes the electromotive force of the electrolysing current; if therefore a continuous electrolysis is desired, the electromotive force of the electrolysing current must be larger than the back electromotive force of the products of electrolysis. The potential difference, which is just sufficiently large to effect a continuous electrolysis, is termed the **decomposition voltage** or the **decomposition potential** of the solution under investigation.

The decomposition potential is the sum of the two electrode potentials and the potential drop between the electrodes, where the latter quantity is given by the product of the resistance of the electrolyte between the electrodes and the current which is flowing. The decomposition potential is found to depend on the concentration of the solution and this must necessarily be the case, for both electrode potentials depend on the ionic concentration of the solution (see Chapter VI.).

The decomposition potential is determined by applying a small electromotive force, from an accumulator, to the electrodes of a decomposition cell and slowly increasing it until a continuous current passes; the voltage at which this occurs is known as the decomposition voltage. It is generally found that the point at which a continuous current begins to flow is not very sharply marked, for the current indicator always shows a small residual current, so that the decomposition voltage has to be deduced from a current-potential curve.

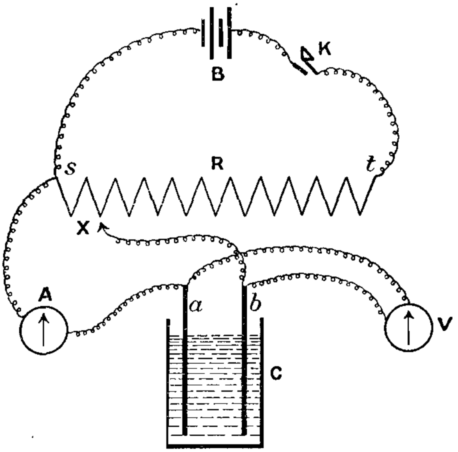

FIG. 69.

The apparatus employed in making such a measurement is shown in the diagram (Fig. 69). It consists of a stout glass decomposition cell C, 2·5 inches diameter and 2 inches deep, fitted with two platinised platinum electrodes *a*, *b* (1″ × ¾″). The electrodes are connected with a sensitive voltmeter, V, capable of measuring up to about 5 volts in tenths of a volt. Two lead accumulators, B, are connected through a key, K, with the ends, *s*, *t*, of a sliding resistance, *R*, of about 100 ohms. One electrode, *a*, of the decomposition cell is connected through a milliammeter, A, with one end, *s*, of the resistance and the other electrode with the sliding contact X. The milliammeter should have a range of about 200 milli-amperes.

EXPERIMENT

Determine the Decomposition Voltage of 0·1 N *Sulphuric Acid.* Assemble and connect the apparatus described above and adjust the indicators of the measuring instruments to the zero mark, or if this is not possible take the zero readings. Fill the decomposition cell with tenth normal sulphuric acid and short circuit the electrodes through the solution for a few minutes by connecting them together with a short length of copper wire; this is for the purpose of removing any absorbed layer of gas, oxygen or hydrogen, which may be upon them. Remove the short circuiting wire, move the sliding contact, X, to the end *s* of the resistance R and close the key K. At this stage there is no impressed electromotive force on the electrodes, *a*, *b*. Carefully move the sliding contact until the voltmeter indicates an electromotive force 0·1 volt and note the reading of the ammeter. This will be very small, probably not so large as one milli-ampere. It is generally necessary to wait for a few minutes before taking the current reading, so that the ammeter needle may have become quite steady. When this reading has been obtained, move the sliding contact of the resistance until the voltmeter indicates 0·2 volt, and again take the current reading. Continue to increase the electromotive force in steps of $\frac{1}{10}$ volt until about 1·9 volts have been impressed on the electrodes. It will be found that for a time the current will remain very small (2–3 milliamperes) and not increase perceptibly with increasing electromotive force, and then it will suddenly commence to rise at a definite electromotive force and to increase very rapidly with each increase in electromotive force.

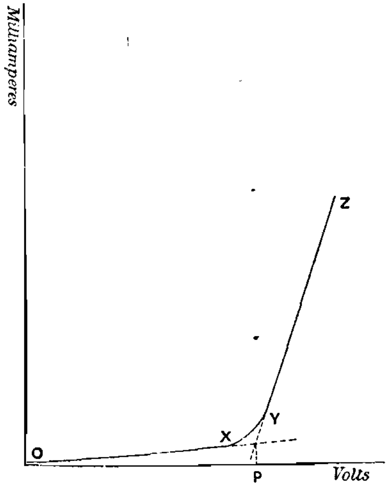

FIG. 70.

The point at which the electromotive force becomes large enough to cause a current to flow is the decomposition voltage, but this cannot as a rule be seen directly from the readings taken. To obtain the actual value the electromotive force is plotted as abscissae against the current as ordinates and a current-potential curve drawn (Fig. 70). Produce the two limbs, OX and ZY, until they meet, when the point of intersection P will give the decomposition voltage. After the final readings have been obtained, slowly and carefully reduce the applied electromotive force by moving the sliding contact toward *s*, until the milliammeter gives the zero reading. When this is reached the voltmeter reading is the decomposition voltage.

This experiment may be repeated with tenth normal solutions of zinc sulphate, silver nitrate and copper chloride.

Discharge Potentials

As has been seen the decomposition voltage is the sum of three potentials, two of these are the discharge potentials of the two ions. These two quantities may be determined individually in the following manner. An apparatus is arranged as in the diagram (Fig. 71), which will be seen to be identical with that used in the previous experiment as far as the current circuit is concerned. Liquid contact is made between the solution in

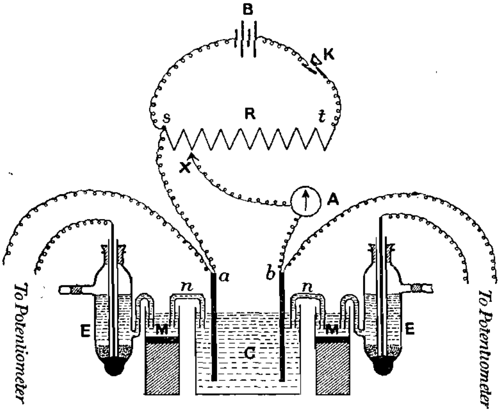

FIG. 71.

the decomposition cell **C** and a saturated solution of ammonium nitrate contained in the two "middle vessels" **M** by means of small glass syphons, *n*. Two small $\frac{N}{10}$ calomel electrodes, **E**, are also placed in liquid contact with the solution in the "middle vessels," so that two cells are formed; calomel electrode | solution | Pt electrode (*a*) and calomel electrode | solution | Pt electrode (*b*). These cells are connected with a potentiometer arrangement for measuring electromotive force, as described in Chapter VI. The determination of the single discharge potentials consists in measuring the electromotive force of both composite cells and the current flowing through the decomposition cell for a series of gradually increasing impressed electromotive forces and determining by means of current-potential curves the values of the electromotive force of the composite cells at which a continuous current just flows through the solution.

EXPERIMENT

Determine the Discharge Potential of the Silver Ion and the Nitrate Ion of a 0·1 N *solution of Silver nitrate.* Fit up the apparatus as described above and fill the decomposition cell with a tenth normal solution of silver nitrate. After the electrodes have been freed from absorbed gases by short-circuiting for a few minutes, apply a small electromotive force by moving the sliding contact a small distance from *s*, Fig. 71. Then measure the electromotive force of the combinations: Calomel electrode | solution | Pt electrode (*a*); Calomel electrode | solution | Pt electrode (*b*), by the compensation method (Chapter VI.), and read the ammeter. Continue to increase the applied electromotive force by small amounts and make the same three measurements for each applied electromotive force until a considerable current is flowing through the decomposition cell. Plot the electromotive force values of each composite cell against the current readings and produce two current-electromotive force curves, one for each composite cell. Produce the two limbs of each of these curves and obtain the electromotive force of the two cells at which the current begins to flow. Now subtract the value of the potential difference of the tenth normal calomel electrode (+0·6130 volt) from each. These values are the discharge potentials of the silver ion and the nitrate ion respectively. This experiment may be repeated with solutions of various concentrations of zinc sulphate, sulphuric acid, copper sulphate and cadmium nitrate.

Overvoltage

If an oxygen and a hydrogen electrode, both in dilute sulphuric acid, are combined to form an electrolytic cell, it will be found that the potential difference of the cell is about 1·1 volts. If an opposing electromotive force of 1·1 volts from an external source is impressed on the electrodes it will be found that no current will flow through the composite cell because the back electromotive force of the gas cell exactly compensates the impressed electromotive force. If the external potential difference is now increased, the back electromotive force of the gas cell will also increase to a definite limiting value, and until this limiting value is reached and just exceeded by the impressed electromotive force no permanent current will flow through the gas cell. The amount by which the back electromotive force of the cell increases above the normal value of the cell is known as the **overvoltage** of the cell, and the increase of potential at the individual electrodes of the cell is known as the cathodic overvoltage and anodic overvoltage respectively. The overvoltage of the electrodes is an important factor in the processes of electrolytic oxidation and reduction. Thus cathodes made of material which has a high overvoltage are more efficient for electrolytic reductions than those with smaller overvoltages, and sometimes it is possible with these to effect reductions, particularly of organic substances, which cannot be brought about by other means. Similarly anodes made of materials which have large overvoltages are very efficient for carrying out electrolytic oxidations. A knowledge, therefore, of the overvoltage of electrodes made of various materials is of great importance from the technical as well as from the scientific point of view. (See Newbery, *J.C.S.* 1914, **105**, 2419; *J. Amer. Chem. Soc.* 1920, **42**, 2007, *J.C.S.* 1921, **119**.)

Experiment

Determine the Cathodic Overvoltage of Lead, Copper and Mercury. Fit up the apparatus required for the determination of decomposition voltage (page 237, Fig. 69). Using two freshly platinised electrodes determine the decomposition voltage of a normal solution of sulphuric acid as previously described. Then substitute the platinum cathode of the decomposition cell by a cathode of the same size made of soft lead and redetermine the decomposition voltage; a somewhat higher value will be obtained. The difference between the two values of the decomposition voltage gives the overvoltage of lead with respect to platinised platinum. Repeat the experiment using a copper and a mercury cathode

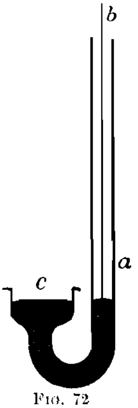

FIG. 72

respectively. A mercury cathode is made by placing a layer of mercury on the bottom of the electrolytic cell and making contact by means of a protected platinum wire, or by using a glass vessel as shown in the diagram (Fig. 72), which is placed in the decomposition cell in the position previously occupied by the platinum cathode. The glass vessel consists of a length of glass tubing 3 mm. diameter, blown out at each end to a bulb 2 cms. diameter, and then worked into a hemi-spherical cup, C. The tube is then bent as in the diagram. Pure mercury is poured into the cup and electrical contact made by a thin platinum wire, *b*, which passes down the tube, *a*.

APPENDIX A

VELOCITY OF REACTIONS

Bi-molecular Reactions. The reaction between certain halogen substitution products of aliphatic acids and esters and sodium thiosulphate takes place according to the laws of bimolecular reactions. Such reactions proceed according to equations of the type

$$Na_2S_2O_3 + CH_2Br . CO_2Et = NaS_2O_3 . CH_2 . CO_2Et + NaBr,$$

and with a velocity which, at ordinary temperatures, can be readily followed. Consequently changes of this kind serve admirably for the study of bi-molecular reactions. (See Slator, *J.C.S.* 1904, 1286; 1905, 484.)

EXPERIMENT

Determine the Velocity Constant of the Reaction between Ethyl Bromo-acetate and Sodium Thiosulphate. Make up an approximately centi-normal solution of sodium thiosulphate (2·48 grams of $Na_2S_2O_35H_2O$ per litre) and an approximately centi-normal solution of iodine. Place about 250 c.c. of the thiosulphate solution in a bottle and hang it in a thermostat at 25° until it has attained the temperature of the bath, then remove quantities of 20 c.c. and titrate them with the centi-normal iodine solution, using starch paste as indicator. Let 20 c.c. of thiosulphate solution be equivalent to x c.c.

of iodine solution. Now weigh out 1·20–1·30 grams of ethyl bromo-acetate and dissolve it in a litre of water. Place about 250 c.c. of this solution in a stoppered bottle and hang it in the same thermostat. When the solution has acquired the temperature of the bath measure out carefully 80 c.c. and place it in a 200 c.c. stoppered bottle and hang it in the thermostat. Then, by means of a pipette, add to the 80 c.c. of bromo-acetate solution 100 c.c. of thiosulphate solution, *noting the time at which* the addition begins and ends. Record the time when one half of the thiosulphate has been added as the beginning of the experiment, t_0. Shake the bottle and replace it in the thermostat. After five minutes remove 20 c.c. of the solution, and run it into a conical flask containing 20 c.c. of water, carefully noting the time, t_5, and titrate with the standard iodine solution, using starch as indicator as before. The titration value n_5 will give the amount of unchanged sodium thiosulphate present in the solution at the time, t_5. Remove further quantities of 20 c.c. of the solution at 10, 15, 25, 40 and 60 minutes after the start of the experiment and titrate each as described above, thus obtaining a series of titration values n_{10}, n_{15}, n_{25}, n_{40} and n_{60}. Now leave the reaction mixture to itself for 24 hours in the thermostat to complete the reaction, and then remove a further 20 c.c. and titrate this and obtain the infinity value n_∞.

The value of the velocity constant (k) is obtained by means of the formula

$$k = \frac{1}{n_\infty . t} . \log \frac{n_t(n_0 - n_\infty)}{n_0(n_t - n_\infty)},$$

in which the value of t corresponding to n_t is inserted (see page 19). The quantity n_0 is the number of cubic centimetres of iodine solution equivalent to 20 c.c. of the reaction mixture at the commencement of the experiment. This is obtained from the ratio between the iodine solution and the thiosulphate solution found before the experiment was begun, and is given by $n_0 = \frac{100}{180} x$.

Further experiments may be made with sodium bromacetate, methyl chloro-acetate, mono-chloro-acetone, for details of which see Slator (*loc. cit.*).

APPENDIX B

TABLE I

Values of $\log \frac{l}{1000-l}$, where l is the point of balance on a metre bridge

l	0	1	2	3	4	5	6	7	8	9
00	—	$\bar{3}$·00043	$\bar{3}$·30180	$\bar{3}$·47842	$\bar{3}$·60370	$\bar{3}$·70115	$\bar{3}$·78076	$\bar{3}$·84815	$\bar{3}$·90658	$\bar{3}$·95817
01	$\bar{2}$·00436	$\bar{2}$·04619	$\bar{2}$·08442	$\bar{2}$·11962	$\bar{2}$·15225	$\bar{2}$·18265	$\bar{2}$·21112	$\bar{2}$·23790	$\bar{2}$·26316	$\bar{2}$·28708
02	$\bar{2}$·30980	$\bar{2}$·33144	$\bar{2}$·35208	$\bar{2}$·37184	$\bar{2}$·39076	$\bar{2}$·40894	$\bar{2}$·42641	$\bar{2}$·44325	$\bar{2}$·45949	$\bar{2}$·47518
03	$\bar{2}$·49035	$\bar{2}$·50504	$\bar{2}$·51927	$\bar{2}$·53308	$\bar{2}$·54650	$\bar{2}$·55954	$\bar{2}$·57222	$\bar{2}$·58457	$\bar{2}$·59660	$\bar{2}$·60834
04	$\bar{2}$·61979	$\bar{2}$·63096	$\bar{2}$·64188	$\bar{2}$·65256	$\bar{2}$·66296	$\bar{2}$·67321	$\bar{2}$·68721	$\bar{2}$·69301	$\bar{2}$·70260	$\bar{2}$·71202
05	$\bar{2}$·72125	$\bar{2}$·73030	$\bar{2}$·73919	$\bar{2}$·74793	$\bar{2}$·75650	$\bar{2}$·76493	$\bar{2}$·77322	$\bar{2}$·78136	$\bar{2}$·78938	$\bar{2}$·79726
06	$\bar{2}$·80502	$\bar{2}$·81266	$\bar{2}$·82019	$\bar{2}$·82760	$\bar{2}$·83490	$\bar{2}$·84210	$\bar{2}$·84919	$\bar{2}$·85619	$\bar{2}$·86309	$\bar{2}$·86990
07	$\bar{2}$·87662	$\bar{2}$·88324	$\bar{2}$·88978	$\bar{2}$·89624	$\bar{2}$·90262	$\bar{2}$·90892	$\bar{2}$·91514	$\bar{2}$·92129	$\bar{2}$·92736	$\bar{2}$·93337
08	$\bar{2}$·93930	$\bar{2}$·94517	$\bar{2}$·95097	$\bar{2}$·95671	$\bar{2}$·96238	$\bar{2}$·96800	$\bar{2}$·97355	$\bar{2}$·97905	$\bar{2}$·98449	$\bar{2}$·98987
09	$\bar{2}$·99520	$\bar{1}$·00048	$\bar{1}$·00570	$\bar{1}$·01087	$\bar{1}$·01600	$\bar{1}$·02107	$\bar{1}$·02610	$\bar{1}$·03108	$\bar{1}$·03602	$\bar{1}$·04092
10	$\bar{1}$·04576	$\bar{1}$·05056	$\bar{1}$·05532	$\bar{1}$·06005	$\bar{1}$·06472	$\bar{1}$·06937	$\bar{1}$·07397	$\bar{1}$·07853	$\bar{1}$·08306	$\bar{1}$·08755
11	$\bar{1}$·09200	$\bar{1}$·09642	$\bar{1}$·10081	$\bar{1}$·10516	$\bar{1}$·10947	$\bar{1}$·11376	$\bar{1}$·11801	$\bar{1}$·12223	$\bar{1}$·12641	$\bar{1}$·13057
12	$\bar{1}$·13470	$\bar{1}$·13880	$\bar{1}$·14287	$\bar{1}$·14691	$\bar{1}$·15092	$\bar{1}$·15490	$\bar{1}$·15886	$\bar{1}$·16279	$\bar{1}$·16669	$\bar{1}$·17057
13	$\bar{1}$·17442	$\bar{1}$·17825	$\bar{1}$·18205	$\bar{1}$·18583	$\bar{1}$·18958	$\bar{1}$·19331	$\bar{1}$·19703	$\bar{1}$·20071	$\bar{1}$·20437	$\bar{1}$·20751
14	$\bar{1}$·21163	$\bar{1}$·21523	$\bar{1}$·21880	$\bar{1}$·22236	$\bar{1}$·22589	$\bar{1}$·22940	$\bar{1}$·23289	$\bar{1}$·23637	$\bar{1}$·23982	$\bar{1}$·24326
15	$\bar{1}$·24667	$\bar{1}$·25007	$\bar{1}$·25344	$\bar{1}$·25681	$\bar{1}$·26015	$\bar{1}$·26347	$\bar{1}$·26678	$\bar{1}$·27007	$\bar{1}$·27335	$\bar{1}$·27660
16	$\bar{1}$·27984	$\bar{1}$·28307	$\bar{1}$·28628	$\bar{1}$·28946	$\bar{1}$·29263	$\bar{1}$·29579	$\bar{1}$·29894	$\bar{1}$·30207	$\bar{1}$·30519	$\bar{1}$·30829
17	$\bar{1}$·31137	$\bar{1}$·31445	$\bar{1}$·31750	$\bar{1}$·32054	$\bar{1}$·32357	$\bar{1}$·32657	$\bar{1}$·32958	$\bar{1}$·33257	$\bar{1}$·33555	$\bar{1}$·33851
18	$\bar{1}$·34146	$\bar{1}$·34440	$\bar{1}$·34732	$\bar{1}$·35023	$\bar{1}$·35313	$\bar{1}$·35601	$\bar{1}$·35889	$\bar{1}$·36175	$\bar{1}$·36460	$\bar{1}$·36744
19	$\bar{1}$·37026	$\bar{1}$·37308	$\bar{1}$·37589	$\bar{1}$·37869	$\bar{1}$·38146	$\bar{1}$·38423	$\bar{1}$·38700	$\bar{1}$·38975	$\bar{1}$·39250	$\bar{1}$·39522
20	$\bar{1}$·39794	$\bar{1}$·40065	$\bar{1}$·40335	$\bar{1}$·40604	$\bar{1}$·40872	$\bar{1}$·41138	$\bar{1}$·41405	$\bar{1}$·41670	$\bar{1}$·41933	$\bar{1}$·42197
21	$\bar{1}$·42459	$\bar{1}$·42720	$\bar{1}$·42981	$\bar{1}$·43241	$\bar{1}$·43499	$\bar{1}$·43757	$\bar{1}$·44013	$\bar{1}$·44270	$\bar{1}$·44525	$\bar{1}$·44799
22	$\bar{1}$·45040	$\bar{1}$·45285	$\bar{1}$·45537	$\bar{1}$·45788	$\bar{1}$·46039	$\bar{1}$·46288	$\bar{1}$·46537	$\bar{1}$·46785	$\bar{1}$·47031	$\bar{1}$·47279
23	$\bar{1}$·47524	$\bar{1}$·47768	$\bar{1}$·48013	$\bar{1}$·48256	$\bar{1}$·48499	$\bar{1}$·48741	$\bar{1}$·48982	$\bar{1}$·49223	$\bar{1}$·49463	$\bar{1}$·49702
24	$\bar{1}$·49940	$\bar{1}$·50178	$\bar{1}$·50415	$\bar{1}$·50651	$\bar{1}$·50887	$\bar{1}$·51122	$\bar{1}$·51357	$\bar{1}$·51591	$\bar{1}$·51823	$\bar{1}$·52056
25	$\bar{1}$·52288	$\bar{1}$·52519	$\bar{1}$·52750	$\bar{1}$·52980	$\bar{1}$·53209	$\bar{1}$·53438	$\bar{1}$·53667	$\bar{1}$·53894	$\bar{1}$·54122	$\bar{1}$·54348
26	$\bar{1}$·54574	$\bar{1}$·54800	$\bar{1}$·55024	$\bar{1}$·55249	$\bar{1}$·55472	$\bar{1}$·55696	$\bar{1}$·55918	$\bar{1}$·56141	$\bar{1}$·56362	$\bar{1}$·56583
27	$\bar{1}$·56804	$\bar{1}$·57024	$\bar{1}$·57244	$\bar{1}$·57463	$\bar{1}$·57681	$\bar{1}$·57899	$\bar{1}$·58117	$\bar{1}$·58334	$\bar{1}$·58650	$\bar{1}$·58766
28	$\bar{1}$·58983	$\bar{1}$·59198	$\bar{1}$·59413	$\bar{1}$·59627	$\bar{1}$·59841	$\bar{1}$·60053	$\bar{1}$·60267	$\bar{1}$·60479	$\bar{1}$·60691	$\bar{1}$·60903
29	$\bar{1}$·61114	$\bar{1}$·61324	$\bar{1}$·61535	$\bar{1}$·61745	$\bar{1}$·61955	$\bar{1}$·62163	$\bar{1}$·62372	$\bar{1}$·62580	$\bar{1}$·62788	$\bar{1}$·62995
30	$\bar{1}$·63202	$\bar{1}$·63409	$\bar{1}$·63615	$\bar{1}$·63821	$\bar{1}$·64026	$\bar{1}$·64232	$\bar{1}$·64436	$\bar{1}$·64641	$\bar{1}$·64844	$\bar{1}$·65048
31	$\bar{1}$·65251	$\bar{1}$·65454	$\bar{1}$·65656	$\bar{1}$·65858	$\bar{1}$·66061	$\bar{1}$·66262	$\bar{1}$·66463	$\bar{1}$·66664	$\bar{1}$·66865	$\bar{1}$·67064
32	$\bar{1}$·67264	$\bar{1}$·67464	$\bar{1}$·67663	$\bar{1}$·67861	$\bar{1}$·68060	$\bar{1}$·68258	$\bar{1}$·68456	$\bar{1}$·68653	$\bar{1}$·68850	$\bar{1}$·69048
33	$\bar{1}$·69244	$\bar{1}$·69440	$\bar{1}$·69636	$\bar{1}$·69831	$\bar{1}$·70028	$\bar{1}$·70222	$\bar{1}$·70417	$\bar{1}$·70612	$\bar{1}$·70806	$\bar{1}$·71000
34	$\bar{1}$·71194	$\bar{1}$·71386	$\bar{1}$·71580	$\bar{1}$·71772	$\bar{1}$·71796	$\bar{1}$·72158	$\bar{1}$·72350	$\bar{1}$·72542	$\bar{1}$·72733	$\bar{1}$·72925
35	$\bar{1}$·73116	$\bar{1}$·73307	$\bar{1}$·73496	$\bar{1}$·73687	$\bar{1}$·73887	$\bar{1}$·74067	$\bar{1}$·74256	$\bar{1}$·74446	$\bar{1}$·74634	$\bar{1}$·74823
36	$\bar{1}$·75012	$\bar{1}$·75201	$\bar{1}$·75389	$\bar{1}$·75577	$\bar{1}$·75764	$\bar{1}$·75952	$\bar{1}$·76139	$\bar{1}$·76327	$\bar{1}$·76513	$\bar{1}$·76700
37	$\bar{1}$·76886	$\bar{1}$·77072	$\bar{1}$·77258	$\bar{1}$·77444	$\bar{1}$·77630	$\bar{1}$·77815	$\bar{1}$·78001	$\bar{1}$·78185	$\bar{1}$·78370	$\bar{1}$·78555
38	$\bar{1}$·78739	$\bar{1}$·78923	$\bar{1}$·79107	$\bar{1}$·79291	$\bar{1}$·79475	$\bar{1}$·79658	$\bar{1}$·79842	$\bar{1}$·80025	$\bar{1}$·80208	$\bar{1}$·80391
39	$\bar{1}$·80573	$\bar{1}$·80756	$\bar{1}$·80939	$\bar{1}$·81120	$\bar{1}$·81303	$\bar{1}$·81484	$\bar{1}$·81666	$\bar{1}$·81847	$\bar{1}$·82028	$\bar{1}$·82210
40	$\bar{1}$·82391	$\bar{1}$·82571	$\bar{1}$·82753	$\bar{1}$·82934	$\bar{1}$·83113	$\bar{1}$·83294	$\bar{1}$·83474	$\bar{1}$·83654	$\bar{1}$·83834	$\bar{1}$·84013
41	$\bar{1}$·84193	$\bar{1}$·84372	$\bar{1}$·84552	$\bar{1}$·84731	$\bar{1}$·84910	$\bar{1}$·85089	$\bar{1}$·85268	$\bar{1}$·85447	$\bar{1}$·85626	$\bar{1}$·85803
42	$\bar{1}$·85982	$\bar{1}$·86160	$\bar{1}$·86338	$\bar{1}$·86516	$\bar{1}$·86695	$\bar{1}$·86872	$\bar{1}$·87050	$\bar{1}$·87228	$\bar{1}$·87404	$\bar{1}$·87582
43	$\bar{1}$·87760	$\bar{1}$·87939	$\bar{1}$·88113	$\bar{1}$·88291	$\bar{1}$·88467	$\bar{1}$·88644	$\bar{1}$·88821	$\bar{1}$·88997	$\bar{1}$·89173	$\bar{1}$·89350
44	$\bar{1}$·89526	$\bar{1}$·89703	$\bar{1}$·89879	$\bar{1}$·90062	$\bar{1}$·90231	$\bar{1}$·90407	$\bar{1}$·90582	$\bar{1}$·90758	$\bar{1}$·90934	$\bar{1}$·91110
45	$\bar{1}$·91285	$\bar{1}$·91461	$\bar{1}$·91636	$\bar{1}$·91811	$\bar{1}$·91987	$\bar{1}$·92161	$\bar{1}$·92336	$\bar{1}$·92512	$\bar{1}$·92687	$\bar{1}$·92861
46	$\bar{1}$·93037	$\bar{1}$·93211	$\bar{1}$·93386	$\bar{1}$·93561	$\bar{1}$·93736	$\bar{1}$·93910	$\bar{1}$·94085	$\bar{1}$·94259	$\bar{1}$·94434	$\bar{1}$·94608
47	$\bar{1}$·94782	$\bar{1}$·94956	$\bar{1}$·95131	$\bar{1}$·95298	$\bar{1}$·95479	$\bar{1}$·95653	$\bar{1}$·95828	$\bar{1}$·96052	$\bar{1}$·96172	$\bar{1}$·96350
48	$\bar{1}$·96524	$\bar{1}$·96698	$\bar{1}$·96872	$\bar{1}$·97046	$\bar{1}$·97220	$\bar{1}$·97393	$\bar{1}$·97568	$\bar{1}$·97741	$\bar{1}$·97915	$\bar{1}$·98089
49	$\bar{1}$·98263	$\bar{1}$·98436	$\bar{1}$·98611	$\bar{1}$·98784	$\bar{1}$·98958	$\bar{1}$·99132	$\bar{1}$·99305	$\bar{1}$·99479	$\bar{1}$·99653	$\bar{1}$·99826
50	0·00000	0·00174	0·00347	0·00521	0·00695	0·00868	0·01042	0·01216	0·01389	0·01564

APPENDIX B

TABLE II

Values of $\log \frac{\alpha^2}{1-\alpha}$, for values of α from 0·0100—0·999

α	0	1	2	3	4	5	6	7	8	9
0·010	$\bar{4}$·00436	$\bar{4}$·01305	$\bar{4}$·02165	$\bar{4}$·03018	$\bar{4}$·03860	$\bar{4}$·04796	$\bar{4}$·05525	$\bar{4}$·06343	$\bar{4}$·07156	$\bar{4}$·07962
0·011	$\bar{4}$·08776	$\bar{4}$·09549	$\bar{4}$·10333	$\bar{4}$·11110	$\bar{4}$·11878	$\bar{4}$·12642	$\bar{4}$·13399	$\bar{4}$·14149	$\bar{4}$·14892	$\bar{4}$·15630
0·012	$\bar{4}$·16360	$\bar{4}$·17087	$\bar{4}$·17805	$\bar{4}$·18519	$\bar{4}$·19226	$\bar{4}$·19928	$\bar{4}$·20625	$\bar{4}$·21315	$\bar{4}$·22001	$\bar{4}$·22682
0·013	$\bar{4}$·23352	$\bar{4}$·24027	$\bar{4}$·24691	$\bar{4}$·25351	$\bar{4}$·26006	$\bar{4}$·26656	$\bar{4}$·27303	$\bar{4}$·27943	$\bar{4}$·28580	$\bar{4}$·29210
0·014	$\bar{4}$·29838	$\bar{4}$·30461	$\bar{4}$·31079	$\bar{4}$·31694	$\bar{4}$·32302	$\bar{4}$·32908	$\bar{4}$·33509	$\bar{4}$·34107	$\bar{4}$·34700	$\bar{4}$·35290
0·015	$\bar{4}$·35874	$\bar{4}$·36457	$\bar{4}$·37033	$\bar{4}$·37608	$\bar{4}$·38178	$\bar{4}$·38744	$\bar{4}$·39307	$\bar{4}$·39867	$\bar{4}$·40424	$\bar{4}$·40976
0·016	$\bar{4}$·41524	$\bar{4}$·42071	$\bar{4}$·42613	$\bar{4}$·43152	$\bar{4}$·43686	$\bar{4}$·44219	$\bar{4}$·44749	$\bar{4}$·45275	$\bar{4}$·45798	$\bar{4}$·46318
0·017	$\bar{4}$·46735	$\bar{4}$·47349	$\bar{4}$·47859	$\bar{4}$·48368	$\bar{4}$·48872	$\bar{4}$·49375	$\bar{4}$·49873	$\bar{4}$·50370	$\bar{4}$·50864	$\bar{4}$·51354
0·018	$\bar{4}$·51843	$\bar{4}$·52329	$\bar{4}$·52812	$\bar{4}$·53292	$\bar{4}$·53771	$\bar{4}$·54245	$\bar{4}$·54717	$\bar{4}$·55183	$\bar{4}$·55656	$\bar{4}$·56121
0·019	$\bar{4}$·56583	$\bar{4}$·57044	$\bar{4}$·57442	$\bar{4}$·57958	$\bar{4}$·58411	$\bar{4}$·58861	$\bar{4}$·59312	$\bar{4}$·59758	$\bar{4}$·60203	$\bar{4}$·60643
0·020	$\bar{4}$·61803	$\bar{4}$·61522	$\bar{4}$·61956	$\bar{4}$·62391	$\bar{4}$·62821	$\bar{4}$·63250	$\bar{4}$·63678	$\bar{4}$·64102	$\bar{4}$·64525	$\bar{4}$·64947
0·021	$\bar{4}$·65336	$\bar{4}$·65782	$\bar{4}$·66199	$\bar{4}$·66611	$\bar{4}$·67021	$\bar{4}$·67432	$\bar{4}$·67838	$\bar{4}$·68245	$\bar{4}$·68649	$\bar{4}$·69050
0·022	$\bar{4}$·69450	$\bar{4}$·69849	$\bar{4}$·70245	$\bar{4}$·70639	$\bar{4}$·71034	$\bar{4}$·71424	$\bar{4}$·71825	$\bar{4}$·72203	$\bar{4}$·72588	$\bar{4}$·72974
0·023	$\bar{4}$·73357	$\bar{4}$·73737	$\bar{4}$·74117	$\bar{4}$·74496	$\bar{4}$·74872	$\bar{4}$·75247	$\bar{4}$·75619	$\bar{4}$·75992	$\bar{4}$·76362	$\bar{4}$·76731
0·024	$\bar{4}$·77097	$\bar{4}$·77463	$\bar{4}$·77828	$\bar{4}$·78190	$\bar{4}$·78551	$\bar{4}$·78911	$\bar{4}$·79270	$\bar{4}$·79626	$\bar{4}$·79981	$\bar{4}$·80335
0·025	$\bar{4}$·80688	$\bar{4}$·81038	$\bar{4}$·81388	$\bar{4}$·81737	$\bar{4}$·82083	$\bar{4}$·82430	$\bar{4}$·82774	$\bar{4}$·83117	$\bar{4}$·83459	$\bar{4}$·83800
0·026	$\bar{4}$·84138	$\bar{4}$·84477	$\bar{4}$·84813	$\bar{4}$·85149	$\bar{4}$·85482	$\bar{4}$·85816	$\bar{4}$·86147	$\bar{4}$·86477	$\bar{4}$·86806	$\bar{4}$·87134
0·027	$\bar{4}$·87561	$\bar{4}$·87787	$\bar{4}$·88112	$\bar{4}$·88434	$\bar{4}$·88757	$\bar{4}$·89077	$\bar{4}$·89398	$\bar{4}$·89716	$\bar{4}$·90032	$\bar{4}$·90349
0·028	$\bar{4}$·90672	$\bar{4}$·90980	$\bar{4}$·91292	$\bar{4}$·91605	$\bar{4}$·91915	$\bar{4}$·92224	$\bar{4}$·92534	$\bar{4}$·92841	$\bar{4}$·93147	$\bar{4}$·93454
0·029	$\bar{4}$·93758	$\bar{4}$·94061	$\bar{4}$·94363	$\bar{4}$·94665	$\bar{4}$·94996	$\bar{4}$·95264	$\bar{4}$·95563	$\bar{4}$·95861	$\bar{4}$·96158	$\bar{4}$·96452
0·030	$\bar{4}$·96747	$\bar{4}$·97041	$\bar{4}$·97334	$\bar{4}$·97624	$\bar{4}$·97915	$\bar{4}$·98205	$\bar{4}$·98494	$\bar{4}$·98782	$\bar{4}$·99079	$\bar{4}$·99355
0·031	$\bar{4}$·99640	$\bar{4}$·99824	$\bar{3}$·00207	$\bar{3}$·00487	$\bar{3}$·00772	$\bar{3}$·01052	$\bar{3}$·01333	$\bar{3}$·01611	$\bar{3}$·01889	$\bar{3}$·02166
0·032	$\bar{3}$·02442	$\bar{3}$·02719	$\bar{3}$·02993	$\bar{3}$·03266	$\bar{3}$·03540	$\bar{3}$·03811	$\bar{3}$·04083	$\bar{3}$·04354	$\bar{3}$·04622	$\bar{3}$·04892
0·033	$\bar{3}$·05159	$\bar{3}$·05428	$\bar{3}$·05694	$\bar{3}$·05959	$\bar{3}$·06225	$\bar{3}$·06488	$\bar{3}$·06752	$\bar{3}$·07015	$\bar{3}$·07277	$\bar{3}$·07538
0·034	$\bar{3}$·07798	$\bar{3}$·08057	$\bar{3}$·08317	$\bar{3}$·08574	$\bar{3}$·08832	$\bar{3}$·09089	$\bar{3}$·09345	$\bar{3}$·09600	$\bar{3}$·09854	$\bar{3}$·10109
0·035	$\bar{3}$·10361	$\bar{3}$·10614	$\bar{3}$·10864	$\bar{3}$·11154	$\bar{3}$·11365	$\bar{3}$·11616	$\bar{3}$·11864	$\bar{3}$·12113	$\bar{3}$·12359	$\bar{3}$·12606
0·036	$\bar{3}$·12852	$\bar{3}$·13099	$\bar{3}$·13343	$\bar{3}$·13588	$\bar{3}$·13833	$\bar{3}$·14073	$\bar{3}$·14315	$\bar{3}$·14558	$\bar{3}$·14798	$\bar{3}$·15039
0·037	$\bar{3}$·15277	$\bar{3}$·15520	$\bar{3}$·15754	$\bar{3}$·15993	$\bar{3}$·16229	$\bar{3}$·16466	$\bar{3}$·16702	$\bar{3}$·16937	$\bar{3}$·17171	$\bar{3}$·17406
0·038	$\bar{3}$·17638	$\bar{3}$·17871	$\bar{3}$·18104	$\bar{3}$·18336	$\bar{3}$·18567	$\bar{3}$·18797	$\bar{3}$·19028	$\bar{3}$·19256	$\bar{3}$·19485	$\bar{3}$·19713
0·039	$\bar{3}$·19940	$\bar{3}$·20168	$\bar{3}$·20395	$\bar{3}$·20619	$\bar{3}$·20846	$\bar{3}$·21070	$\bar{3}$·21295	$\bar{3}$·21517	$\bar{3}$·21740	$\bar{3}$·21962
0·040	$\bar{3}$·22185	$\bar{3}$·22405	$\bar{3}$·22628	$\bar{3}$·22848	$\bar{3}$·23067	$\bar{3}$·23288	$\bar{3}$·23506	$\bar{3}$·23723	$\bar{3}$·23941	$\bar{3}$·24158
0·041	$\bar{3}$·24374	$\bar{3}$·24591	$\bar{3}$·24807	$\bar{3}$·25202	$\bar{3}$·25236	$\bar{3}$·25451	$\bar{3}$·25663	$\bar{3}$·25878	$\bar{3}$·26090	$\bar{3}$·26301
0·042	$\bar{3}$·26513	$\bar{3}$·26724	$\bar{3}$·26935	$\bar{3}$·27145	$\bar{3}$·27356	$\bar{3}$·27564	$\bar{3}$·27773	$\bar{3}$·27981	$\bar{3}$·28188	$\bar{3}$·28396
0·043	$\bar{3}$·28603	$\bar{3}$·28809	$\bar{3}$·29014	$\bar{3}$·29220	$\bar{3}$·29425	$\bar{3}$·29630	$\bar{3}$·29834	$\bar{3}$·30037	$\bar{3}$·30239	$\bar{3}$·30442
0·044	$\bar{3}$·30644	$\bar{3}$·30847	$\bar{3}$·31047	$\bar{3}$·31248	$\bar{3}$·31448	$\bar{3}$·31649	$\bar{3}$·31847	$\bar{3}$·32048	$\bar{3}$·32247	$\bar{3}$·32445
0·045	$\bar{3}$·32642	$\bar{3}$·32840	$\bar{3}$·33037	$\bar{3}$·33233	$\bar{3}$·33430	$\bar{3}$·33624	$\bar{3}$·33819	$\bar{3}$·34016	$\bar{3}$·34210	$\bar{3}$·34403
0·046	$\bar{3}$·34597	$\bar{3}$·34790	$\bar{3}$·34982	$\bar{3}$·35175	$\bar{3}$·35367	$\bar{3}$·35558	$\bar{3}$·35750	$\bar{3}$·35941	$\bar{3}$·36132	$\bar{3}$·36320
0·047	$\bar{3}$·36511	$\bar{3}$·36699	$\bar{3}$·36888	$\bar{3}$·37076	$\bar{3}$·37265	$\bar{3}$·37452	$\bar{3}$·37640	$\bar{3}$·37827	$\bar{3}$·38013	$\bar{3}$·38200
0·048	$\bar{3}$·38384	$\bar{3}$·38571	$\bar{3}$·38755	$\bar{3}$·38940	$\bar{3}$·39125	$\bar{3}$·39307	$\bar{3}$·39492	$\bar{3}$·39674	$\bar{3}$·39857	$\bar{3}$·40039
0·049	$\bar{3}$·40222	$\bar{3}$·40403	$\bar{3}$·40585	$\bar{3}$·40766	$\bar{3}$·40946	$\bar{3}$·41137	$\bar{3}$·41305	$\bar{3}$·41486	$\bar{3}$·41664	$\bar{3}$·41843
0·050	$\bar{3}$·42022	$\bar{3}$·42200	$\bar{3}$·42377	$\bar{3}$·42555	$\bar{3}$·42732	$\bar{3}$·42909	$\bar{3}$·43085	$\bar{3}$·43262	$\bar{3}$·43436	$\bar{3}$·43613
0·051	$\bar{3}$·43787	$\bar{3}$·43962	$\bar{3}$·44137	$\bar{3}$·44311	$\bar{3}$·44484	$\bar{3}$·44658	$\bar{3}$·44831	$\bar{3}$·45003	$\bar{3}$·45176	$\bar{3}$·45349
0·052	$\bar{3}$·45519	$\bar{3}$·45692	$\bar{3}$·45862	$\bar{3}$·46033	$\bar{3}$·46203	$\bar{3}$·46374	$\bar{3}$·46545	$\bar{3}$·46713	$\bar{3}$·46882	$\bar{3}$·47052
0·053	$\bar{3}$·47221	$\bar{3}$·47388	$\bar{3}$·47556	$\bar{3}$·47725	$\bar{3}$·47891	$\bar{3}$·48058	$\bar{3}$·48225	$\bar{3}$·48391	$\bar{3}$·48558	$\bar{3}$·48724
0·054	$\bar{3}$·48889	$\bar{3}$·49055	$\bar{3}$·49220	$\bar{3}$·49385	$\bar{3}$·49549	$\bar{3}$·49614	$\bar{3}$·49876	$\bar{3}$·50041	$\bar{3}$·50204	$\bar{3}$·50366
0·055	$\bar{3}$·50529	$\bar{3}$·50691	$\bar{3}$·50854	$\bar{3}$·51017	$\bar{3}$·51177	$\bar{3}$·51338	$\bar{3}$·51498	$\bar{3}$·51661	$\bar{3}$·51820	$\bar{3}$·51980
0·056	$\bar{3}$·52141	$\bar{3}$·52299	$\bar{3}$·52460	$\bar{3}$·52619	$\bar{3}$·52777	$\bar{3}$·52936	$\bar{3}$·53094	$\bar{3}$·53151	$\bar{3}$·53410	$\bar{3}$·53566
0·057	$\bar{3}$·53723	$\bar{3}$·53881	$\bar{3}$·54038	$\bar{3}$·54193	$\bar{3}$·54549	$\bar{3}$·54506	$\bar{3}$·54660	$\bar{3}$·54817	$\bar{3}$·54972	$\bar{3}$·55126
0·058	$\bar{3}$·55281	$\bar{3}$·55436	$\bar{3}$·55588	$\bar{3}$·55743	$\bar{3}$·55895	$\bar{3}$·56050	$\bar{3}$·56203	$\bar{3}$·56335	$\bar{3}$·56508	$\bar{3}$·56660
0·059	$\bar{3}$·56811	$\bar{3}$·56964	$\bar{3}$·57114	$\bar{3}$·57265	$\bar{3}$·57418	$\bar{3}$·57568	$\bar{3}$·57619	$\bar{3}$·57867	$\bar{3}$·58018	$\bar{3}$·58169
0·060	$\bar{3}$·58317	$\bar{3}$·58466	$\bar{3}$·58616	$\bar{3}$·58765	$\bar{3}$·58914	$\bar{3}$·59062	$\bar{3}$·59209	$\bar{3}$·59358	$\bar{3}$·59504	$\bar{3}$·59653
0·061	$\bar{3}$·59799	$\bar{3}$·59946	$\bar{3}$·60093	$\bar{3}$·60239	$\bar{3}$·60386	$\bar{3}$·60533	$\bar{3}$·60677	$\bar{3}$·60824	$\bar{3}$·60968	$\bar{3}$·61113
0·062	$\bar{3}$·61258	$\bar{3}$·61402	$\bar{3}$·61547	$\bar{3}$·61692	$\bar{3}$·61834	$\bar{3}$·61979	$\bar{3}$·62122	$\bar{3}$·62266	$\bar{3}$·62409	$\bar{3}$·62551
0·063	$\bar{3}$·62694	$\bar{3}$·62837	$\bar{3}$·62979	$\bar{3}$·63120	$\bar{3}$·63263	$\bar{3}$·63403	$\bar{3}$·63546	$\bar{3}$·63686	$\bar{3}$·63827	$\bar{3}$·63968
0·064	$\bar{3}$·64108	$\bar{3}$·64249	$\bar{3}$·64390	$\bar{3}$·64528	$\bar{3}$·64669	$\bar{3}$·64808	$\bar{3}$·64946	$\bar{3}$·65085	$\bar{3}$·65227	$\bar{3}$·65362
0·065	$\bar{3}$·65501	$\bar{3}$·65639	$\bar{3}$·65778	$\bar{3}$·65915	$\bar{3}$·66053	$\bar{3}$·66190	$\bar{3}$·66327	$\bar{3}$·66465	$\bar{3}$·66602	$\bar{3}$·66739

TABLE II (*Cont'nued*)

α	0	1	2	3	4	5	6	7	8	9
0·38	$\bar{1}$·36717	$\bar{1}$·37015	$\bar{1}$·37313	$\bar{1}$·37611	$\bar{1}$·37908	$\bar{1}$·38204	$\bar{1}$·38501	$\bar{1}$·38796	$\bar{1}$·39091	$\bar{1}$·39386
0·39	$\bar{1}$·39679	$\bar{1}$·39974	$\bar{1}$·40268	$\bar{1}$·40559	$\bar{1}$·40853	$\bar{1}$·41144	$\bar{1}$·41436	$\bar{1}$·41726	$\bar{1}$·42016	$\bar{1}$·42307
0·40	$\bar{1}$·42597	$\bar{1}$·42885	$\bar{1}$·43176	$\bar{1}$·43465	$\bar{1}$·43751	$\bar{1}$·44040	$\bar{1}$·44327	$\bar{1}$·44613	$\bar{1}$·44900	$\bar{1}$·45185
0·41	$\bar{1}$·45471	$\bar{1}$·45756	$\bar{1}$·46042	$\bar{1}$·46326	$\bar{1}$·46610	$\bar{1}$·46894	$\bar{1}$·47177	$\bar{1}$·47461	$\bar{1}$·47744	$\bar{1}$·48024
0·42	$\bar{1}$·48307	$\bar{1}$·48588	$\bar{1}$·48869	$\bar{1}$·49150	$\bar{1}$·49432	$\bar{1}$·49711	$\bar{1}$·49991	$\bar{1}$·50271	$\bar{1}$·50548	$\bar{1}$·50828
0·43	$\bar{1}$·51107	$\bar{1}$·51345	$\bar{1}$·51661	$\bar{1}$·51941	$\bar{1}$·52216	$\bar{1}$·52493	$\bar{1}$·52770	$\bar{1}$·53045	$\bar{1}$·53320	$\bar{1}$·53596
0·44	$\bar{1}$·53871	$\bar{1}$·54147	$\bar{1}$·54421	$\bar{1}$·54694	$\bar{1}$·54969	$\bar{1}$·55243	$\bar{1}$·55515	$\bar{1}$·55789	$\bar{1}$·56062	$\bar{1}$·56335
0·45	$\bar{1}$·56606	$\bar{1}$·56879	$\bar{1}$·57140	$\bar{1}$·57421	$\bar{1}$·57693	$\bar{1}$·57962	$\bar{1}$·58232	$\bar{1}$·58504	$\bar{1}$·58774	$\bar{1}$·59042
0·46	$\bar{1}$·59313	$\bar{1}$·59581	$\bar{1}$·59850	$\bar{1}$·60119	$\bar{1}$·60388	$\bar{1}$·60655	$\bar{1}$·60924	$\bar{1}$·61191	$\bar{1}$·61459	$\bar{1}$·61725
0·47	$\bar{1}$·61992	$\bar{1}$·62258	$\bar{1}$·62525	$\bar{1}$·62791	$\bar{1}$·63057	$\bar{1}$·63322	$\bar{1}$·63589	$\bar{1}$·63854	$\bar{1}$·64119	$\bar{1}$·64384
0·48	$\bar{1}$·64648	$\bar{1}$·64913	$\bar{1}$·65177	$\bar{1}$·65441	$\bar{1}$·65705	$\bar{1}$·65967	$\bar{1}$·66232	$\bar{1}$·66494	$\bar{1}$·66757	$\bar{1}$·67020
0·49	$\bar{1}$·67283	$\bar{1}$·67544	$\bar{1}$·67808	$\bar{1}$·68069	$\bar{1}$·68331	$\bar{1}$·68593	$\bar{1}$·68853	$\bar{1}$·69115	$\bar{1}$·69376	$\bar{1}$·69636
0·50	$\bar{1}$·69897	$\bar{1}$·70158	$\bar{1}$·70417	$\bar{1}$·70678	$\bar{1}$·70938	$\bar{1}$·71179	$\bar{1}$·71457	$\bar{1}$·71717	$\bar{1}$·71975	$\bar{1}$·72236
0·51	$\bar{1}$·72494	$\bar{1}$·72753	$\bar{1}$·73012	$\bar{1}$·73271	$\bar{1}$·73528	$\bar{1}$·73788	$\bar{1}$·74045	$\bar{1}$·74303	$\bar{1}$·74561	$\bar{1}$·74819
0·52	$\bar{1}$·75076	$\bar{1}$·75334	$\bar{1}$·75591	$\bar{1}$·75848	$\bar{1}$·76105	$\bar{1}$·76363	$\bar{1}$·76620	$\bar{1}$·76876	$\bar{1}$·77132	$\bar{1}$·77390
0·53	$\bar{1}$·77646	$\bar{1}$·77901	$\bar{1}$·78157	$\bar{1}$·78414	$\bar{1}$·78669	$\bar{1}$·78925	$\bar{1}$·79180	$\bar{1}$·79436	$\bar{1}$·79692	$\bar{1}$·79948
0·54	$\bar{1}$·80202	$\bar{1}$·80459	$\bar{1}$·80713	$\bar{1}$·80968	$\bar{1}$·81224	$\bar{1}$·81479	$\bar{1}$·81732	$\bar{1}$·81988	$\bar{1}$·82242	$\bar{1}$·82496
0·55	$\bar{1}$·82751	$\bar{1}$·83005	$\bar{1}$·83260	$\bar{1}$·83515	$\bar{1}$·83769	$\bar{1}$·84022	$\bar{1}$·84276	$\bar{1}$·84532	$\bar{1}$·84784	$\bar{1}$·85038
0·56	$\bar{1}$·85293	$\bar{1}$·85546	$\bar{1}$·85801	$\bar{1}$·86054	$\bar{1}$·86307	$\bar{1}$·86561	$\bar{1}$·86815	$\bar{1}$·87067	$\bar{1}$·87322	$\bar{1}$·87574
0·57	$\bar{1}$·87827	$\bar{1}$·88082	$\bar{1}$·88336	$\bar{1}$·88587	$\bar{1}$·88841	$\bar{1}$·89095	$\bar{1}$·89347	$\bar{1}$·89602	$\bar{1}$·89855	$\bar{1}$·90108
0·58	$\bar{1}$·90361	$\bar{1}$·90615	$\bar{1}$·90866	$\bar{1}$·91120	$\bar{1}$·91373	$\bar{1}$·91627	$\bar{1}$·91880	$\bar{1}$·92133	$\bar{1}$·92386	$\bar{1}$·92640
0·59	$\bar{1}$·92892	$\bar{1}$·93146	$\bar{1}$·93398	$\bar{1}$·93651	$\bar{1}$·93905	$\bar{1}$·94158	$\bar{1}$·94412	$\bar{1}$·94663	$\bar{1}$·94917	$\bar{1}$·95172
0·60	$\bar{1}$·95524	$\bar{1}$·95677	$\bar{1}$·95932	$\bar{1}$·96185	$\bar{1}$·96438	$\bar{1}$·96692	$\bar{1}$·96944	$\bar{1}$·97199	$\bar{1}$·97451	$\bar{1}$·97706
0·61	$\bar{1}$·97960	$\bar{1}$·98213	$\bar{1}$·98467	$\bar{1}$·98721	$\bar{1}$·98975	$\bar{1}$·99230	$\bar{1}$·99483	$\bar{1}$·99738	$\bar{1}$·99992	0·00246
0·62	0·00500	0·00754	0·01009	0·01264	0·01517	0·01773	0·02027	0·02283	0·02538	0·02793
0·63	0·03048	0·03303	0·03559	0·03813	0·04070	0·04325	0·04582	0·04837	0·05093	0·05349
0·64	0·05606	0·05863	0·06120	0·06375	0·06633	0·06889	0·07146	0·07403	0·07663	0·07917
0·65	0·08175	0·08433	0·08692	0·08949	0·09208	0·09466	0·09724	0·09985	0·10243	0·10503
0·66	0·10760	0·11020	0·11280	0·11539	0·11800	0·12060	0·12319	0·12582	0·12842	0·13103
0·67	0·13363	0·13624	0·13887	0·14149	0·14410	0·14672	0·14935	0·15198	0·15460	0·15723
0·68	0·15987	0·16251	0·16513	0·16778	0·17043	0·17307	0·17571	0·17838	0·18103	0·18368
0·69	0·18634	0·18900	0·19167	0·19432	0·19700	0·19966	0·20235	0·20502	0·20771	0·21039
0·70	0·21308	0·21577	0·21846	0·22166	0·22385	0·22656	0·22925	0·23197	0·23468	0·23741
0·71	0·24012	0·24284	0·24557	0·24830	0·25103	0·25378	0·25650	0·25925	0·26199	0·26475
0·72	0·26750	0·27028	0·27306	0·27580	0·27857	0·28075	0·28413	0·28690	0·28969	0·29249
0·73	0·29528	0·29809	0·30089	0·30369	0·30652	0·30933	0·31216	0·31498	0·31782	0·32064
0·74	0·32349	0·32634	0·32918	0·33205	0·33490	0·33778	0·34075	0·34352	0·34640	0·34929
0·75	0·35218	0·35508	0·35799	0·36088	0·36380	0·36673	0·36965	0·37259	0·37552	0·37846
0·76	0·38141	0·38436	0·38732	0·39029	0·39327	0·39625	0·39924	0·40224	0·40523	0·40825
0·77	0·41125	0·41426	0·41731	0·42033	0·42337	0·42642	0·42947	0·43254	0·43561	0·43869
0·78	0·44176	0·44486	0·44796	0·45106	0·45419	0·45730	0·46043	0·46356	0·46672	0·46988
0·79	0·47304	0·47621	0·47940	0·48257	0·48577	0·48899	0·49219	0·49542	0·49865	0·50190
0·80	0·50515	0·50841	0·51167	0·51497	0·51826	0·52157	0·52488	0·52818	0·53152	0·53487
0·81	0·53823	0·54158	0·54496	0·54834	0·55173	0·55515	0·55856	0·56199	0·56543	0·56888
0·82	0·57235	0·57583	0·57932	0·58283	0·58635	0·58986	0·59341	0·59697	0·60053	0·60410
0·83	0·60771	0·61131	0·61493	0·61858	0·62223	0·62590	0·62958	0·63327	0·63696	0·64069
0·84	0·64444	0·64820	0·65196	0·65576	0·65956	0·66339	0·66722	0·67107	0·67496	0·67884
0·85	0·68275	0·68667	0·69059	0·69458	0·69857	0·70257	0·70658	0·71062	0·71467	0·71869
0·86	0·72287	0·72699	0·73114	0·73530	0·73948	0·74371	0·74794	0·75219	0·75647	0·76077
0·87	0·76510	0·76945	0·77383	0·77822	0·78265	0·78711	0·79158	0·79609	0·80062	0·80519
0·88	0·80978	0·81441	0·81906	0·82373	0·82844	0·83318	0·83796	0·84276	0·84690	0·85248
0·89	0·85739	0·86233	0·86730	0·87232	0·87737	0·88243	0·88759	0·89274	0·89796	0·90320
0·90	0·90848	0·91380	0·91919	0·92461	0·93007	0·93558	0·94113	0·94674	0·95239	0·95808
0·91	0·96384	0·96965	0·97550	0·98142	0·98740	0·99342	0·99952	1·00566	1·01187	1·01815
0·92	1·02449	1·03089	1·03737	1·04391	1·05053	1·05722	1·06399	1·07084	1·07777	1·08478
0·93	1·09186	1·09905	1·10633	1·11369	1·12116	1·12871	1·13638	1·14414	1·15201	1·16001
0·94	1·16811	1·17633	1·18467	1·19243	1·20175	1·21010	1·21939	1·22842	1·23762	1·24697
0·95	1·25647	1·26616	1·27604	1·28608	1·29634	1·30679	1·31747	1·32835	1·33949	1·35086
0·96	1·36248	1·37438	1·38658	1·39906	1·41186	1·42499	1·43838	1·45235	1·46661	1·48128
0·97	1·49642	1·51204	1·52818	1·54486	1·56215	1·58006	1·59869	1·61805	1·63826	1·65934
0·98	1·68143	1·70359	1·72895	1·75465	1·78188	1·81079	1·84163	1·87470	1·91034	1·94901
0·99	1·99128	2·03790	2·08993	2·14880	2·21663	2·29667	2·39446	2·52028	2·69723	2·99914

TABLE III

NORMAL POTENTIALS[1] (ELECTRO-AFFINITIES) AT 18°.

	EP_h
$Zn \rightarrow Zn^{\cdot\cdot}$	−0·76 volts
$Cd \rightarrow Cd^{\cdot\cdot}$	−0·40 „
$Fe \rightarrow Fe^{\cdot\cdot}$	−0·43 „
$Tl \rightarrow Tl^{\cdot\cdot}$	−0·32 „
$Co \rightarrow Co^{\cdot\cdot}$	−0·29 „
$Ni \rightarrow Ni^{\cdot\cdot}$	−0·22 „
$Pb \rightarrow Pb^{\cdot\cdot}$	−0·12 „
$H_2 \rightarrow 2H^{\cdot\cdot}$	*±0·00* „
$Cu \rightarrow Cu^{\cdot\cdot}$	+0·34 „
$Hg \rightarrow Hg^{\cdot\cdot}$	+0·86 „
$Ag \rightarrow Ag^{\cdot}$	+0·80 „
$Au \rightarrow Au^{\cdot}$	+1·54 „
$2F' \rightarrow F_2$ (gas)	+1·9 „
$2Cl' \rightarrow Cl_2$ (gas)	+1·35 „
$2Br' \rightarrow Br_2$ (liq.)	+1·08 „
$2I' \rightarrow I_2$ (solid)	+0·54 „
$S'' \rightarrow S$ (solid)	−0·55 „

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[1] Abegg, Auerbach and Luther, *Messungen Elektromotorische Kräfte.*

TABLE IV

TRANSPORT NUMBERS OF ANIONS[1]

v = Gram equivalents per litre

v =	0·01	0·02	0·05	0·1	0·2	0·5	1·0	1·5	2·0
KCl	0·506	0·507	0·507	0·508	0·509	0·513	0·514	0·515	0·515
KBr	0·506	0·507	0·507	0·508	0·509	0·513	0·514	0·515	0·515
KI	0·506	0·507	0·507	0·508	0·509	0·513	0·514	0·515	0·515
NH_4Cl	0·506	0·507	0·507	0·508	0·509	0·513	0·514	0·515	0·515
NaCl	—	—	0·614	0·617	0·620	0·626	0·637	0·640	0·642
KNO_3	—	—	—	0·497	0·496	0·492	0·487	0·482	0·479
$NaNO_3$	—	—	—	0·615	0·614	0·612	0·611	0·610	0·608
$AgNO_3$	0·528	0·528	0·528	0·528	0·527	0·519	0·501	0·487	0·482
KOH	—	—	—	0·735	0·736	0·738	0·740	—	—
NaOH	—	—	0·81	0·82	0·82	0·82	0·825	—	—
HCl	—	—	0·172	0·172	0·172	0·173	0·176	0·180	0·185
$\frac{1}{2}BaCl_2$	0·56	0·565	0·575	0·585	0·595	0·615	0·640	0·650	0·657
$\frac{1}{2}CaCl_2$	0·58	0·59	0·61	0·64	0·66	0·675	0·686	0·695	0·700
$\frac{1}{2}K_2CO_3$	—	—	0·39	0·40	0·41	0·435	0·434	0·421	0·413
$\frac{1}{2}Na_2CO_3$	—	—	0·52	0·53	0·53	0·54	0·548	0·546	0·542
$\frac{1}{2}CuSO_4$	—	0·62	0·626	0·632	0·643	0·668	0·696	0·714	0·720
$\frac{1}{2}H_2SO_4$	—	—	0·193	0·191	0·188	0·182	0·174	0·169	0·168

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[1] Kohlrausch and Holborn, *Leitvermogen der Elektrolyte.*

TABLE V

IONIC CONDUCTIVITIES (MOBILITIES)[1]

Normal Concentration	K	Na	Li	NH_4	Ag	$\frac{1}{2}Ba$	$\frac{1}{2}Ca$	$\frac{1}{2}Mg$	H
0·0000	65·3	44·4	35·5	64·2	55·7	57·3	53·0	49	318
0·0001	64·7	43·8	34·9	63·6	55·4	55·0	50·6	47	316
0·0002	64·4	43·6	34·7	63·4	55·1	54·3	50·0	46	316
0·0005	64·1	43·3	34·4	63·0	54·9	53·3	48·9	45	315
0·001	63·7	42·9	34·0	62·7	54·7	52·2	47·8	43	314
0·002	63·2	42·4	33·5	62·2	54·2	50·7	46·4	42	313
0·005	62·3	41·4	32·6	61·2	53·2	48·2	43·9	40	311
0·01	61·3	40·5	31·6	60·2	51·9	45·7	41·4	37	310
0·02	60·0	39·2	30·3	59·0	50·0	42·7	38·3	34	307
0·03	59·2	38·3	29·4	58·1	48·6	40·5	36·1	32	305
0·05	57·9	37·0	28·2	56·8	46·6	37·7	33·4	29	302
0·1	55·8	35·6	26·1	54·8	43·3	33·8	29·4	25	296

Normal Concentration	Cl	I	NO_3	$C_2H_3O_2$	$\frac{1}{2}SO_4$	$\frac{1}{2}C_2O_4$	$\frac{1}{2}CO_3$	OH
0·0000	65·9	66·7	60·8	33·7	69·7	63	—	174
0·0001	65·3	66·1	60·2	33·1	67·2	61	—	172
0·0002	65·1	65·9	60·0	33·0	66·6	60	—	172
0·0005	64·8	65·5	59·6	32·8	65·4	59	—	171
0·001	64·4	65·1	59·3	32·6	64·0	58	69	171
0·002	63·9	64·7	58·8	32·4	62·3	56	66	170
0·005	63·0	63·7	57·8	31·6	59·3	54	60	168
0·01	62·0	62·7	56·8	30·8	56·1	51	55	167
0·02	60·7	61·6	55·6	29·8	52·3	48	50	165
0·05	58·6	59·3	53·4	28·0	46·1	43	43	161
0·1	56·5	57·3	51·4	26·4	41·9	39	38	157

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[1] Kohlrausch and Holborn, *Leitvermogen der Elektrolyte.*

TABLE VI*a*

EQUIVALENT CONDUCTIVITY[1] AT 18°

Normal Concentration	KCl	NaCl	KNO_3	$NaNO_3$	$AgNO_3$	$\frac{1}{2}K_2SO_4$	$\frac{1}{2}Na_2SO_4$	$\frac{1}{2}Na_2CO_3$
0·0001	129·5	109·7	124·7	103·7	115·5	133·5	110·5	—
0·0002	129·1	109·2	124·3	103·3	115·2	132·7	109·6	—
0·0005	128·3	108·5	123·6	102·5	114·5	130·8	108·3	—
0·001	127·6	107·8	122·9	101·8	114·0	129·0	106·7	112·0
0·002	126·6	106·7	122·0	100·7	113·0	126·3	104·8	108·5
0·005	124·6	104·8	120·1	98·9	111·0	121·9	100·8	102·5
0·01	122·5	102·8	118·1	97·1	108·7	117·4	96·8	96·2
0·02	120·0	100·2	115·2	95·0	105·6	111·8	91·9	89·5
0·05	115·9	95·9	110·0	91·4	100·1	102·5	83·9	80·3
0·1	111·9	92·5	104·4	87·4	94·7	95·9	78·4	72·9
0·2	107·7	88·2	98·6	82·3	88·1	88·9	71·4	65·6
0·5	102·3	80·9	89·7	74·2	77·8	78·7	59·7	54·5
1·0	98·2	74·4	80·4	66·0	67·8	71·8	50·8	45·5
2·0	92·6	64·8	69·4	54·5	55·8	—	40·0	34·5

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[1] Kohlrausch and Holborn, *Leitvermögen der Elektrolyte*.

TABLE VI*b*

EQUIVALENT CONDUCTIVITY[1] AT 18°

Normal Concentration	$\frac{1}{2}CuSO_4$	KOH	NaOH	NH_4OH	HCl	HNO_3	$\frac{1}{2}H_2SO_4$	$C_2H_4O_2$
0·0001	113·3	—	—	66·0	—	—	—	107·0
0·0002	111·1	—	—	53·0	—	—	—	80·0
0·0005	106·8	—	—	38·0	—	—	368	57·0
0·001	101·6	234	208	28·0	377	375	361	41·0
0·002	93·4	233	206	20·6	376	374	351	30·2
0·005	81·5	230	203	13·2	373	371	330	20·0
0·01	72·2	228	200	9·0	370	368	308	14·3
0·02	63·0	225	197	7·1	367	364	286	10·4
0·05	51·4	219	190	4·6	360	357	253	6·45
0·1	45·0	213	183	3·3	351	350	225	4·60
0·2	39·2	206	178	2·3	342	340	214	3·24
0·5	30·8	197	172	1·35	327	324	205	2·01
1·0	25·8	184	160	0·89	301	310	198	1·32
2·0	20·1	161	131·4	0·532	254	258	183	0·80

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[1] Kohlrausch and Holborn, *Leitvermogen der Elektrolyte*.

TABLE VII

VAPOUR PRESSURE OF WATER

Temperature	Vapour Pressure	Temperature	Vapour Pressure
4°	6·0 mm.	19°	16·4 mm.
5°	6·5 ,,	20°	17·4 ,,
6°	6·9 ,,	21°	18·5 ,,
7°	7·5 ,,	22°	19·6 ,,
8°	8·0 ,,	23°	20·9 ,,
9°	8·5 ,,	24°	22·2 ,,
10°	9·2 ,,	25°	23·5 ,,
11°	9·8 ,,	26°	25·0 ,,
12°	10·5 ,,	27°	26·5 ,,
13°	11·2 ,,	28°	28·1 ,,
14°	11·9 ,,	29°	29·8 ,,
15°	12·7 ,,	30°	31·5 ,,
16°	13·5 ,,	31°	33·4 ,,
17°	14·4 ,,	32°	35·4 ,,
18°	15·3 ,,	33°	37·4 ,,

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