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ELECTROCHEMISTRY

I

THEORETICAL ELECTROCHEMISTRY AND ITS PHYSICO-CHEMICAL FOUNDATIONS

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INTRODUCTION.

THE science of electrochemistry has come to have a far wider range of application than formerly. A comparatively short time ago it comprised little more than methods of bringing about chemical reactions by means of electricity, and the utilization of chemical affinity for the production of an electric current. It has now become one of our most important aids in the investigation of some of the fundamental problems of general chemistry. The measurement of electromotive forces is the safest, and oftentimes the only, means of determining the chemical force with which reactions take place; conductivity measurements have given us an insight into the nature of solutions; electrochemistry has given rise to one of the most fruitful of the modern chemical theories, the theory of electrolytic dissociation.

In practical as well as theoretical lines electrochemistry has been of immense value. Aside from the fact that many substances, such as the alkali metals, aluminium, magnesium, calcium carbide, etc., which can only be made with the greatest difficulty by purely chemical means, are easily manufactured with the help of electricity, let us remember that electrochemistry gives us a nearly perfect means of utilizing the enormous power of our waterfalls for chemical purposes, and enables us to store up and transport this energy which we receive from the sun. Finally electrochemistry gives us many compounds in a quicker, and therefore cheaper, way than the old purely chemical processes.

Theoretical, or general chemistry, and electrochemistry are not separable; comprehension of one presupposes knowledge of the other. Therefore before we take up electrochemistry proper we will go over some of the physical and physico-chemical principles which form the basis of our present ideas in the field of electrochemistry. We will then discuss the various theories of electrochemistry and give such illustrations as are necessary for their better comprehension. Experimental results and their applications, as well as methods of measurement, etc., will be contained in the second volume. The third will be devoted to the technical applications.

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ELECTROCHEMISTRY.

CHAPTER I.

WORK, CURRENT, AND VOLTAGE.

THE most important question for scientific and technical progress is, How much work can a given chemical reaction perform? This question is of equal or perhaps greater importance than the question as to what happens when two substances are brought together. If we know the work which a certain reaction can do, for instance the reaction $CO + O = CO_2$, and the temperature coefficient of its ability to do work, we know at once whether or not the reaction occurs and the conditions necessary for its occurrence. We see from the value of the energy, that this reaction, the oxidation of carbon monoxide, takes place at ordinary temperatures with great violence, in fact explosively; further, that the reaction is less complete the higher the temperature, and that at very high temperatures it even goes in the opposite direction; i.e., carbon monoxide not only will not burn, but carbon dioxide is decomposed into carbon monoxide and oxygen.

We can distinguish six different kinds of energy:

1, mechanical energy; 2, volume energy; 3, chemical energy; 4, electrical energy; 5, heat energy, and 6, radiant energy. These different forms of energy are mutually transformable and if we have a suitable mechanism, the transformation is quantitative. Heat energy forms an exception to this rule; the complete transformation of heat into electrical or mechanical energy is theoretically and practically impossible, although mechanical or electrical energy may be completely transformed into heat.

The scientific unit of mechanical work is the erg (=1 dyne×1 centimetre) and this is the unit of the so-called C.G.S. system. The practical unit is the kilogram-metre, which is the work necessary to raise 1000 grams through a height of 100 centimetres, or the work which a kilogram can do in falling a distance of 1 metre.

A kilogram *weight* (not to be confused with the *mass* of a kilogram) is the force with which the mass of 1 kilogram (=1 litre of water at 4° C.) is attracted by the earth. A falling body attains as a result of the earth's attraction an acceleration of 980.6 cms. per second, so that a gram weight represents a force of 980.6 dynes. The unit of force=1 dyne is that force which, acting on the mass of 1 gram, gives it an acceleration of 1 cm. per second. Acceleration is the increase of velocity per second. $\text{Velocity} = \frac{\text{distance}}{\text{time}}$. A kilogram-metre is 100 000 times as great as a gram-centimetre, i.e., =98 060 000 ergs.

The unit of volume energy is the litre-atmosphere. When any body, for instance a gas, which always exerts a pressure on the walls of the vessel enclosing it (cf. p. 16) expands, the weight of the atmosphere above it is displaced by an amount corresponding to the number of litres of expansion of the gas. The expanding gas therefore does work against the pressure of the atmosphere. (In general, every increase of volume taking place against a pressure, or every contraction brought about by a pressure, is accompanied by a gain or loss of work.) In the barometer the pressure of the atmosphere forces a column of mercury 1 sq. cm. in cross-section up to a height of 76 cms. Such a column of mercury weighs 1.0333 kilograms, since the specific gravity of mercury is 13.596. The pressure of one atmosphere therefore is 1.0333 kg. per sq. cm., or 103.33 kg. per sq. decimetre. If then 103.33 kilograms are raised 1 decimetre, i.e., if a body expands by 1 litre, the work done is the same as when 1 gram is raised 1 033 000 cms. 1 gr. cm. = 980.6 ergs; the value of 1 litre atmosphere is therefore 980.6×1 033 000 = 1 013 200 000 ergs.

The ordinary unit of electric work is the watt-second. Watt is the "power" of an electric current of 1 ampere under the pressure of 1 volt. By power is meant the work done in unit time, i.e., = work/time. An ampere is the amount of electricity measured in coulombs flowing through a conductor in unit time. A coulomb is the unit quantity of electricity. A coulomb in passing through a silver voltameter precipitates 0.001118 gr. of silver; a coulomb is the electric charge (cf. p. 53) on 0.01036 milligram equivalents of every ion and will precipitate this quantity of any ion on an electrode. A current of 1 ampere flows through a conductor when the quantity of electricity passing is 1 coulomb per second. An ampere is the tenth part of the unit of current in the C.G.S. system.

Electric pressure or difference of potential is ordinarily measured in volts. A volt is that pressure which suffices to send a current of 1 ampere through a resistance of 1 ohm (legal definition). One volt is equal to 10^8 C.G.S. units. A Daniell cell has an electromotive force or difference of potential of 1.1 volts; a storage battery has 2.0 volts. A watt is 1 volt×1 ampere (a power), and a watt-second is the work which a current of 1 ampere is able to do when flowing for 1 second through a resistance of 1 ohm. A watt-second is therefore $10^8 \times 10^{-1} = 10^7$ ergs.

Heat energy is measured in calories. A calorie is the quantity of heat which is necessary to raise the temperature of 1 gram of water from 15° C. to 16° C. Since the specific heat of water is not independent of the temperature, the quantity of heat necessary to raise the temperature of 1 gr. of water 1° C. is different at different temperatures.*

The mechanical equivalent of heat has been determined by many investigators; we will use the value adopted by Nernst,† 42 600. The meaning of this number is as follows: If 1 gram falls 42 600 centimetres, or if 1 kg. falls 42.6 cms. and the total kinetic energy (*vis viva*) of the falling weight is converted by impact into heat, this quantity of heat is just sufficient to raise the temperature of 1 gram of water from 15° C. to 16° C., i.e., one calorie

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* Beside the above-defined calorie, which is the one most generally in use, there are the "mean calorie" $= \frac{1}{100}$ the quantity of heat necessary to warm 1 gr. of water from 0° to 100°, and the "zero-point calorie," the quantity of heat necessary to warm 1 gr. of water from 0° to 1°. The "kilogram calorie" is 1000 times the 15° calorie.

† Theoretische Chemie, p. 12. Enke, Stuttgart.

is evolved. The energy of the 1 gram weight is then $42\,600 \times 980.6 = 41\,777\,000$ ergs (980.6 is the acceleration due to gravity).

There is no fixed unit for chemical energy, it is generally measured in volt-coulombs. As yet there is also no common unit for radiant energy.

With the help of the following table* it is easy to express a given quantity of work in any of the different units.

		Absolute Units, Ergs	Electrical Units, Watt-seconds	Heat-units, Gr. Calories
1 erg	=	1	10^{-7}	2.387×10^{-8}
1 watt-second	=	10^{7}	1	0.2387
1 gr. calorie	=	4.187×10^{7}	4.189	1
1 litre-atmosphere	=	1.013×10^{9}	0.01013	24.19
1 kg.-metre	=	9.806×10^{7}	9.806	2.341
1 horse-power-second	=	7.355×10^{9}	735.5	175.58
Gas constant R	=	8.3155×10^{7}	8.3155	1.985

		Litre-atmospheres	Kilogram-metres	Horse-power-seconds
1 erg	=	9.869×10^{-10}	1.0198×10^{-8}	1.3597×10^{-10}
1 watt-second	=	0.009869	0.10198	0.0013597
1 gr. calorie	=	0.041342	0.4272	0.005696
1 litre-atmosphere	=	1	10.333	0.13778
1 kg.-metre	=	0.09678	1	0.01333
1 horse-power-second	=	7.2585	75.00	1
Gas constant R	=	0.0821	0.848	0.011308

From the foregoing it is clear that an expression denoting work is always made up of two factors. A summary of these will perhaps be of use in making the relationship clearer.

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* Table of H. Steinwehr, recalculated after Nernst, Zeitschr. f. Electrochemie, 10, 629, 1904.

Mechanical work:

Velocity $= \frac{\text{Distance}}{\text{Time}}$.

Acceleration $= \frac{\text{Increase of velocity}}{\text{Time}}$.

Force = Acceleration × mass.

Work = Force × distance.

Power $= \frac{\text{Work}}{\text{Time}}$.

Work = Mass × length of fall × acceleration due to gravity.

Weight = Mass × acceleration due to gravity.

Work of expansion = Increase of volume × pressure.

Pressure $= \frac{\text{Weight}}{\text{Surface}}$.

Electrical work = Voltage × coulombs.

Current strength $= \frac{\text{Coulombs}}{\text{Time}}$.

Electrical power = Voltage × current.

Chemical work = Chemical potential × quantity of substance.

The conceptions of chemical and electric potential will occur repeatedly and will be explained in their proper place.

Work Done by Natural Processes.

Fundamental Law.—*All processes in Nature which take place of themselves can furnish work, and only such processes occur spontaneously, which, with the aid of suitable apparatus, can be made to perform work.* Among such processes are the union of electric charges; movements of liquid from a higher to a lower level; all movements of masses in general which occur spontaneously; further, chemical reactions; equalization of different temperatures, etc.

The most important question for us is, how much work we can obtain from a given process under the most favorable conditions, the so-called "maximum work." In order to appreciate the meaning of this term we must review two laws concerning the relation between heat and work, the two principles of thermodynamics.

First Law, Principle of the Conservation of Energy.—Just as no substance can be created from nothing nor be absolutely destroyed (law of the conservation of matter), so energy can neither be created from nothing nor annihilated. "Perpetual motion," i.e., a machine which continually does work without having energy given to it in any way, is scientifically an absurdity. Many inventors who have had such an end in view have tried to achieve the impossible.

A few illustrations will make the meaning of this law clear.

We lift a weight of 10 kg. vertically from the floor through a distance of 1 metre. In so doing our muscles do 10 kg. metres of work. The weight has now a capacity for doing work, or *potential energy*, of 10 kg. metres, if we disregard the energy it may have had to start with. If we let the weight fall again it attains as a result of the earth's attraction a certain "vis viva" (the potential energy changes to *kinetic energy*) and when it strikes the floor this energy is converted into heat. If we measure the heat we find it to be 23.5 calories, and this, as we see from the table on p. 5, is just equal to the original

10 kg. metres we spent in raising the weight. If we denote by U the change in energy resulting from the fall (in this case 10 kg. metres) and by W the heat generated by the impact of the weight on the floor, then

$$U = W.$$

We now tie to the falling weight a cord, lead it over a pulley, and fasten a 9 kg. weight to the other end, so that this last is raised a metre by the fall of the first; let the work necessary to raise this weight be A (in this case 9 kg. metres). We will now find that the heat developed by the impact of the first weight on the floor is 2.35 calories; if we denote this by W, then

$$U = A + W.$$

If we supply extra work to the process—for instance, by accelerating either the 10 or 9 kg. weight by a blow—this work A' must also appear in the heat developed,

$$W = U - A + A'.$$

In every case the change in the total energy plus the heat expended and work expended is equal to the work obtained plus the heat obtained.

If we let a chemical reaction take place in such a way that no work is done, we obtain the change in total energy as heat, which in this case we call the "heat of reaction" (Wärmetönung). In the combustion of coal we obtain with the help of a steam-boiler only about 20% of the heat of reaction as mechanical energy; the other 80% goes over into heat which is lost up the chimney and by radiation. If we obtain more work than that which corresponds to the heat of reaction (which is possible in some cases) the extra heat must be supplied by the surroundings, i.e., the reaction mixture cools itself off.

Second Law, Principle of the Transformation of Energy.—We wish, of course, to know how much work we can get out of a given process under the most favorable conditions, i.e., what the maximum work is. Thomson, and after him Berthelot, proposed the law (principe du travail maximum) that the maximum work may be calculated from the heat of reaction, and that the two are equal. Helmholtz,* however, later proved that this is not the case.

The basis of Helmholtz's theory is the well-known fact that *heat can do no work when it is at rest.* Just as water can do no work when it is at rest and only does so when it falls from a higher to a lower level, and just as electricity can only perform work as it falls from a higher to a lower potential, so heat will only do work when it falls from a higher to a lower temperature.

If heat is to be converted into work we must have differences of temperature. To cite an illustration of Nernst's, we cannot utilize the enormous reservoir of heat in the sea to turn the propellers of the ocean steamers. One might conceive of the ships' engines taking heat from the ocean water, using it in the performance of work, i.e., in propelling the ship, and then returning it to the water in the form of friction. Experience shows that such a machine, which would not contradict the law of the

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* Thomson has accepted the views of Helmholtz, but Berthelot and many of the French scientists still cling to the principe du travail maximum although it has been clearly shown to be incorrect.

conservation of energy, is unfortunately an impossibility; such a machine, however, has received the name of "perpetual motion of the second kind."

By a simple thermodynamic cycle it can be shown that when an amount of heat Q at the absolute temperature* T falls to the temperature $T-dT$,† in the most favorable case the quantity of work dA to be obtained is

$$dA=Q\frac{dT}{T}.$$

By combining this equation with the equation $U=A+W$ (cf. p. 8) we have

$$A-U=T\frac{dA}{dT};$$

$\frac{dA}{dT}$ is, however, nothing else than the temperature coefficient of the capacity for doing work, i.e., it is the amount by which A changes when the temperature is changed one degree. If we represent the temperature coefficient by α, then

$$A-\alpha T=U.$$

The formula $A-U=T\frac{dA}{dT}$ is the exact expression in one equation of both laws of thermodynamics.

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* The gas laws make it probable that there can be no temperature lower than $-273°$ C. -273 is therefore called the absolute zero of temperature. Temperatures counted from the absolute zero are denoted by T; if t is the ordinary Celsius temperature, counted from the freezing-point of water, $T=273+t$.

† An infinitely small value, which is not zero, but approaches zero, is denoted by a prefixed d. dQ is an infinitely small quantity of heat, dU an infinitely small change of total energy, etc.

From this equation we can derive several very important results: 1. The change in total energy U, which in chemical reactions is simply the heat of reaction, is only equal to the work obtainable, or, as it is often called, the "free energy," when the free energy is independent of the temperature, i.e., when $\alpha = 0$. 2. At the absolute zero (−273° C.) A is always $= U$. 3. If α is positive, i.e., if the free energy increases when the temperature is raised, we may obtain more work than corresponds to the heat of the reaction. The excess must be supplied by the surroundings, and the reaction mixture cools itself off. This happens, of course, only when we do extract the maximum work. 4. If α is negative, excess heat results, and the system becomes warm, even when the maximum work is obtained. With the exception of No. 2, all these cases are realized.

The Daniell cell furnishes a good illustration of these points. This affords electric energy as the result of the following equation:

$$Zn + CuSO_4 = ZnSO_4 + Cu,$$

i.e., copper is precipitated from a solution of $CuSO_4$ by zinc. A Daniell cell in using up 32.7 grs. of zinc gives at 0° C. electric energy equivalent to 25 263 calories; electrical measurements further show that the free energy increases 0.786 calorie per degree rise of temperature. $\therefore \alpha T = 0.786 \times 273 = 213$ calories. The heat of reaction is therefore

$$U = 25\,263 - 213 = 25\,050 \text{ cal.}$$

Calorimetric measurements gave 25 055 calories, in excellent agreement with the calculated value.

The questions now arise, How do we determine the maximum work? or, How can we compel a reaction to do its best? To do this we must contrive an arrangement which converts chemical into mechanical or electrical energy, and which works so perfectly that there are no losses due to secondary causes, such as leakage, friction, radiation, etc. Further, the reaction must take place in such a manner that we may stop it at any time, and by putting back exactly the same amount of work we have already obtained from it, bring the system to its original condition. Such a process is called a "reversible" one. Absolute reversibility would be possible experimentally only if we ourselves were perfect beings; since, unfortunately, even electrochemists can make no such claim, we must content ourselves with approaching the above requirements of reversibility as closely as possible. An arrangement which fulfils these requirements very perfectly is the galvanic cell (battery). In it reactions often take place with practically perfect reversibility, and for this reason the scientific chemist should realize the importance of electrochemistry.

The work which a reaction can do is the point which has a special interest for us. One of the chief aims of electrochemistry is to obtain work from chemical reactions, such, for instance, as the combustion of coal; the reaction between zinc and copper sulphate or between lead, lead peroxide, and sulphuric acid. Another aim is the compulsion of chemical reactions by means of electrical work, as in the manufacture of aluminium from its oxide, or the preparation of bleaching solutions from common salt. In the first case we are satisfied when we know the maximum work which the given reaction can do; in the second we must learn the maximum work of the reverse reaction.

If we have a solution in which two reactions may take place, for instance a solution of $FeSO_4$ and $CuSO_4$, and wish to obtain the copper electrolytically, we must know which of the two reactions takes place easier; i.e., how much work is sufficient to precipitate the copper on the cathode, but does not suffice to precipitate the iron. In other words, we must know the work necessary for each reaction.

If we know the maximum work of a reaction we know also, as already stated, whether it will take place of itself or not. If we know, for instance, that the displacement of copper by zinc according to the equation $Zn + CuSO_4 = Cu + ZnSO_4$ can perform work, we know from this fact that the reaction will go on of its own accord, and that therefore the reverse reaction which requires the expenditure of work will not occur spontaneously; that is, zinc cannot be precipitated by copper from a zinc salt solution.

Another example is the following: When we dissolve hydrogen peroxide in water we observe no reaction; decomposition according to the equation $H_2O_2 = H_2O + O$ apparently does not take place of itself. It would therefore appear probable that the reverse reaction would occur spontaneously. However, if we pass oxygen gas into water, H_2O_2 is not formed in measurable amounts. Accordingly the only way of deciding which of the two reactions, decomposition or formation, is spontaneous, is to measure the work involved. It is found that work is necessary for the formation of H_2O_2; work can be done by its decomposition and therefore this reaction goes on of itself. A similar case is found in detonating gas. Hydrogen and oxygen may be kept together many years without the visible formation of water. In this case, also, the only means of determining which reaction is spontaneous is by measuring the work. The reason why we do not observe either a decomposition of the H_2O_2 or a formation of H_2O lies in the slowness of the reaction.

Reaction Velocity and Chemical Force.

At the end of the last paragraph mention was made of the slowness of a reaction, and we must now see what bearing the reaction velocity has on the work of a process. In utilizing a chemical reaction for the production of work the first point to be considered is the speed with which the reaction proceeds. A reaction which can furnish a million kg.-metres can be of no use to us if it requires a milliard years before it is completed, nor, on the other hand, if it only requires a fraction of a second, for our machines are too imperfect to take care of such a power, and the greater part would be lost in the form of heat. The reaction $2H_2+O_2=2H_2O$ at ordinary temperatures goes too slow, and at high temperatures, too fast (explosively). An electrochemical arrangement, however, enables us to regulate the velocity within certain limits, and so quantitatively obtain the work of the reaction.

A law similar to Ohm's law regulates the velocity of chemical reactions.

$$\text{Reaction velocity}=\frac{\text{impelling force}}{\text{chemical resistance}}.$$

We can always calculate the impelling force from the work which the given reaction can do, but we know very little about chemical resistance. In most reactions, probably in all, the chemical resistance increases as the temperature decreases, and would appear to become infinite at the absolute zero, where all chemical action would cease. In many cases we can reduce the chemical resistance; this may be done, for example, in the case of H_2O formation by constructing a gas cell. The chemical resistance is also lowered by raising the temperature, or by bringing finely divided platinum into the gas mixture. The platinum does not take a visible part in the reaction, for it is the same after the reaction as before. But by the simple presence of platinum we can increase the reaction velocity at ordinary temperatures till explosion occurs. Such substances which diminish chemical resistance are known as catalytic agents or catalyzers. Their presence changes neither the impelling force nor the nature of the reaction. In technical work there are many reactions which, were it not for suitable catalyzers, would go so slowly as to be commercially worthless. We need only mention the "contact process" for sulphuric acid, in which a number of catalyzers have found application in bringing about the union of sulphur dioxide and oxygen.*

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* The reader will find a collection of the most important technical reactions in which catalysis plays an important part in an address of Bodländer's, delivered before the Berlin International Chemical Congress, which has appeared with other collections in "Der deutsche Verlag." Compare also Ostwald's article on Catalysis in Science and the Arts, in the Zeitschrift für Electrochemie, 7, 995, 1901.

The Gas Laws. Work Obtainable from the Expansion of Gases.

We will later find that the method of calculating the work obtainable from the expansion of a gas is also applicable in calculating the work done when substances in a solution change their concentration. We will therefore briefly go over the gas laws and put them in a form from which the work obtainable is easily calculated.

1. **Boyle's Law.**—At constant temperature, when the volume of a gas is changed, the pressure varies inversely as the volume; that is,

$$p \cdot v = \text{a constant.}$$

If we bring into the volume of 1 litre successively one, two, three, . . . grams of oxygen, the pressure increases in the proportion one, two, three, . . . ; i.e., each gram of oxygen presses on the walls of the containing vessel as though it were present alone.

2. **Gay-Lussac's Law.**—If the pressure on a gas is kept constant and the temperature raised, the gas expands per degree centigrade by an amount which is 0.003663 times $(=\frac{1}{273})$ the volume it occupies at 0° C. If the volume at 0° C. is v_0, its volume (v) at the temperature τ° C. is

$$V = v_0(1 + 0.003663 \cdot \tau).$$

On the other hand, if the volume is kept constant during the heating, the pressure increases. Boyle's law holds for any given temperature, and it therefore follows by combining these two equations that

$$P = p_0(1 + 0.003663\tau).$$

If both pressure and volume vary, we obtain for the product at the temperature τ° C.

$$p \cdot v = p_0 \cdot v_0 (1 + 0.003663\tau).$$

This equation holds on the supposition that a gas exerts no pressure at the absolute zero, and affords a means of calculating this temperature. The value thus found is -273° C. If T represents the absolute temperature $(=273+\tau)$ (cf. p. 10) we obtain the equation

$$pv = \frac{p_0 v_0}{273} T.$$

3. From section 1 it is seen that each gram of a gas exerts a pressure on the walls of the containing vessel as though it were present alone. This applies also to a mixture of two or more different gases, and the pressure of a gas mixture is therefore equal to the sum of the pressure which each gas would exert by itself. This single pressure of each gas which goes to make up the total is called the partial pressure of the gas in question.

ILLUSTRATION: The pressure of the atmosphere at sea-level under normal conditions is 760 mm. of mercury, and this is made up of the partial pressures due to nitrogen, oxygen, carbon dioxide, water-vapor, and the rare gases. Air contains about 79.2% nitrogen, 20.8% oxygen, and about 0.04% carbon dioxide. The partial pressure of nitrogen is therefore $760 \frac{79.2}{100}$ mm. of mercury, and that of oxygen $760 \frac{20.8}{100}$ mm.

4. When gases combine to form a chemical compound the volumes which react are either equal or stand in a simple numerical proportion to one another, and the

same is true of the resulting product if it remains in the gaseous form. These facts form the basis of *Avogadro's Hypothesis* (1811), which states *that under the same conditions of temperature and pressure the unit volume of all gases contains the same number of molecules.*[*]

ILLUSTRATION: 2 grs. of hydrogen, 32 grs. oxygen, 44 grs. carbon dioxide, 28 grs. nitrogen always occupy the same volume when the temperature and pressure of each has the same value. At atmospheric pressure and 0° C. this volume is 22.42 litres. Or if a mol of any gas at 0° C. is confined in the volume of 1 litre, it exerts a pressure of 22.42 atmospheres on the containing walls. The equation of section 2, therefore, when applied to 1 mol, becomes

$$p \cdot v = \frac{p_0 v_0}{273} T = \frac{22.42}{273} T = 0.0821 T \text{ litre atmospheres.}$$

This factor 0.0821 which is the same for all gases is a very important one. It is called the "gas constant" and is denoted by the letter R. If we consider n mols instead of one the equation is of course

$$pv = nRT.$$

ILLUSTRATION: The average volume of 1 mol of the different gases at 0° C. and 1 atmosphere pressure has been found to be 22.42 litres. Atmospheric nitrogen gave a somewhat different value, 22.34. This led to an investigation into the purity of atmospheric nitrogen and resulted in the discovery of argon and the other rare gases.

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[*] A mol or gram-molecule is that number of grams of a substance which is equal to the molecular weight. 1 mol of Zn = 65.4 grs. Zn. 1 mol $Cl_2 = 35.45 + 35.45$ grs. = 70.9 grs. chlorine. 1 mol $CuSO_4 =$ $63.6 + 32 \times 64$ grs. = 158.6 grs. $CuSO_4$, etc.

To calculate the work obtainable from an expanding gas one must remember that work = pressure × change in volume, provided during the process the pressure does not change. If the volume is kept constant and the pressure changes, the work is = volume × pressure change.

If we let a gas under constant pressure and temperature expand from the volume v_1 to volume v_2 the work obtained is

$$A = p(v_2 - v_1).$$

Or if a quantity of gas at constant temperature and constant volume has its pressure raised from p_1 to p_2 then

$$A = v(p_2 - p_1).$$

ILLUSTRATION 1. Let us consider a cylinder whose cross-section is one square decimetre and whose height is about 3 metres, at the bottom of which is 1 mol = 18 grs. of water. Suppose the water is converted into vapor at 0° and under the atmospheric pressure. Neglecting the volume of the liquid water (0.018 litre) and remembering that at 0° and atmospheric pressure 1 mol of every gas occupies the volume of 22.42 litres, we find that the weight of the atmosphere above the cylinder is raised through a distance of 22.42 decimetres. Since the work which is necessary to overcome the pressure of 1 atmosphere through the volume of 1 litre is 1 litre-atmosphere, we find the work on evaporation

$$A = 22.42 \text{ litre-atmospheres.}$$

If n mols are evaporated the work is of course $n \cdot 22.42$ litre-atm. = $n \cdot 231.60$ kg.-metres, or 542.34 calories (cf. Table 5).

ILLUSTRATION 2. If we decompose by electrolysis 1 gr.-molecule of water, we obtain 2 grs. of hydrogen and 16 grs. of oxygen = 1 mol hydrogen + $\frac{1}{2}$ mol oxygen; these occupy under standard conditions 33.63 litres, That is, in order to liberate the gas into the atmosphere we have done 33.63 litre-atmospheres of work, aside from the chemical work necessary to decompose the water. This consideration frequently enters into the calculation of the work necessary in such reactions where a gas is evolved or absorbed. If we let the hydrogen and oxygen again combine, the volume decreases by 33.43 litres; i.e., the atmosphere in this case does 33.43 litre-atmospheres of work, which we can obtain as electrical work by using a gas-battery.

In general it will not be true that the volume alone or the pressure alone varies. If we have a quantity of gas and increase its volume at a constant temperature, the pressure falls off at the same time according to the equation $pv = \text{constant}$. To calculate the work we need the help of differential calculus, and find the following result: When a mol of a gas expands from v_1 to v_2 the work obtainable is *

$$A = RTln\frac{v_2}{v_1}.$$

Osmotic Pressure and Osmotic Work.

It has been shown by van't Hoff that the gas laws mentioned above also apply to substances in dilute solutions.

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* *Ln* is the symbol of the "natural logarithm." To change it to the Briggs or common logarithm it must be multiplied by 0.4343. The derivation of the above equation is here given for the benefit of those

The pressure of a gas is to be looked upon as its endeavor to expand. Gases expand as far as they can, i.e., they distribute themselves through the whole of the volume at their disposal if there is a medium present through which they can pass. Such a medium is the vacuum or any space filled with other gases. When their expansion is hindered by a medium through which they cannot pass, such as an air-tight wall, they exert on this wall a pressure.

All other substances behave in this respect similar to gases. All have the tendency to distribute themselves as much as possible, but can only do so in a suitable medium. Water is a suitable medium for cane-sugar. Sugar tries to distribute itself in this medium to the greatest possible degree, i.e., it dissolves in water. If a layer of pure water is carefully put over a solution of

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who have studied calculus. When the gas expands from v to the volume $v+dv$, the pressure decreases from p to $p-dp$; the work obtained, dA therefore lies between pdv and $(p-dp)dv$. In comparison with p, dp is infinitely small and can therefore be neglected; i.e.,

$$dA = pdv.$$

If we insert the value of p which is obtainable from $p \cdot v = RT$ in this equation we obtain

$$dA = RT\frac{dv}{v}.$$

This, integrated between the values v_1 and v_2, gives

$$A = RTln\frac{v_2}{v_1}.$$

Since $v_2 : v_1 = p_1 : p_2$, the equation can also be written

$$A = RTln\frac{p_1}{p_2}.$$

If n mols of gas are used, the equation is

$$A = nRTln\frac{v_2}{v_1}.$$

sugar, the sugar has an opportunity for further expansion, and it accordingly diffuses upwards against the force of gravity till the concentration at all points is the same. If the two layers are separated by a wall which is permeable to water but not to the sugar molecules, the process is reversed, the sugar no longer diffuses upwards, but draws water through the wall to itself. If the vessel containing the solution is closed on all sides, very little water can enter, since a hydrostatic pressure is soon developed which prevents the further entrance of water. This tendency to expand has therefore the nature of a pressure, and is called the osmotic pressure of the sugar solution. The relation between osmotic and gas pressure is clear when we remember that the gas corresponds to the dissolved sugar and the solvent (water) to the vacuum.

If we avoid the development of hydrostatic pressure, by allowing the containing vessel to give way, the solution actually draws in a great quantity of water.

To test this conclusion experimentally we require a substance which is permeable to water but impermeable to the dissolved sugar molecules. A diaphragm built of such a substance is called "semi-permeable."

We will first go over the history of our knowledge concerning osmotic pressure and at the same time become acquainted with many terms and laws which will be met later on.

It is well known that plant cells which have become dry and need water can take up water when they are put in contact with it, without losing any of the cell contents. The walls of plant cells are therefore semi-permeable membranes. The first investigations on the osmotic pressure of the solution in plant cells were made by physiologists. The cells were placed in salt solutions, and it was found that salt solutions of a particular concentration were in equilibrium with the cells, i.e., the cells neither expanded nor contracted. If they were put in a more dilute solution, they took up water and expanded; put in a more concentrated solution they gave off water and became smaller. Solutions which were in equilibrium with the cells were called "isotonic" or "isosmotic" solutions. It was discovered that solutions of similar salts were isotonic when they had the same molecular concentration; * for instance, normal solution of KNO_3, $NaNO_3$, KCl, NaCl are approximately isotonic.

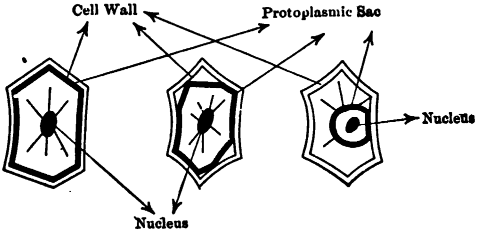

FIG. 1.

As Fig. 1 shows, the cells are surrounded by a cell wall which is permeable to solutions as well as water; within this is the protoplasmic sac which is permeable to water but not to the salts dissolved in the cell solution. The cell solution is called the "protoplast," and the process of expansion or contraction is called "plasmolysis." A fact was further discovered which was later explained by the theory of electrolytic dissociation, namely, that

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* Measured in mols per litre. Cf. remark on p. 18.

dilute solutions of the above-mentioned inorganic salts have an osmotic pressure which is practically twice as great as solutions containing an amount of organic substances—urea, sugar, etc.—equal in molecular concentration to that of the inorganic salts. It should be mentioned here that the osmotic pressures were later measured in atmospheres and that the ordinary plant cells which contain dissolved glucose, malates of calcium and potassium, sodium chloride, etc., have an osmotic pressure of about 4 to 5 atmospheres. Certain cells used for storage purposes in plants such as the sugar-beet have a pressure of 15 to 20 atmospheres. In young plants the pressure is still higher. The cells of bacteria have an especially high osmotic pressure, which fact may perhaps explain their great physiological action.

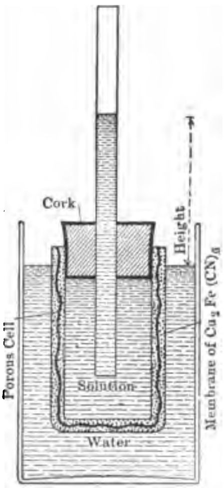

FIG. 2.

Plant cells could only be used in making comparative measurements; in order to measure the pressure directly in atmospheres, it was necessary to construct an artificial protoplasmic sac, i.e., a semi-permeable membrane. A membrane composed of copper ferrocyanide is impermeable to sugar and most salts, but readily permeable to H_2O. Traube made such a membrane by putting a solution of $K_4Fe(CN)_6$ in a carefully cleaned porous cell and placing the cell in a dilute solution of $CuSO_4$. The two substances diffuse toward each other in the cell wall and form, on meeting, a precipitate of $Cu_2Fe(CN)_6$, thus making a durable semi-permeable wall. Using this cell, measurements were made as follows (cf. Fig. 2). A sugar solution was put in the cell; the open end was closed by a rubber cork, through which passed a long glass tube, and the whole was placed in pure water. The osmotic pressure of the sugar in solution causes water to be drawn in through the walls of the cell till the hydrostatic pressure of the column of water in the upright tube is as great as this drawing force, i.e., as great as the osmotic pressure of the solution. The hydrostatic pressure is easily calculated from the specific gravity of the solution and the height of the water column in the tube.

An experiment made by Ramsay at the suggestion of Arrhenius affords a striking comparison of osmotic pressure with the action of gases. He made an air-tight cell the bottom of which consisted of a thin sheet of Pt, attached a manometer, filled the cell with nitrogen, and placed the whole in an atmosphere of hydrogen. Platinum is impermeable to nitrogen but permeable to hydrogen, consequently hydrogen is drawn into the cell just as H_2O is drawn through the copper ferrocyanide membrane, and the increase of pressure can be read off on the manometer.

The first quantitative osmotic measurements were made by the physiologist Pfeffer. He measured the osmotic pressure of sugar solutions of various concentrations and obtained the following table.

Concentration of sugar in grams per 100 c.c.	1	2	2.74	4	6
Pressure in atmospheres. . . .	0.704	1.34	1.97	2.75	4.06
Pressure per gram of sugar .	0.704	0.67	0.72	0.69	0.68

From these figures it is clear that the pressure is proportional to the percentage of sugar in the solution, or inversely proportional to the volume which contains a gram of sugar in solution $p=\frac{\text{Constant}}{v}$; $p\cdot v=\text{Constant}$, which is the expression of Boyle's law.

Pfeffer found further that the osmotic pressure rises with a rise in temperature, as the following table shows.

t	Pressure		Difference
	Observed	Calculated	
6.8	0.664 atmosphere	0.665 atmosphere	+0.001
13.7	0.691 "	0.681 "	−0.010
14.2	0.671 "	0.682 "	+0.011
15.5	0.684 "	0.686 "	+0.002
22.0	0.721 "	0.701 "	−0.020
32.0	0.716 "	0.725 "	+0.009
36.0	0.746 "	0.735 "	−0.011

The calculated pressures in the third column were obtained from the value for a 1% solution, according to the equation

$$p=0.649(1+0.00367\tau)\text{ atm.};$$

for an *n*% solution,

$$p=n\cdot 0.649(1+0.00367\tau).$$

At 13.7° C. the pressure of a 4% solution was 2.74 atmospheres, while the formula gives 2.73. If we calculate from this the value of the osmotic pressure for 1 gram-molecule of sugar = 342 grs. in 1 litre we obtain the equation

$$p\cdot v=0.0823T \text{ (Gay-Lussac's law)},$$

where *p* is the osmotic pressure in atmospheres, *v* the volume in litres, and *T* the absolute temperature. Gay-Lussac's law, therefore, holds for the osmotic pressure of sugar; that is, the sugar exerts the same osmotic pressure as it would exert gaseous pressure if the H_2O were absent and the sugar in the form of a gas.

We will now describe a few experiments which strikingly illustrate the action of osmotic pressure and at the same time form a transition to considerations on the relation between osmotic pressure and the freezing- or boiling-points of solutions.

1. When a crystal of $FeCl_3$ is thrown into a dilute solution of $K_4Fe(CN)_6$ a membrane of Prussian blue is formed on the outside of the crystal. Inside this membrane the concentration of $FeCl_3$ is very high, and water is drawn in from the outer solution, and the membrane is extended till it can no longer stand the pressure from within. It breaks at some point and concentrated solution from within bursts out. A fresh membrane is at once formed around this and the process is repeated so that a tree-like structure of Prussian blue gradually grows up from the crystal.

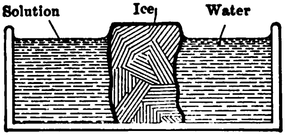

FIG. 3.

2. If a wall of ice is placed in a rectangular vessel (Fig. 3) in one side of which is water and in the other a solution, the ice wall will appear to move toward the

side where the water is, because on the one side ice melts in contact with the solution, while water crystallizes out on the other side. This ice wall is in a way a semi-permeable wall which is permeable to water. (An important point in calculating the depression of the freezing-point.)

3. The atmosphere can also be considered as a semi-permeable medium. If two beakers, one of which contains a sugar solution and the other water, are placed in a confined space, it will be found that water distils over from the second to the first. The atmosphere can be considered in this case as a wall permeable to water but not to sugar molecules. (Important in calculating the elevation of the boiling-point.)

4. The so-called "Schlierenapparat" of Tammann is an arrangement for observing the concentration changes on a semi-permeable wall. If a drop of a concentrated solution of K_4FeCy_6 is carefully brought into a dilute solution of $CuSO_4$ by means of a pipette, a membrane of Cu_2FeCy_2 is at once formed around the drop. Water will be drawn in through the membrane on account of the higher osmotic pressure of the salt inside, and as a result the $CuSO_4$ solution in the immediate vicinity of the drop becomes more concentrated and this heavier solution can be seen falling in a stream away from the drop. If no descending streams are observed, the two solutions are isotonic.*

We have seen (p. 27) that the gas laws hold for dilute solutions. Just as gases can do work on expanding,

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* For further methods of measuring osmotic pressure, as well as freezing- and boiling-point changes, see any of the larger text-books of physical chemistry, as Nernst, p. 132 ff.

so a dilute solution can be made to perform work when it is being further diluted, since dilution is nothing more than the distribution of the dissolved substance through a greater volume, i.e., expansion. If v is the volume in which n gram-molecules of a simple substance, for instance cane-sugar, are dissolved, and if the osmotic pressure of these molecules is lowered by dilution from p_1 to p_2, the work which may be obtained is (cf. p. 20)

$$A = nRTln\frac{p_1}{p_2},$$

or, since osmotic pressure and concentration are directly proportional,

$$A = nRTln\frac{c_1}{c_2},$$

or, finally, since the osmotic pressure varies inversely as the dilution,

$$\left(\text{Dilution} = \text{volume per gram-molecule} = \frac{1}{\text{concentration}}\right).$$

$$A = nRTln\frac{v_2}{v_1}.$$

With the help of this equation it is possible in most cases to calculate the work obtainable from chemical reactions.

Calculation of Chemical Work from Osmotic Pressure. van't Hoff's Equation.

We will take a reaction of the form

$$mA + nB = oC + qD;$$

i.e., a reaction in which m mols of the substance A unite with n mols of thesubstance B, forming o mols of the substance *C* and *q* mols of *D*. For instance in the reaction

$$4SbCl_3 + 5H_2O = Sb_4O_5Cl_2 + 10HCl,$$

$m=4$, $n=5$, $o=1$, and $q=10$. Further, let the small italic and Greek letters represent the concentrations before and after the reaction and we have the following scheme:

	Disappearing Substances.		Resulting Substances.	
	A.	B.	C.	D.
Concentration before reaction. . .	a	b	c	d
Concentration after reaction.	α	β	γ	δ
Number of reacting molecules. . . .	m	n	o	q

As the reaction goes on, the concentration of both *A* and *B* sinks. Lowering of a concentration or pressure can do work. For the substance *A* this work is

$$A_A = mRTln\frac{a}{\alpha},$$

for *B* it is

$$A_B = nRTln\frac{b}{\beta}.$$

The concentrations of *C* and *D* are increased by the progress of the reaction. The work to be gained from this cause is negative, i.e., to increase their concentration requires work; consequently

$$A_C = -oRTln\frac{c}{\gamma} = oRTln\frac{\gamma}{c},$$

$$A_D = -qRTln\frac{d}{\delta} = qRTln\frac{\delta}{d}.$$

The total work of the reaction is therefore

$$A = A_A + A_B + A_C + A_D = RTln\frac{a^m b^n \gamma^o \delta^q}{c^o d^q \alpha^m \beta^n}.$$

This is the so-called "energy equation" of van't Hoff. This equation becomes still simpler when we introduce the laws of mass action. When the reaction goes to completion, i.e., till equilibrium between all the reacting substances prevails (cf. following chapter), and $K = \frac{\gamma^o \delta^q}{\alpha^m \beta^n}$ represents the equilibrium constant, then

$$A = RTlnK + RTln\frac{\text{Product of active masses* of disappearing substances}}{\text{Product of active masses of resulting substances}}.$$

When all the substances have the same concentration at the start, then

$$A = RTlnK.$$

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* In this equation by "active mass" of a substance is meant the concentration of the same raised to a power represented by the number of molecules with which it enters into the reaction.

CHAPTER II.

CHEMICAL EQUILIBRIUM, STATICS, AND KINETICS.

THE first equation on page 31 gives the work of a reaction when it is interrupted at a particular point where the concentrations are α, β, γ, δ. We will now consider the far more important question, how much work a reaction can afford when we let it go on till it stops of itself. We have a fundamental distinction to make between the so-called complete and incomplete reactions.

An example of a complete reaction is the conversion of water into steam at atmospheric pressure and temperatures above 100°, when the water "phase" completely disappears.

The freezing of water below 0° is likewise a complete reaction. Water is turned completely into ice, there is no unfrozen remainder.

The evaporation of water at temperatures below 100° and at atmospheric pressure is an example of an incomplete reaction. In this case water will evaporate till the partial pressure (cf. p. 17) of the water-vapor attains a value which is just the same as the vapor pressure of water at the temperature which prevails. When such a concentration of the water-vapor is attained just as much water evaporates as is formed by condensation of the vapor, i.e., visible evaporation has stopped. We say the liquid water is in equilibrium with water-vapor at the corresponding vapor pressure. If too little water is present, it will of course evaporate completely.

A classical example of an incomplete reaction is the "ester formation." When one mol each of alcohol and acetic acid are brought together they unite to form ethyl acetate and water, but the reaction is not complete; it stops when ⅔ mol of ester and ⅔ mol of water have been formed and ⅓ mol of alcohol and ⅓ mol of acid remain unaltered. The reaction has reached equilibrium when the concentrations have attained these values.

We will have to do principally with the incomplete reactions. It was formerly thought that such reactions were exceptional, because the end concentrations were too small to be measured chemically. For instance, before Davy's time certain substances were considered absolutely insoluble. It was believed that when solutions of barium chloride and sulphuric acid were mixed, barium sulphate was absolutely removed from the solution. According to this idea such a reaction would be complete. In reality there is no such thing as an absolutely insoluble substance, although in many cases the solubility is so small that chemical methods are unable to measure it. The precipitation of substances is in reality an incomplete reaction. It was formerly thought that when zinc in excess was put in a solution of copper sulphate absolutely all the copper was precipitated out of the solution. But this is not the case, the reaction goes on till the concentration of the copper salt is 10^{-40}. Of course it is out of the question to even demonstrate by chemical means the presence of copper in such a dilute solution, but certain electrochemical methods enable us to approximately measure such low concentrations. All such reactions in which one metal is precipitated by another are incomplete. They are also reversible. We saw above that alcohol and acetic acid unite to form ethyl acetate and water. When we dissolve a mol of ethyl acetate in 1 mol of water the reverse reaction occurs, i.e., alcohol and acetic acid are formed. But this reaction is also incomplete, and will come to the same state of equilibrium as the first, i.e., will stop when $\frac{1}{3}$ mol of ethyl acetate has been converted into acid and alcohol.

Such reactions which can occur in either direction are denoted by two arrows in place of the equality sign:

$$C_2H_5OH + CH_3COOH \rightleftarrows CH_3COOC_2H_5 + H_2O.$$

We have defined an incomplete reaction as one which ceases of itself when equilibrium is reached. This definition requires some modification: when equilibrium is reached the reaction does not actually cease, but the two reactions, from left to right and the reverse, both go on with the same velocity, so that although a continual reaction is going on the composition of the equilibrium mixture remains constant. We must likewise assume a similar condition of affairs before equilibrium is reached. Both reactions take place, but the velocity in one direction is much greater than in the other, so that this determines the direction of the total reaction which we observe.

Keeping in mind these considerations we will have little difficulty in understanding the very important *law of mass action.*

Let us take the reaction of page 29,

$$mA + nB = oC + qD,$$

in which the concentrations of A, B, C, D are represented by a, b, c, d respectively. The kinetic theory * and also practical experience teach that the reaction from left to right can be expressed by the equation

$$v_1 = k_1 a^m b^n,$$

i.e., is proportional to the product of the active masses of the reacting substances. In the same way the velocity of the reverse reaction can be expressed:

$$v_2 = k_2 c^o d^q.$$

But the actual apparent velocity is the difference between these two single velocities:

$$V = v_1 - v_2 = k_1 a^m b^n - k_2 c^o d^q.$$

This is the *law of chemical kinetics.*

When equilibrium is attained $v_1 = v_2$ and the total velocity V becomes 0. Consequently when the equilibrium concentrations are $\alpha, \beta, \gamma, \delta$,

$$k_1 \alpha^m \beta^n = k_2 \gamma^o \delta^q.$$

If $\frac{k_2}{k_1} = K$ represents the equilibrium constant of the reaction, then

$$K = \frac{\alpha^m \beta^n}{\gamma^o \delta^q}.$$

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* The kinetic theory assumes that the molecules of all substances are in a continual state of motion; a reaction can only occur when two or more molecules collide. See Nernst, Theoretische Chemie, 1903, p. 427.

This is the *law of chemical statics.* It states that for every incomplete reaction there exists a state of equilibrium when the reaction ceases of itself, and this condition is regulated by the active masses * of the disappearing substances and of those being produced. The equilibrium constant remains the same no matter what the concentrations of the reacting substances were at the start. For instance, in the reaction

$$CH_3COOH + C_2H_5OH \rightleftarrows CH_3COOC_2H_5 + H_2O$$

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* We must explain the conception of "active mass" somewhat more definitely. By the active mass of a substance is meant its volume concentration; in the case of a solution it is the ordinary molecular concentration (gr.-mols per litre). In the formulæ of the law of mass action, the energy equation, etc., the active mass of each molecule which takes part in the reaction is used; the concentration a of the substance A, for instance, appears m times since m molecules of A take part in the reaction.

If a solvent takes part in a reaction, as for instance water in the ester formation or in hydrolysis, its active mass should also be introduced. In dilute solutions, however, the change in the active mass of water is so slight that for practical purposes it may be neglected, and its active mass be considered as a constant (in all such calculations the change in active mass is the important point rather than the absolute value itself). In very concentrated solutions the change in active mass of the solvent can no longer be neglected, but in most of the electrochemical reactions of importance, concentrated solutions play a minor part, and we may nearly always consider the active mass of the solvent as constant.

The active mass of a solid in contact with a solution in which the solid reacts is constant.

The active mass of a metal in a galvanic cell, or of a soluble substance in excess in a solution saturated with respect to this substance, is constant, for as soon as any more of the substance is formed or used up the concentration of saturation is at once reproduced by further precipitation or solution of the solid, and the active mass remains unchanged.

if we start with 1 gr.-mol each of acid and alcohol, equilibrium is reached when $\frac{1}{3}$ mol of acid and alcohol is left and $\frac{2}{3}$ mol of ester and water are formed. K is therefore

$$K=\frac{\frac{1}{3}\times\frac{1}{3}}{\frac{2}{3}\times\frac{2}{3}}=\frac{1}{4}.$$

If instead of taking one mol each, to start with, we take any concentration we please, the reaction will go on in any case till the ratio of the concentrations is $\frac{1}{4}$. For instance, if we take 2 mols of acid to 1 of alcohol, there will of course be more than $\frac{1}{3}$ mol of acid left over. If x represents the amount of acid and alcohol which has been used up when equilibrium is reached the quantity of ester and water formed is also x.

In equilibrium, then, we have $2-x$ mols acetic acid, $1-x$ mol alcohol, and x mol each of ester and water,

then $\frac{(2-x)(1-x)}{x^2}=K=\frac{1}{4}$. From this quadratic equation

we can calculate x, and then know how far the reaction has gone.

Another classical example is the formation of hydriodic acid from iodine vapor and hydrogen, according to the reaction $H_2+I_2\rightleftarrows 2HI$. Here we can use instead of the concentration the partial pressures of each gas, which are directly proportional to the concentration. If P with the corresponding indices represents each particular partial pressure, then

$$\frac{P_{\mathrm{H}}\times P_{\mathrm{I}}}{P^2_{\mathrm{HI}}}=K.$$

A further example is the reaction

$$P\,Cl_5 \rightleftarrows P\,Cl_3 + Cl_2$$

and

$$K = \frac{p_{P\,Cl_3} \times p_{Cl_2}}{p_{P\,Cl_5}}.$$

The last two equations have to do with the breaking up or "dissociation" of gases. All cases of dissociation equilibrium whether in gases or in solution are calculated in a similar way.

A very important example is the dissociation of carbon dioxide. The union of carbon monoxide with oxygen is an incomplete reaction; thus, $2CO_2 \rightleftarrows O_2 + 2CO$, and the equilibrium conditions are given by $K \times P_1^2 = P_2 \times P_3^2$, where P_1, P_2, P_3 are the partial pressures of the three gases respectively. If the constant K has been determined at some particular temperature and pressure, the dissociation can be calculated by the above equation for any pressure at this particular temperature. The following table gives the percent to which carbon dioxide is dissociated into carbon monoxide and oxygen not only for different pressures but also for temperatures between 1000° and 4000°.

Temperature	Pressures in Atmospheres					
	0.001	0.01	0.1	1	10	100
1000	0.7	0.3	0.13	0.06	0.03	0.015
1500	7	3.5	1.7	0.8	0.4	0.2
2000	40	12.5	8	4	3	2.5
2500	81	60	40	19	9	4.0
3000	94	80	60	40	21	10
3500	96	85	70	53	32	15
4000	97	90	80	63	45	25

The table shows that at high temperatures it is impossible to burn carbon monoxide completely to the dioxide, and that for this reason we are unable to utilize at high temperatures the full energy of the combustion of carbon; we can see from the table about how far the combustion goes in different processes.

In the iron blast-furnace the temperature is about 2000° and the partial pressure of carbon dioxide is about 0.2 of an atmosphere. Under these conditions CO_2 is about 5% dissociated, and as a result the efficiency of the furnace is slightly impaired. In illuminating flames which also have a temperature of 2000° or more, the partial pressure of CO_2 is only about 0.1 of an atmosphere owing to the large quantity of hydrogen. The dissociation of CO_2 can then exceed 10%, and the temperature is correspondingly lower, while the illuminating power, which varies enormously with the temperature, is very appreciably decreased. In the case of explosives the temperature is probably between 2500° and 3000°, but here the pressure of CO_2 is several thousand atmospheres, and the dissociation very small, so that the combustion is practically perfect.

The law of mass action has been found to hold for a great number of reactions; for further details, reference is made to the text-books of theoretical and physical chemistry by Nernst, Ostwald, and others. As yet we have only considered reactions between substances which were in the same physical condition, i.e., in "homogeneous systems" when all were either liquid or gaseous. We will now consider the "heterogeneous" systems.

For the first illustration we will take the solution of a salt. If we bring solid salt in contact with water it dissolves:

$$NaCl_{solid} \rightleftarrows NaCl_{dissolved}.$$

The equilibrium equation is $K \cdot C_{solid} = C_{dissolved}$; but the solid salt does not change its concentration C_{solid} as solution goes on; its quantity may diminish but the remaining solid salt always keeps the same density or concentration. C_{solid} is therefore also a constant, and for equilibrium we have $K_1 = C_{dissolved}$. This equation, however, is nothing less than a statement that at equilibrium the concentration of the dissolved salt is constant, i.e., every salt has a constant solubility. What has been said for ordinary salt is true for all solid substances. They do not change their concentration as solids although they may lose in weight. This fact is expressed when we say the active mass of a solid substance is constant (cf. note, p. 36).

2. Another classical example is the dissociation of calcium carbonate: $CaCO_{3\,solid} \rightleftarrows CaO_{solid} + CO_{2\,gaseous}$. Here, too, we can include the active mass of the solid substances in the constant of equilibrium and obtain

$$K = p_{CO_2},$$

where p_{CO_2} is the pressure of the carbon dioxide, and is proportional to its concentration. This is simply a statement that the dissociation pressure of marble, i.e., the pressure with which it evolves CO_2, is a constant at constant temperature. The same remarks apply also to liquids. When liquid water evaporates, part of it disappears as such, but the density of the remaining water, i.e., its concentration (mols per litre), is not changed. We obtain in this case also

$$K = p_{H_2O};$$

in other words, the vapor pressure of water has at constant temperature a fixed value.

Change of Equilibrium with the Temperature.

In the previous considerations it has been understood that the temperature remains constant. If we consider a reaction at different temperatures, as for instance the formation of carbon dioxide (cf. table, p. 38), we

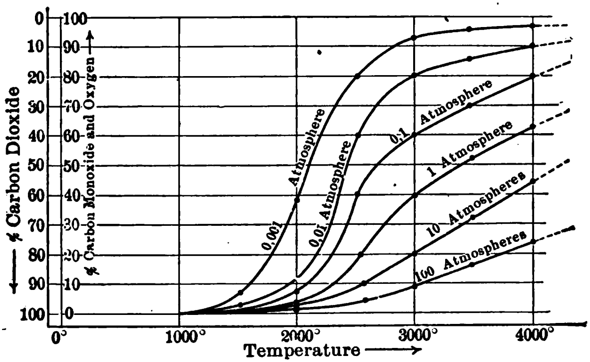

FIG. 4.

find that the equilibrium constants are different for each temperature. These facts are clearly shown by the accompanying curves (Fig. 4). The abscissæ represent temperatures, and the ordinates give the percentage to which carbon dioxide is dissociated. At low temperatures the combustion for all practical purposes is complete, and the gas mixture contains practically 100% CO_2. But the higher the temperature, the less complete is the combustion. At a temperature of 3000° when the pressure of CO_2 is one atmosphere the combustion is only 60% of the whole; the dissociation increases with increasing temperature, till finally at very high temperatures carbon monoxide and oxygen combine to a very slight extent. However, since this reaction, either at high or low temperature, is not absolutely complete, the curve which represents the relation between degree of combination and temperature can never actually touch the two horizontal lines representing 0% and 100% dissociation, but can only approach them asymptotically. This is best seen in the curve for 0.001 of an atmosphere. The relations which hold for this particular reaction are true for all incomplete reactions; similar curves can be obtained in all cases.

From what has been said it can be seen that the chemical facts with which we are acquainted are somewhat a matter of chance, since they are governed by the temperature and pressure which happen to prevail on our planet. We are accustomed to say that coal burns, uniting with oxygen to form carbon dioxide, and this is true for the comparatively low temperatures of our stoves or blast-furnaces. But if we lived on a body whose temperature like that of the sun is in the neighborhood of 10 000° our chemical text-books would say that carbon and oxygen do not combine. Carbon dioxide would be an unknown substance to an inhabitant of the sun, since at that temperature it is almost completely dissociated. Water is an unknown body on the sun, since the equilibrium of the reaction $2H_2+O_2 \rightleftarrows 2H_2O$ at the sun's temperature lies at a point where the concentration of the water is immeasurably small. We consider a mixture of hydrogen and oxygen unstable, but an inhabitant of the sun would consider water an exceedingly unstable compound if he could ever succeed in obtaining it.

Our experimental chemistry is the chemistry of the earth; we cannot write a "chemistry of the universe" until we know the equilibrium constants of all reactions at all temperatures. For since all reactions proceed toward the point of equilibrium we could then know the direction in which any reaction would go at any temperature.

We are indebted to J. H. van't Hoff, the master of the science of physical chemistry, for the method of solving this important problem. An expression derived by him and known as "van't Hoff's Equation" gives the relation between the equilibrium constant, the heat of reaction, and the temperature. This expression, obtained by integrating a differential equation,* is:

$$lnK_2 - lnK_1 = \frac{q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

In this equation T_1 and T_2 are two absolute temperatures, K_1 and K_2 the equilibrium constants of the given reaction at these temperatures, *ln* represents the "natural log" (see p. 20, note), R is the gas constant 1.991 cal. (see table on p. 5), and q is the "heat of reaction" (see p. 8). If we know the last-named value and determine the equilibrium constant for any particular temperature we can calculate the equilibrium for any other temperature. The table on page 38 has been calculated in this

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* The equation is derived from the second law of thermodynamics (p. 9) and the energy equation (p. 31). By combining them the differential equation $\frac{dlnK}{dT} = \frac{-q}{RT^2}$ is obtained.

way, since it is experimentally impracticable to measure the equilibrium at a temperature of 4000°.

On the other hand, if we know the equilibrium constant of a reaction at two different temperatures we can calculate the "heat of reaction." The equilibrium constant of the reaction where a solid substance dissolves in water is equal to the concentration at saturation (see p. 40). If $c_1 = 2.88$ and $c_2 = 4.22$ are the solubilities of succinic acid at 0° C. (=273) and 8.5° C. (=281.5), then

$$lnc_1 - lnc_2 = \frac{q}{2}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

From this equation we can calculate q_1 and find the value −6900 cal. The reaction mixture cools itself off, since q is negative. Berthelot found experimentally −6700 cal. as the heat of solution, in very good agreement with the calculated value.

CHAPTER III.

THEORY OF ELECTROLYTIC DISSOCIATION.

A NUMBER of experimental facts which we will mention later on has led to the supposition that in the water solution of a salt only a certain fraction of the salt plays a part in electrochemical processes. This active part varies with the nature of the salt, the temperature, the dilution, and the nature of the solvent. (Solutions in solvents other than water have not as yet been systematically investigated.) The rest of the salt remains inactive and has nothing to do in transporting the electric current. For instance, if we measure the conductivity of a sodium-chloride solution, we find that all the salt does not take part in conducting the current, but only a fraction; in the case of a normal solution of NaCl this active part is ⅔ of the whole; in a normal solution of $AgNO_3$ it is only 58%. It is this same fraction which is active in influencing the electromotive force of an electrode; for instance, in a normal $AgNO_3$ solution it is 58% of the total salt present. Of every 100 molecules in the above NaCl solution 67 are in a condition different from the remaining 33, and the same is true of the 58 molecules in every 100 in the $AgNO_3$ solution. This active part of the whole is found from the conductivity and measurement of electromotive forces, and also from measurements of the osmotic pressure and changes in the freezing- and boiling-points of the solutions, and all these methods give practically the same values.

The chemical conduct of dissolved salts seems to indicate that these 67 or 58 molecules are just the ones which enter into chemical reactions. In cases where no molecules are present which can transport the current, or if they are present in very small amounts, chemical reactions do not take place, or if they do, are extremely slow. A salt on dissolving in water must therefore suffer some change, and the physical conduct of solutions shows that the change is very profound.

Like all soluble substances, a dissolved salt depresses the freezing-point of water and raises the boiling-point. When 1 gr.-mol of a substance like urea, or boric acid, or sugar, which does not conduct the current, is dissolved in 1 litre of water, the freezing-point of the solution is $-1.86°$. 1.86 is called the "molecular lowering of the freezing-point" of water. If, however, we take a solution of 1 gr.-mol of a salt in 1 litre, which does conduct the current, we find that the freezing-point is lowered more than 1.86°. It seems as though that part of the salt which does not take part in the conductivity acts normally in lowering the freezing-point, but the rest which is the active agent in conducting the current acts as though its component radicals had parted company and were each existing separately in the solution. For instance, in a normal solution of NaCl, 33% of the salt affects the freezing-point as cane-sugar would, lowering it $1.86 \times 0.33 = 0.614°$; but the remaining 67% acts as though it had broken up into Na and Cl atoms and thus affects the freezing-point twice as much as an equal molecular quantity of sugar would do, so that the lowering from this cause is $2 \times 67 \times 1.86 = 2.49$. The total lowering is therefore $2.49 + 0.614 = 3.104°$ instead of 1.86°. In a normal $AgNO_3$ solution 42% has the usual effect, but the rest has twice the normal effect, as if this part of the $AgNO_3$ had broken up into Ag and NO_3 radicals. In a $\frac{N}{10}$ solution of H_2SO_4 about 75% of the acid takes part in conduction. The remaining 25% acts as usual in depressing the freezing-point, but the 75% has triple the usual effect, as though it had broken up into $H + H + SO_4$. The 0.1 normal acid acts therefore in regard to its conductivity as though it were 0.075 normal, but with respect to its freezing-point as if it were 0.25 normal.

The relations which hold for the lowering of the freezing-point are true also of the rise of the boiling-point or lowering of the vapor pressure. A gram-molecule of any non-conducting substance when dissolved in 1 litre of water raises the boiling-point a certain fixed amount, no matter what the substance is, provided only that it gives a non-conducting solution. But a 0.1 normal solution of H_2SO_4 raises the boiling-point as though 75% of the acid had decomposed with the formation of three new substances, i.e., as though the solution were 0.25 normal.

The osmotic pressure is affected in just the same way. On p. 26 we saw that a normal solution of cane-sugar exerted an osmotic pressure of 22.42 atmospheres. A normal solution of other non-conducting substances has the same value, but a conducting salt solution has a much higher osmotic pressure. The ratio of this higher pressure to 22.42 is the same as the ratio of the abnormal to the normal lowering of the freezing-point. Here again the conducting molecules act as though they had broken up into their component radicals.

These facts, as well as many others of a physical and chemical nature, leave little room for doubt that a decomposition or "electrolytic dissociation" actually takes place when a salt is dissolved in water, and that only the dissociated atoms or molecules (known as "ions") are the active agents in conducting the electric current or determining the electromotive force of an electrode. The percentage of the salt which undergoes decomposition is called the "degree of dissociation."

Aside from the fact that many chemical reactions can only be explained on this supposition, the theory of electrolytic dissociation finds its principal support in the fact that all the different methods give concordant results for the degree of dissociation. At the present time it is impossible for the electrochemist to do without the theory of electrolytic dissociation.

To illustrate these facts we give the following table of measurements. The numbers state how many molecules are formed from one molecule of the dissolved salt as the result of electrolytic dissociation.

The question now comes up: "What is the nature of this separation?" It cannot be an ordinary separation, since the union of atoms in forming a compound is generally accompanied by a great production of energy. On decomposition this energy would have to appear again, which is apparently not true in this case. It seems, therefore, that the chemical affinity which has brought about the union of the atoms has been compensated for in some way so that the atoms are at liberty to separate,

DEGREE OF DISSOCIATION AS DETERMINED BY OSMOTIC AND ELECTRICAL METHODS.

Salts	Concentration	Degree of Dissociation		
		Osmotic	Freezing-point	Conductivity
KCl	0.14	1.81	——	1.86
NH_4Cl	0.148	1.82	——	1.89
$Ca(NO_3)_2$	0.18	2.48	2.47	2.46
$K_4Fe(CN)_6$	0.356	3.09	——	3.07
$MgSO_4$	0.38	1.25	1.20	1.35
LiCl	0.13	1.92	1.94	1.84
$SrCl_2$	0.18	2.69	2.52	2.51
$MgCl_2$	0.19	2.79	2.68	2.48
$CaCl_2$	0.184	2.78	2.67	2.42
$CuCl_2$	0.188	——	2.56	2.41
$Na_6C_{12}O_{12}$	0.0018	——	5.92	——

Because of the electromotive effects and the conductivity we assume that the chemical affinity has been changed to an electrical affinity, in that the atoms take on charges of positive and negative electricity. The neutral compound dissociates into positively and negatively charged atoms or radicals, which are known as "ions."

In what follows we will review briefly the history of the theory, and at the same time explain the different conceptions which have been introduced.

History of Electrochemistry. The Theory of Electrolytic Dissociation and its Foundations.

In order to understand the foundation of the theory and its advantages—a theory which at present is an indispensable part of theoretical chemistry—we will follow its development historically. We will not, however, confine ourselves strictly to the history of the theory of electrolytic dissociation, but will also take up that of electrochemistry in general and use this opportunity to learn some of the important laws of electrochemistry.

The dissociation theory has met with more opposition than most theories of a purely hypothetical nature, probably because at first sight it seems to clash with our "chemical sense." But is not the atomic theory—that matter is divisible until the final indivisible particles known as atoms are reached—still more antagonistic to our "chemical sense"? And yet we find ourselves quite at ease where the atomic theory is concerned. Possibly the reason for this is that the physical and mathematical knowledge required for the comprehension of the dissociation theory is not necessary to an understanding of the atomic theory. We are probably justified in saying that most of the opponents of the theory of electrolytic dissociation refrain from accepting it on grounds of conservatism—which is simply another name for inertia—while others oppose it as they do the atomic theory, because they are unwilling to accept anything which they have not seen or tested by experiment.

The dissociation theory had its beginning a long time ago. Nicholson and Carlysle[*] found, and Davy[†] confirmed the facts accurately, that solutions which conduct do not remain unchanged by the passage of the current, as the metals do, but are decomposed; that is, the chemical affinity which has brought about the union of the elements in the salt is simply overcome by the action of electricity.

The fact that the products of the decomposition are

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[*] Nicholson, Journ. of Nat. Phil., 4, 179 (1800).

[†] Gilbert's Ann., **7**, 114, **28**, 1 and 161 (1808).

attracted to the electrodes, where they are deposited, proves that they were already electrically charged before deposition, as otherwise there would be no attraction; and further, the elements which move toward the negative electrode must be charged positively and those which go to the positive electrode must be negatively charged.

Fig. 5 is a facsimile of one of Faraday's drawings in which he has written the terms now in common use. These words were made at his suggestion by the philologist Whewell. He called the negative "electrode" the "cathode," and this is the electrode toward which the "cations," or the metallic elements in the "electrolyte," move; the "anode" is the electrode toward which the "anions" move. The whole process was named "electrolysis."*

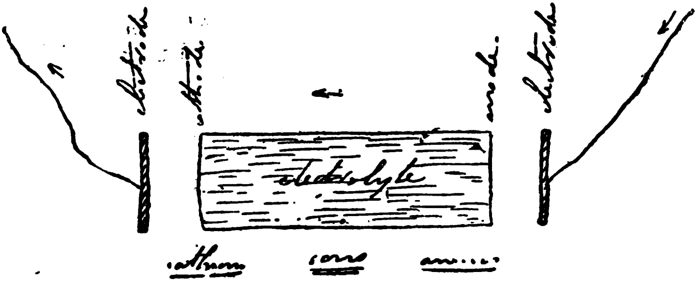

Fig. 5.

About 1833, Faraday discovered the law of equivalent deposition, now generally known as Faraday's law. He

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* Faraday's spelling of "cathion" is wrong. The word anode is derived from the Greek words ἀνά = up and ὁδός = road; cathode is from κατά = down and ὁδός (the *th* in this case comes from the aspirate in ὁδός). The word ion is from ἴεγαι = to go, and the corresponding words are cation and anion. Cation should have no *h*.

showed: 1st, that the amount of the electrolyte which is decomposed is proportional to the quantity of electricity which has passed through the solution; and 2d, that when the same current is passed through two different electrolytes the amounts of the different substances set free are chemically equivalent.

ILLUSTRATION: This law can be expressed as follows: Equal quantities of electricity precipitate equal quantities of all substances in electrolysis. By equal quantities of substances is meant not equal quantities in grams but in gram equivalents. A current of 1 ampere precipitates per second 0.01036 milligram equivalents of any substance; for instance (cf. table on p. 163):

$$107.93 \times 0.01036 = 1.118 \text{ mgr. of silver,}$$

or $$35.45 \times 0.01036 = 0.368 \text{ mgr. of chlorine,}$$

or $$127 \times 0.01036 = 1.316 \text{ mgr. of iodine,}$$

or $$(14.04 + 3 \times 16) \times 0.01036 = 0.643 \text{ mgr. of } NO_3.$$

In the case of substances whose valence is greater than 1 we must divide the atomic weight by the valence. One ampere-second deposits

$$\frac{63.6}{2} \times 0.01036 = 0.3294 \text{ mgr. of copper,}$$

or $$\frac{(32.06 + 4 \times 16)}{2} \times 0.01036 = 0.5 \text{ mgr. of } SO_4,$$

or $$\frac{27.1}{3} \times 0.01036 = 0.0935 \text{ mgr. of Al.}$$

Since the precipitation of metals or radicals is governed by the law of equivalents, it follows that equivalent quantities of different compounds are decomposed by one and the same quantity of electricity. Thus 1 ampere-second decomposes

$$\frac{2+16}{2}\times 0.01036 = 0.0933 \text{ mgr. of water,}$$

or $$\frac{(23\times 2+32+16\times 4)}{2}\times 0.01036 = 0.737 \text{ mgr. of } Na_2SO_4.$$

Since 1 ampere-second deposits 0.01036 mgr. equivalents or 0.00001036 gr. equivalents, it is seen that 96 540 ampere-seconds are required to deposit 1 gr. equivalent; or since 1 ampere-second = 1 coulomb, 96 540 coulombs are required. This fact proves that one equivalent of each and every ion carries the same charge of electricity. Faraday's law applies not only to water solutions, but also to solutions in other solvents, and to salts in a fused state, and holds for all temperatures.

The fact that the decomposition products of the electrolyte, as hydrogen and oxygen, appear at points some distance apart, caused at first a great deal of difficulty. It was evident that the two products could scarcely be derived from the same molecule of water or dissolved substance, but must come from different ones. Several theories were at first proposed to account for the facts; for instance, the theory that the two substances hydrogen and oxygen were not derived from the water at all; that electricity itself was nothing less than an acid.

Von Grotthus* attempted to clear up the difficulty. He assumed that the anion which was being deposited came from the molecule which was nearest to the anode;

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* Ann. d. chem. u. Physik, 58, 64 (1806), 63, 20 (1808).

the cation which was being deposited came from the molecule nearest to the cathode. Just at the instant when these were deposited on the electrodes the remainder of the decomposed molecule appropriated the atom or radical it had lost from its neighboring molecule, this in turn robbing its next-door neighbor. This view was also apparently held by Faraday.

The first to point out the shortcomings of this theory was Grove.* From his study of the oxygen-hydrogen cell, which derives its energy from the union of these two elements, he concluded that a decomposition of the water molecules is not necessary for the evolution of oxygen and hydrogen, but that the molecules are present from the start in a decomposed state.

Clausius † then followed up this idea: if a force is necessary to decompose the molecules, electrolysis should not be possible at very low voltages. But the electrolysis of silver nitrate between silver electrodes takes place at voltages which are far below the voltage which corresponds to the energy of formation of silver nitrate; that is, we decompose at the expense of a small amount of work a salt which is formed with the liberation of a great deal of energy, a fact which conflicts with the principle of the conservation of energy. Clausius concludes therefore that "the supposition that the components of the molecules of an electrolyte are firmly united and exist in a fixed orderly arrangement is wrong."

A few years earlier Williamson ‡ had expressed a somewhat similar view. He proposed the hypothesis

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* Phil. Mag., 27, 348 (1845).

† Poggendorf's Ann., 101, 338 (1857).

‡ Liebig's Ann., 77, 37 (1851).

that in hydrochloric acid "each atom of hydrogen does not remain quietly attached all the time to the same atom of chlorine, but that they are continually exchanging places with one another." If this is the case, then the two radicals must be present separately for a certain length of time, and this time will be longer the farther apart the molecules are, or, in other words, the more dilute the solution is.

This hypothesis was adopted by Clausius, but at that time no experimental means were known for determining how much of the electrolyte was dissociated, or, in other words, to determine the ratio of the time during which the molecules were dissociated to the time during which the atoms remain united.

About this time Hittorf's* important work was published. Hittorf found that during electrolysis changes of concentration occur at the anode and cathode, and concluded that these changes could only be explained by assuming that the anions and cations move with a different velocity. At the same time Kohlrausch discovered the law† of the "independent wandering of the ions." He found that in dilute solutions the conductivity of a given salt is additively composed of two values which are peculiar to the different ions; that is, the potassium ion plays the same part in conducting the current whether it is present with the chlorine ion or the NO_3 ion. If we add to the conductivity of the potassium ion that of the chlorine ion, which is also independent of the nature of the cation present with it, we obtain the conductivity of potassium chloride. This result shows that any one ion troubles

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* Ostwald's Klassiker, Nos. 21 and 23.

† See the chapter on Conductivity.

itself very little about the nature of any other ions which may also be present in the solution.

Electrochemical theories had reached this point when van't Hoff in his classic work applied the gas laws to solutions. We saw (pp. 20 and 46) that the gas laws no longer hold when we consider a salt whose solution conducts the electric current. If p is the osmotic pressure and v the dilution, i.e., the volume in which a gram-molecule is contained, then $pv=RT$ for non-conducting solutions (cf. p. 26). In the case of conducting solutions van't Hoff found it necessary to multiply RT by a factor i, so that for this class of solutions $p \cdot v=iRT$.

Arrhenius calculated from Kohlrausch's measurements that only a part of the total number of molecules of a dissolved salt is active in conducting the current, and that this part is $i-1$; i.e., if $i=1.7$, then 70% of the total dissolved salt takes part in conduction. Arrhenius then concluded: "If we must assume that free ions are present in the solution, as Clausius and Williamson have shown, and if the osmotic and other methods show that many more molecules seem to be present in the solution than we have introduced, then we may assume that the salt is dissociated, not as Clausius believed, to a very slight extent, but to such a large extent that this will account for the deviation from the van't Hoff gas laws." Now, since only a part of the dissolved salt and not the whole is active in conduction, and since this part corresponds to the extra molecules which van't Hoff has shown to be present, Arrhenius drew the conclusion that the electrolyte is dissociated into ions, the amount of dissociation depending on the concentration of the solution and nature of the salt, and that the ions are the only active agents in conducting the current. This theory has become indispensable to electrochemistry, and has also become of great help in our understanding of general chemistry.

When we bring ordinary salt in contact with water, it dissolves, but at the same time the reaction *

$$NaCl \rightleftarrows Na^{\cdot} + Cl'$$

takes place. This is the equation of an ordinary chemical reaction and like all reactions finally reaches a condition of equilibrium. In the case of a normal solution of NaCl, the reaction goes on till 67% of the salt has dissociated into ions, i.e., the degree of dissociation is 67%. Such a reaction must follow the law of mass action (p. 35). If x represents that part of a gram-molecule which is dissociated when the volume of the solution is v (in the above case $x = 0.67$), then at equilibrium the concentration of the undissociated molecules will be $\frac{1-x}{v}$, but the concentration of each kind of ions will be $\frac{x}{v}$ and the law of mass action requires

$$K\frac{1-x}{v} = \frac{x^2}{v^2},$$

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* The ions were formerly denoted by $\overset{+}{Na}$ and $\overset{-}{Cl}$ to indicate that we have to do with a positively charged sodium ion and a negatively charged chlorine ion; substances whose valence is greater than 1 were denoted by $\overset{++}{Cu}$ and $\overset{--}{SO_4}$, indicating that the copper or SO_4 ions carry twice the charge of the sodium or chlorine ions. For typographical reasons it has become customary to replace the + by · and the − by ′, printed above and to the right of the symbol.

or, in general, if c_i is the concentration of the ions and c_s that of the undissociated molecules, then

$$K = \frac{c_i^n}{c_s},$$

n being the number of ions which results from the dissociation of 1 molecule of the salt. K is called the "dissociation constant" of the salt.

The following examples will show how the dissociation occurs:

$$AgNO_3 \rightleftarrows Ag^{\cdot} + NO_3{}'; \quad Na_2SO_4 \rightleftarrows Na^{\cdot} + Na^{\cdot} + SO_4{}'';$$

$$BaCl_2 \rightleftarrows Ba^{\cdot\cdot} + Cl' + Cl'.$$

But "dissociation by steps" may also occur, as:

$$BaCl_2 \rightleftarrows BaCl^{\cdot} + Cl'.$$

In many cases we cannot decide from the formula of a salt how it will dissociate. In the case of $KHSO_4$ the following reactions are possible:

$$KHSO_4 \rightleftarrows K^{\cdot} + H^{\cdot} + SO_4{}'',$$

or

$$KHSO_4 \rightleftarrows K^{\cdot} + HSO_4{}',$$

or

$$KHSO_4 \rightleftarrows H^{\cdot} + KSO_4{}'.$$

By measuring the "transport number" we can generally determine what the ions are, and Hittorf has applied this method in a number of cases where the composition of the ions was doubtful. If we put some potassium silver cyanide $KAg(CN)_2$ at the bottom of a U tube and pour water into each arm of the tube, the cations will move to the cathode and the anions to the anode when a current is passed through the tube. After the current has passed for some time we find on analyzing the contents of each half of the tube that no silver has wandered toward the cathode, but has gone in the opposite direction toward the anode. This shows that the silver forms part of the anion, and that the dissociation occurs thus:

$$KAg(CN)_2 \rightleftarrows K^{\cdot} + Ag(CN)_2'.$$

In a similar way it has been shown that the chromium in the chromates belongs to the anion just as sulphur belongs to the SO_4 ion. In the case of many acid salts, provided the solution is not too dilute, the hydrogen goes as part of the anion to the anode. Acid potassium sulphate then would dissociate

$$KHSO_4 \rightleftarrows K^{\cdot} + HSO_4'.$$

It must not be understood, however, that no further dissociation takes place. In the above instance of $KAg(CN)_2$ the dissociation constant K of the reaction

$$K = \frac{[Ag(CN)_2'] [K^{\cdot}]^{*}}{[KAg(CN)_2]}$$

has a very large value, and the dissociation is nearly complete. On the other hand the dissociation constant

$$K_1 = \frac{[Ag^{\cdot}][CN']^2}{[Ag(CN)_2']}$$

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* The concentration of a substance is denoted by enclosing its symbol in brackets.

of the reaction $Ag(CN)_2' \rightleftarrows Ag^{\cdot} + CN' + CN'$ is very small, so that this second dissociation only takes place to an exceedingly small extent. In such a solution we have very many potassium ions and "complex" silver-cyanogen ions, but free silver ions and cyanide ions are present in exceedingly small amounts. It follows therefore that the current is conducted almost entirely by the potassium and complex ions, while the others on account of their scarcity are practically without effect on the conductivity. As a result we find in the above experiment no silver in the cathode arm of the U tube.

Some other typical forms of dissociation are:

$$AlCl_3 \rightleftarrows Al^{\cdots} + Cl' + Cl' + Cl',$$

$$KMnO_4 \rightleftarrows K^{\cdot} + MnO_4',$$

$$*\, K_6Fe_2(CN)_{12} \rightleftarrows K^{\cdot} + K^{\cdot} + K^{\cdot} + K^{\cdot} + K^{\cdot} + K^{\cdot} + Fe_2(CN)_{12}''''''.$$

From one molecule of potassium ferricyanide seven ions are formed, and the dissociated part has seven times as great an effect on the osmotic pressure or lowering of the freezing-point as the simple molecules. Other typical examples will be given in the following chapters.

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* This equation seems to the translator to be incorrect, as Ostwald's "Basicity Rule" shows ferricyanic acid to be tribasic. See Jahn, Grundriss der Elektrochemie, 2d edition, p. 146.

Applications of the Dissociation Theory in Chemistry.

In this chapter we cannot enter into details but must limit ourselves to a few examples which will show the usefulness of the theory of electrolytic dissociation and how we can apply it in our work and calculations. At the same time we will touch on a number of physico-chemical questions, a clear understanding of which is necessary to our further study of electrochemistry.

The supporters of the theory of electrolytic dissociation assume that most of the reactions of inorganic chemistry, which, in comparison to organic reactions, take place in a very short space of time, are reactions between the ions. The precipitation of silver chloride from a silver-nitrate solution by ordinary salt was formerly explained by the following equation:

$$AgNO_3 + NaCl \rightleftarrows AgCl + NaNO_3.$$

If we assume that all the salts except the solid AgCl are dissociated into their ions the reaction becomes

$$Ag^{\cdot} + NO_3{}' + Na^{\cdot} + Cl' \rightleftarrows Na^{\cdot} + NO_3{}' + AgCl,$$

or subtracting those ions which occur on both sides of the equation,

$$Ag^{\cdot} + Cl' \rightleftarrows AgCl.$$

The essential reaction is the union of silver ions and chlorine ions to form insoluble silver chloride. The old explanation that "chlorine and silver react in solution to form silver chloride" is not strictly correct. In terms of the theory of electrolytic dissociation "chlorine ions and silver ions can only exist together in a water solution in very small concentrations; if the product of their concentrations, measured in mols per litre, should exceed 1.2×10^{-10} solid silver chloride is deposited until the product of the concentration of the ions is reduced to this value."

Chloroform, for instance, contains no chlorine ions, since it is a non-conductor of electricity, and therefore cannot be electrolytically dissociated; therefore it does not precipitate silver chloride from a solution. The same is true for sodium chlorate, $NaClO_3$, which dissociates according to the formula

$$NaClO_3 \rightleftarrows Na^{\cdot} + ClO_3'.$$

A solution of this salt contains chlorate ions, but no chlorine ions. In a solution of $KAg(CN)_2$, which dissociates after the formula

$$KAg(CN)_2 \rightleftarrows K^{\cdot} + Ag(CN)_2',$$

so few silver ions result from the further dissociation,

$$Ag(CN)_2' \rightleftarrows Ag^{\cdot} + CN' + CN',$$

that they can remain in the presence of a large amount of Cl' ions without being precipitated. This accounts for the fact that NaCl will not precipitate AgCl from a solution of $KAg(CN)_2$. Before the birth of the theory of electrolytic dissociation no satisfactory explanation had been given.

The theory explains the slowness of reactions between organic substances on the ground that they are not dissociated to any measurable extent, and the same is true of reactions between solid substances. A mixture of solid NaCl and $AgNO_3$ from which water is carefully excluded does not react; but as soon as it comes in contact with water the two salts dissolve, are at once dissociated into their ions, and reaction starts. Salts in a state of fusion are also dissociated so that under such circumstances reaction can easily take place.

The old dictum "corpora non agunt nisi fluida" is pretty generally true, but not absolutely, since solid substances do react, but with extreme slowness.

Among the salts we must include the salts of the metal hydrogen, i.e., the acids. These are generally very strongly dissociated in water solution. Just as potassium salts have the common property of giving off potassium ions, so all the acids have the property of sending hydrogen ions into solution, as, for instance,

$$HCl \rightleftarrows H^{\cdot} + Cl',$$

or

$$H_2SO_4 \rightleftarrows H^{\cdot} + HSO_4' \rightleftarrows H^{\cdot} + H^{\cdot} + SO_4'',$$

or

$$H_3PO_4 \rightleftarrows H^{\cdot} + H_2PO_4' \rightleftarrows H^{\cdot} + H^{\cdot} + HPO_4'' \rightleftarrows H^{\cdot} + H^{\cdot} + H^{\cdot} + PO_4'''.$$

Acids like sulphuric acid which can furnish two hydrogen ions per molecule are called dibasic, those which can furnish three hydrogen ions tribasic, etc. The examples just given show that the dissociation of a molecule is not necessarily complete but may take place by stages, or "stepwise."

The bases are also to be reckoned among the strongly dissociated salts. Just as a common characteristic of the chlorides is their ability to furnish chlorine ions, so the bases have the common property of furnishing hydroxyl or OH ions. Acids and bases therefore are simply two particular kinds of salts. Their exceptional importance in chemistry due to the fact that their characteristic ions are also the ions of the most universal solvent, water. A chemical science based on a solvent which contained neither $H^{\cdot}$ nor OH' ions would therefore be wholly unable to distinguish acids or bases from salts. We thus arrive at a new and exact definition of an acid or a base. Acids are salts which are capable of forming $H^{\cdot}$ ions in solution; bases are salts which furnish OH' ions.

We must now consider the dissociation of water, which is one of the most important results of the dissociation theory and the most convincing proof of its value. We can consider water as a dibasic acid which dissociates as follows:

$$H_2O \rightleftarrows H^{\cdot}+OH' \rightleftarrows H^{\cdot}+H^{\cdot}+O'',$$

or also as a mon-acid base, since it can furnish OH' ions. The second step of the acid dissociation which gives rise to O'' ions is very slight, i.e., the concentration of O'' ions is exceedingly small.

The first dissociation of water into $H^{\cdot}$ and OH' is also very slight but of very great chemical importance. The reaction

$$H_2O \rightleftarrows H^{\cdot}+OH'$$

like every other chemical reaction is governed by the law of mass action, thus:

$$K[H_2O]=[H^{\cdot}][OH'].$$

The equilibrium constant K is known as the "dissociation constant of water." (Enclosing a symbol in brackets is the conventional way of indicating the concentration of a substance.)

Now, the dissociation of water is very slight, so that the active mass of water is practically unchanged by the dissociation, and we may therefore consider it a constant and include it along with the reaction constant without causing any appreciable error; then

$$k=[H^{\cdot}][OH'],$$

where k is the product of the concentrations of both ions. In neutral water neither $H^{\cdot}$ nor OH' is present in excess. The two concentrations are equal, so that if c_0 represents the concentration of either ion in neutral water,

$$c_0=[H^{\cdot}]=[OH']=\sqrt{k}.$$

The last equation but one must always hold, no matter what the concentrations of $H^{\cdot}$ or $OH'OH'$ may be, i.e., whether the solution is acid, neutral, or alkaline. A number of different methods which we will consider in the following have given 10^{-7} as the value of c_0 at about 22°. Therefore

$$[H^{\cdot}][OH']=10^{-14}.$$

In an alkaline solution, which contains 17 grams of OH' ions per litre, $[OH']=1$, and $[H^{\cdot}]$ must then be 10^{-14}; in such a solution, then, we would have a concentration of 1 gr. of hydrogen ions in 100 billion litres. In a 0.001 ormal acid solution $[H^{\cdot}]=.001$ and $[OH']=10^{-11}$, etc.

A further application of this formula is as follows: if we mix 1 mol of HCl and 1 mol of NaOH in a litre of water, the product $[H^{\cdot}]\times[OH']$ at first will be $=1$, a much larger value than is possible. $H^{\cdot}$ and OH' will therefore combine till the value of $[H^{\cdot}][OH']$ becomes 10^{-14}. The equations for this and other simple reactions of neutralization are:

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

$$K^{\cdot}+OH'+H^{\cdot}+NO_3' = H_2O+K^{\cdot}+NO_3',$$

$$\tfrac{1}{2}Ba^{\cdot\cdot}+OH'+H^{\cdot}+I' = H_2O+I'+\tfrac{1}{2}Ba^{\cdot\cdot}.$$

After subtracting the ions which appear on both sides there remains in every case

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

The process of neutralization therefore is always based on the same fundamental reaction, provided of course that the reacting base and acid are in a solution so dilute that they are both completely dissociated into their ions. As a result, the heat of reaction of every neutralization must always be the same, and must be independent of the nature of the particular acid or base used. This fact has long been known, but previous to the evolution of the dissociation theory no satisfactory explanation had been given. The following table gives some experimental results:

Acid and Base.	Heat of Neutralization.
Hydrochloric acid and sodium hydroxide	13 700
Hydrobromic " " " "	13 700
Nitric " " " "	13 700
Hydroiodic " " " "	13 800
Hydrochloric " " lithium "	13 700
" " " potassium "	13 800
" " " barium "	13 800
" " " calcium "	13 900

Hydrofluoric acid is only slightly dissociated in solution, consequently in the reaction

$$HF + K^{\cdot} + OH' \rightleftarrows K^{\cdot} + F' + H_2O$$

HF must become further and further dissociated as the reaction goes on. The dissociation of HF of course follows the law of mass action

$$K_1[HF] = [H^{\cdot}][F']$$

and as the $H^{\cdot}$ ions combine with OH' ions to form water new ones are supplied by the undissociated HF. The heat evolved by the dissociation of the hydrofluoric acid appears as an excess over that evolved by the union of $H^{\cdot}$ and OH'. The neutralization of hydrofluoric acid evolves 16 270 calories. The difference between this and the ordinary heat of neutralization, $16\,270 - 13\,700 = 2\,570$, is the heat of dissociation of HF.

The question now arises, when either the acid or base has a very small dissociation constant, how will this affect the neutralization? Like all chemical reactions, that of neutralization goes on till a particular condition of equilibrium is reached. When we mix solutions of NaOH and HCl, they do not combine completely to form NaCl, some free NaOH and HCl remain, but their quantity is so small that it cannot be measured. The incompleteness of some reactions of neutralization, however, can be measured, as, for instance, that of acetic acid.

From conductivity measurements, or, better, from the influence of sodium acetate on the velocity of the saponification of methyl acetate,* it has been found that a mixture of 0.1 N acetic acid and 0.1 N sodium hydroxide combine to the extent of 99.992%, i.e., 0.008% of NaOH and CH_3COOH remain in a free state. We may now ask, is it possible to calculate this percentage of free acid or hydroxide from the dissociation constant of acetic acid? A 0.1 N solution of sodium acetate in H_2O must be decomposed into free acid and base to exactly this same amount (0.008%) and this decomposition of a salt by water is known as "hydrolysis." The calculation of the dissociation constant of organic acids from the dissociation constant of water and the degree of hydrolysis of the salts of the acid, or the reverse, has recently become of such importance for organic chemistry that we will give a numerical illustration of the method to be followed.

The Hydrolysis of sodium acetate: acetic acid dissociates according to the equation

$$CH_3COOH \rightleftarrows H^{\cdot} + CH_3COO',$$

and the constant of the reaction is given by

$$K_1[CH_3COOH] = [H^{\cdot}][CH_3COO'].$$

From conductivity measurements the value of K_1 has been found to be 0.000018. The relation between $[H^{\cdot}]$ and $[OH']$ is governed by the dissociation constant of H_2O, K_2, at 25°:

$$K_2 = 1.2 \times 10^{-14} = [H^{\cdot}][OH'].$$

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* The velocity of this reaction is proportional to the concentration of the OH' ions present, which accelerate the saponification catalytically.

Further, there must be just as many positive ions present in the solution as there are negative ions, i.e.,

$$[H^\cdot]+[Na^\cdot]=[CH_3COO']+[OH'].$$

The two sodium compounds present, NaOH and CH_3COONa, can be considered as completely dissociated at this degree of dilution, i.e., practically all the sodium is present in the form of $Na^\cdot$ ions. This concentration is then 0.1 N, since we took that much Na in the form of sodium acetate. Finally we must remember that the amounts of NaOH or CH_3COOH which do not combine in the reaction of neutralization or which are set free by the hydrolysis are equal. Since the NaOH is completely dissociated, while the CH_3COOH is only dissociated to such a small amount that its total concentration is not appreciably affected, we may consider

$$[OH']=[CH_3COOH].$$

We have then four equations:

(1) $0.000018[CH_3COOH]=[CH_3COO'][H^\cdot]$.

(2) $[H^\cdot][OH']=1.2\times10^{-14}$.

(3) $[H^\cdot]+[Na^\cdot]=[H^\cdot]+0.1=[CH_3COO']+[OH']$.

(4) $[CH_3COOH]=[OH']$.

Substituting the value of $[CH_3COO']$ from (3) in equation (1) gives

$$0.000018[CH_3COOH]=[H^\cdot]([H^\cdot]+0.1-[OH']).$$

A solution of CH_3COONa reacts alkaline; there must therefore be more OH' than $H^\cdot$ present, so that $[H^\cdot]$ is certainly less than 10^{-7}. This value is so small that it may be neglected in comparison with 0.1 (at the most this would only introduce an error of about 0.0001%). Substituting the value of [H˙] from equation (2) and then introducing for [OH′] its value from equation (4), we finally obtain

$$0.000018[CH_3COOH]=\frac{1.2\times10^{-14}}{[CH_3COOH]}(0.1-[CH_3COOH]).$$

On solving this quadratic equation we find for the concentration of CH_3COOH,

$$[CH_3COOH]=0.0000081.$$

That is, of the 0.1 CH_3COONa, 0.0000081 or 0.0081% has decomposed into free acetic acid and sodium hydroxide; this agrees very well with the value 0.008 found by experiment.

We may also reverse this process and from the experimental value 0.008 calculate the dissociation constant of water. In this way we find:

$$C_0=1.1\times10^{-7} \text{ at } 25°.$$

The following table contains the "degrees of hydrolysis" of certain salts at 25° when present in 0.1 normal solution:

Salt.	Degree of Hydrolysis.
Sodium carbonate.	3.17 %
Potassium phenolate. . .	3.05 "
" cyanide. . . .	1.12 "
Borax.	0.5 "
Sodium acetate.	0.008 "

It is seen that the hydrolysis may amount to several percent. It is well known that a solution of potassium cyanide smells of prussic acid, which can only result from a "hydrolytic dissociation" of the salt. A solution of ammonium carbonate smells strongly of ammonia; the odor in this case being due to the free NH_3 resulting from hydrolysis. The slow evolution of carbon dioxide from a solution of sodium carbonate is another instance. Still another example is the conduct of certain salts of bismuth, which precipitate bismuth oxide on being diluted; in this case the hydrolysis is so great that the solubility of the oxide is thereby exceeded.

Let us now go back to the calculation of the dissociation constant of water. The first method was by measuring the hydrolysis of sodium acetate; a second method consists in measuring the velocity of the reaction of "saponification." When ethyl acetate and sodium hydroxide are brought together, sodium acetate and ethyl alcohol are formed according to the equation

$$CH_3COOC_2H_5 + NaOH \rightleftarrows CH_3COONa + C_2H_5OH.$$

In this reaction the ester $CH_3COOC_2H_5$ is said to be saponified by the base NaOH. The velocity of this reaction is dependent on the concentrations of the reacting substances and is further catalytically accelerated by the presence of $H^{\cdot}$ ions (cf. p. 15). On the other hand, the number of OH' ions present also influence the velocity, and it has been found experimentally that the OH' ions saponify an ester 1400 times as fast as the $H^{\cdot}$ ions. It is easy to see that when we successively diminish the concentration of the OH' ions, the velocity of the reaction will reach a minimum when the concentration of the $H^{\cdot}$ ions is 1400 times as large as that of the OH′ ions. If this minimum is determined experimentally and the amount of free acid at that point determined, we have

$$C_{H^{\cdot}} = 1400 C_{OH'}.$$

In this manner van't Hoff has calculated the dissociation constant of water, and obtained as the value of c_0,

$$c_0 = 1.2 \times 10^{-7} \text{ at } 25°.$$

A third method for calculating the dissociation of H_2O consists in measuring the electromotive force of the acid-alkali cell; that is, of an element made of up two platinum electrodes saturated with hydrogen, one of which is placed in an acid and the other in an alkaline solution. We shall see later that the electromotive force of a metal when placed in a solution of one of its salts depends not only on the nature of the metal but also on the concentration of the ions of the metal present in the solution For any one metal the electromotive force varies inversely as the logarithm of the concentration of the ions of the metal in solution. We may consider a platinum electrode saturated with hydrogen as an electrode of the metal hydrogen, and its electromotive force is therefore dependent on the concentration of the hydrogen ions in the solution. If we measure the electromotive force of the acid-alkali cell and determine by titration the concentration of the $H^{\cdot}$ ions on one side and that of the OH′ ions on the other, we can calculate from this result the concentration of the $H^{\cdot}$ ions in the alkaline solution. In a normal solution of NaOH where the concentration of the OH′ ions is nearly = 1 it has been found that the concentration of the H˙ ions is about 1.44×10^{-14}. That is, in this solution

$$[H^{\cdot}][OH']=1.44\times10^{-14},$$

or

$$c_0=1.2\times10^{-7}.$$

The conductivity of pure water furnishes a fourth method. The measurements made by Kohlrausch on the purest water obtainable have given the following figures:

$$c_0=0.78\times10^{-7} \text{ at } 18^\circ$$

and

$$c_0=1.05\times10^{-7} \text{ at } 25^\circ.$$

(The method by which these results were obtained will be discussed later, in the chapter on Conductivity.) These four independent methods have given the following results for the dissociation of water:

$$c_0=1.2\times10^{-7},\quad 1.1\times10^{-7},\quad 1.2\times10^{-7}, \text{ and } 1.05\times10^{-7}.$$

If we take the constant for 25° as $K=1.2\times10^{-14}$, we can calculate the value of the constant for other temperatures by means of van't Hoff's equation, since the heat of the reaction $H^{\cdot}+OH'=H_2O$ is 13 700 cal. From these results it has been calculated that the conductivity of the purest water should increase 5.81% per degree rise of temperature. Kohlrausch found that the increase was 5.32%. The following table gives the dissociation of water at different temperatures:

Temperature=	0	2	10	18	26	34	42	50	100
$c_0\times10^7=$	0.35	0.39	0.56	0.80	1.1	1.47	1.93	2.48	8.5

A number of purely chemical problems which cannot be satisfactorily explained without the help of the theory of equilibrium will be discussed in the chapter on Conductivity, after we have learned the different methods of measuring dissociation constants. Among these are: influence of the strength of acids and bases on the saponification of esters, on the inversion of sugar, and on the hydrolytic dissociation of salts; distribution of an acid between two bases, or of a base between two acids; rapidity of solution of metals, carbonates, and oxalates in acids; the influence of dissolved salts on one another, etc.

The dissociation theory disposes of the question whether a reaction occurs when solutions of salts which have no common ions are brought together; for instance, are KCl and NaBr formed when solutions of KBr and NaCl are mixed? The absence of any evolution or absorption of heat would go to show that no reaction takes place. The dissociation theory shows that the question is meaningless. Before mixing, the solutions contain the ions $K^{\cdot}$, $Na^{\cdot}$, Cl' and Br'; and after mixing, the resulting solution contains the same ions unchanged. No reaction can have occurred.

According to the dissociation theory it is self-evident that the properties of such mixed solutions are additively built up of the properties of the original solutions. The specific gravity, for instance, is simply obtained from the specific gravities of the original solutions. We can go one step farther, since the specific gravity of a solution of a single substance is additively made up of values peculiar to the ions. If we know the number representing the effect of each ion on the specific gravity, we can calculate by simple addition the specific gravity of a mixture of any ions, i.e., the specific gravity of a solution of any salt. In a similar manner it has been shown that the compressibility, the capillarity, the internal friction, the index of refraction, the magnetic rotation of the plane of polarization, and the light absorption of solutions are additive properties. These few examples have shown some of the applications of the dissociation theory to chemical phenomena, and will suffice for the present. We need only mention that the conduct of indicators in titration has been explained satisfactorily by the dissociation theory. Also many analytical reactions, such as the precipitation of metallic sulphides by hydrogen sulphide, can easily be understood from a knowledge of the solubility products and the state of dissociation. (Cf. chapter on Conductivity, p. 103).

Finally a few words must be added on the application of the dissociation theory to physiological problems. The theory has widely increased our knowledge of the poisonous action of certain classes of substances. The acids are more poisonous and have a greater physiological action according as their dissociation constant is great or small. The ions of mercury are very poisonous. If a salt containing mercury is taken into the stomach, the poisonous effect is more intense the higher the salt is dissociated. Corrosive sublimate is exceedingly poisonous, while the slightly soluble calomel which gives rise to few mercury ions is less poisonous although physiologically active. Cyanide of mercury, on the other hand, which contains the two active poisons mercury and prussic acid, is itself not very poisonous. This is accounted for by the fact that cyanide of mercury is practically undissociated, as has been shown by conductivity measurements. An every-day example of the application of the osmotic theory to physiology is the following: The cells of the human body contain dissolved substances and have therefore a certain osmotic pressure. When a wound is washed with water, the cells, whose walls are "semipermeable," draw in water and burst, giving rise to continued bleeding. To avoid this the wound should be washed with a solution whose osmotic pressure is the same as that of the solution in the cells. Such a solution is the 2% solution of boric acid. If a 2% solution of NaCl were used, this would cause smarting, since NaCl is completely dissociated and has twice the osmotic pressure of the boric acid, which is practically undissociated. A 1% solution of salt, the so-called "physiological salt solution," is therefore used for cleansing wounds. Washing out the nose with water causes pain, but this may be avoided by the use of a 1% solution of common salt. A swimmer knows that it is unpleasant to open the eyes under fresh water, but in sea-water, which has nearly the same osmotic pressure as the solution in the cells of the eye, the eyes may be kept open for a long time without smarting.

CHAPTER IV.

CONDUCTIVITY.

JUST as water strives to descend from a higher to a lower level, or as heat tends to pass from a higher to a lower temperature, so electricity tends to sink from a higher to a lower "potential." In these three cases the tendency is greater, the greater the difference in level, or in "potential," and consequently the quantity which falls in unit time is governed by the difference of potential. A quantity of water is measured in litres, a quantity of heat in calories, and a quantity of electricity in coulombs. The quantity of water flowing in a given time is governed by the size of the pipe through which the water flows, as well as by the difference in level. The quantity of water per unit of time is greater, the greater the cross-section of the pipe; and smaller, the longer the pipe. This quantity can be measured by determining the number of litres per unit of time which flows in at the top or out at the bottom of the pipe. This same amount must also pass any cross-section of the pipe in unit time. The amount of water is further dependent on the friction of the water against the material of which the pipe is made. In other words, it is directly proportional to the reciprocal of the value of this friction, which we might call the conductivity for water of the pipe material. Exactly similar relations hold for the conduction of heat and of electricity. When two quantities of electricity which have a different potential are connected by a conductor, a certain quantity of electricity per unit of time will pass through the conductor. This amount per unit of time, or current, will vary directly with the cross-section of the conductor and inversely with its length and with the friction which the material of the conductor offers to passage of the electricity. These relations are expressed in Ohm's Law:

$$\text{Current} = \frac{\text{Amount of electricity in coulombs}}{\text{Time}} = i = \frac{Eq}{lw}.$$

In this formula E represents the impelling electromotive force, or difference of potential, q the cross-section of the conductor, l its length, and w is a value which varies from substance to substance, and expresses the resistance which each substance offers to the passage of electricity. The current is therefore proportional to the electromotive force and the cross-section, and inversely proportional to the length and specific resistance. w is called the "specific resistance"; it is the reciprocal of the conductivity for the unit of cross-section and length, and is the resistance which a cube of the conductor 1 centimetre in thickness offers to the passage of the current. If we put a difference of potential of 1 volt on two opposite sides of this cube and find that the current flowing is 1 ampere, it follows from the above equation that the specific resistance of the conductor is 1. The reciprocal of the specific resistance is the specific conductivity. The specific conductivity of a substance is 1 when a difference of potential of 1 volt will send a current of 1 ampere through a cube of the substance 1 centimetre in diameter. The specific resistance is then 1 ohm.

A distinction was formerly made between good, bad, and medium conductors. This distinction, however, cannot be adhered to, since we have conductors of every order of magnitude. The following table gives the specific conductivity of a number of substances:

SPECIFIC CONDUCTIVITY IN RECIPROCAL OHMS OF A CENTIMETRE CUBE AT 18°.

κ_{18} is the specific conductivity; $\sigma_{18}=\frac{1}{\kappa}$ is the specific resistance; $\sigma_{18}'=10\,000\,\sigma_{18}$ gives the resistance of a wire 1 metre in length and 1 square millimetre in cross-section; α is the temperature coefficient; if τ is the temperature, then $\sigma_\tau=\sigma_{18}[1+\alpha(\tau-18)]$. The figures apply to pure soft metals.

	κ_{18}.	σ_{18}.	σ_{18}'.	α.
Silver	624 000	0.0000016	0.016	+0.0037
Copper	587 000	0.0000017	0.017	+0.0040
Aluminium	312 000	0.0000032	0.032	+0.0036
Zinc	164 000	0.0000061	0.061	+0.0037
Iron	76 800	0.000013	0.13	+0.0060
Mercury	10 420	0.0000958	0.958	+0.00092
Constantan	20 400	0.000049	0.49	+0.00000
Manganine	23 800	0.000042	0.42	+0.00003
Nickeline	23 800	0.000042	0.42	+0.00023
Gas carbon *	200	0.0050	50	−0.00003 to −0.00008
H_2SO_4 30%	1.35	0.74		
Slate *	0.000014	70 000		
Wood charcoal *	0.00004	26 000		
Benzol *	7.5×10^{-10}	1 300 000 000		
Hard rubber *	2.5×10^{-16}	4×10^{15}		

* Approximate values.

Silver is the best conductor known, although copper, which is used most extensively, is not far behind. Aluminium, which has lately come into prominence as a material for power transmission cables, conducts only about half as well as copper, but has the advantage of lightness. Impurities in a metal always diminish its conductivity, consequently all alloys have a lower conductivity than the metals themselves. Thirty percent sulphuric acid has at 18° a conductivity of about ¾, at 40° of about 1; i.e., a centimetre cube of sulphuric acid of this strength has a resistance of 1 ohm. A complete list of substances could be given whose resistances lie between those of nickeline and hard rubber, which shows that all degrees of resistance are possible. The temperature coefficient of the resistance of all the metals and most of the alloys is positive, i.e., the resistance increases as the temperature rises. In the case of practically all liquid conductors the temperature coefficient of the conductivity is positive, and in the case of water solutions its value would indicate a conductivity of zero at about −30°.

It is impossible to make a sharp distinction between good and bad conductors, but another very important distinction can be made. All conducting substances may be divided into two classes: the first includes *all substances which remain unchanged by the passage of the current;* in this class belong all the metals, practically all solid conductors and a few liquids. The second class comprises *all substances which are definitely changed by the passage of the current;* to this class belong the electrolytes, i.e., salt solutions and salts in a state of fusion.

The rule has been proposed that a substance shows metallic conduction when the temperature coefficient of its conductivity is negative; electrolytic conduction when the coefficient is positive. This rule, however, does not always hold, for gas carbon, which conducts like a metal, has a positive temperature coefficient of conductivity (or negative temperature coefficient of resistance). Certain solutions show a negative temperature coefficient of conductivity. Even among the metals there are certain alloys which have a positive temperature coefficient of conductivity.

The difference between the two kinds of conductivity will be clearer if we assume that in a metallic conductor the atoms touch each other, and there are everywhere present bridges over which the electricity may pass. In an electrolyte the dissolved substances which conduct the current are more or less widely separated, so that if electricity is to pass from one atom to another these atoms must first traverse a certain distance in order to come in contact. A rise of temperature causes metals to expand and thus the contact between the atoms becomes less intimate and the resistance increases. In the case of electrolytes, however, the rise in temperature diminishes the friction to which the atoms are subject in their motions and the conductivity increases.

Conductivity of Solutions.

In the study of electrochemistry we have to deal principally with solutions of salts in water, and we will therefore consider more closely the mechanism of the conduction of electricity through a solution.

We saw on p. 58 that salts when dissolved in water dissociate into electrically charged ions. When two electrodes are connected with the poles of a battery so that one is charged positively and the other negatively and the electrodes dipped into a solution of any salt, the positive electrode exerts an attractive force on the negatively charged ions and a repelling force on the positively charged ions, while at the other electrode the positive ions are attracted and the negative repelled. As a result the negatively charged anions move to the positively charged anode and the positively charged cations go to the cathode. At the electrodes the ions are discharged; i.e., they neutralize a part of the electricity with which the electrodes are supplied, and either remain as neutral matter on the electrode or enter into further reactions. The charges on the electrodes which have been neutralized by the ions are of course immediately renewed by the battery.

As a result of the pull exerted on the ions by the charges on the electrodes the ions move through the solution, and since they themselves are electrically charged they thus transport a current through the solution. As was seen on p. 52, each gram equivalent of any ion always carries the same amount of electricity, 96 540 coulombs, i.e., the anions carry 96 540 coulombs of negative electricity per mol, and the cations the same amount of positive electricity per mol. When 1 mol of $K^{\cdot}$ ions and 1 mol of Cl' ions pass through a plane perpendicular to the direction of the current in one second, then 2 × 96 540 coulombs are transported and the current strength is 193 080 amperes, since it makes no difference whether positive electricity moves in one direction or negative in the other. If instead of 1 mol 1/100 000 mol passes through the plane per second the current is only 1.931 amperes.

We must now consider the all-important question: *What is the relation between the conductivity of an electrolyte and the number and nature of the ions?*

Let us consider two metallic plates, serving as electrodes, placed parallel to each other at a distance of 1 centimetre; between these we pour the solution to be considered. Since all the ions are either attracted or repelled by the electrodes, and since they all take part in transporting the current, the conductivity of the solution will be greater the more ions there are between the electrodes; two equivalents of the ions will give twice the conductivity of one equivalent.*

The conductivity will also depend on the amount of electricity which each ion can carry; this, however, is the same for all ions since they all carry 96 540 coulombs per equivalent. Finally, the conductivity is dependent on the velocity with which the ions move, i.e., is conditioned by the different degrees of friction which the ions must overcome as they move through the solution. If we represent by L the conductivity of our solution, by r the friction, and by m the number of equivalents present, then

$$L=\frac{m\times 96540}{r}.$$

If we represent by $\varLambda$ the reciprocal value of r multiplied by 96 540, then when $m=1$, i.e., when we are dealing with 1 equivalent of the ions, $L=\varLambda$. $\varLambda$ is called the equivalent conductivity. The equivalent conductivity of a salt is therefore equal to 1 when an electromotive force of 1 volt

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* "Gram equivalent," or simply "equivalent," is the number of grams of the substance obtained by dividing the atomic or molecular weight by the valence, i.e., it is mol (see p. 18) divided by valence. In other words, it is the weight in grams of a substance which carries a charge of 96 540 coulombs. The atomic weight of the bivalent element zinc, for instance, is 65.4 and its equivalent is 32.7 grs.

suffices to send a current of 1 ampere between two electrodes which are 1 cm. apart, when the solution between the electrodes contains 1 gram equivalent of each ion of the dissolved salt.*

In this definition no account is taken of the volume of the solution between the electrodes, the only provision is that they are 1 cm. apart. Whether the gram equivalent is present in a small or large volume of solvent the pull exerted on the ions by the electromotive force of the electrodes will always be the same, and the same is true of their velocities and electric charges. What has just been said in regard to the salts can be applied to each kind of ion. The conductivity of any sort of ion will be high according as its concentration is high and the less the friction is which the ion has to overcome in moving through the water.

Let $k^{\cdot}$ represent the conductivity of the cation, $m^{\cdot}$ the number of equivalents present, U its velocity (reciprocal of the friction), and $96\,540\ U = l_0'$, and let k', m', V, and l_0' be the corresponding values for the anion, then

Conductivity of the cation $= k^{\cdot} = m^{\cdot}U96\,540 = m^{\cdot}l_0^{\cdot}$,
“ “ “ anion $= k' = m'V96\,540 = m'l_0'$,
“ “ “ solution $= k = m^{\cdot}l_0^{\cdot} + m'l_0'$.

In the solution of a salt $m^{\cdot}$ is always equal to m', since the number of equivalents of cations must necessarily

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* Any changes at the electrodes brought about by the passage of the current and which may result in a back electromotive force are not considered in this definition. This phenomenon of "polarization" will be considered later. Any difficulty arising from this source can be avoided by suitable methods of measurement. See Book II,

equal the number of equivalents of anions; then if $m=m^{\cdot}=m'$,

$$k_0=m(l_0{}^{\cdot}+l_0{}'),$$

or if $m=1$ (1 equivalent in solution),

$$\Lambda_0=l_0{}^{\cdot}+l_0{}'.$$

Each ion, then, has a particular value l_0 known as the "molecular conductivity of the ion," and by adding them together the conductivity of any salt may be obtained.

Since the ions lead a rather independent life and any one ion bothers itself very little about what the others may be doing it follows that l_0 has the same value in all solutions.

To take an example, the conductivity of the $K^{\cdot}$ ion is 65.3, the molecular conductivity of KCl is 131.2, consequently the conductivity of the Cl' ion is $131.2-65.3=65.9$. Since the conductivity of NaCl is 110.3, we find that the value for the $Na^{\cdot}$ ion is $110.3-65.9=44.4$. Further, since the conductivity of $NaNO_3$ is 105.2 and therefore that of $NO_3{}'$ is 60.8, the conductivity of KNO_3 is $65.3+60.8=126.1$. This law, that *the conductivity of any one kind of ion is independent of the nature of the ions of opposite charge which may be present in a solution*, was called by its discoverer, Kohlrausch, the "*law of the independent wandering of the ions.*" A table of the values of l_0 for the different ions will be given in Book II. By adding the different values of l_0 we obtain the value of Λ_0 for any salt.

Thus far we have considered only solutions containing a known quantity of ions. But in general we are not sure of the quantity of ions present, we simply know the total quantity of salt. As we saw on p. 48, however, all salts are not entirely dissociated into ions, but only to an extent which generally represents a large fraction of the whole. This fraction can be determined by measurements of the osmotic pressure, or of the freezing- or boiling-points of the solution. Let α be the degree of dissociation for the concentration η mol per c.c., i.e., for every mol present α mols have dissociated into ions and the salt is $100\alpha\%$ dissociated. For every mol present then $1-\alpha$ mols remain as undissociated salt, and we find as the conductivity of the solution, not $k_0 = m(l_0^{\cdot} + l_0')$, but $k = m\alpha(l_0^{\cdot} + l_0')$.

Thus far we have not considered any particular volume of solution between the electrodes. The specific conductivity of our solution (cf. p. 79) is $\kappa = \frac{kl}{q}$, where q is the cross-section. Since in this particular case $l = 1$, the volume of the solution, $v = q$ and $k = \kappa v$. Further, the concentration in mols per c.c. is

$$\eta = \frac{m}{v}.$$

$$\therefore\ \kappa v = \eta v \alpha(l_0^{\cdot} + l_0') \quad \text{or} \quad \kappa = \eta\alpha(l_0^{\cdot} + l_0'),$$

or if $\eta = 1$ mol per c.c.,

$$\Lambda_\eta = \alpha(l_0^{\cdot} + l_0').$$

Λ_η is called the equivalent conductivity of the salt for the concentration η. This equation is used very often to determine the degree of dissociation. We measure the specific conductivity of the solution and divide this by the equivalent concentration of the solution, i.e., $\frac{\kappa}{\eta} = \Lambda_\eta$, and this gives the equivalent conductivity. We then introduce the values for $l_0^{\cdot}$ and l_0' from the table mentioned on p. 85 and obtain

$$\alpha = \frac{\Lambda_v}{l_0^{\cdot} + l_0'} = \frac{\Lambda_v}{\Lambda_0}.$$

Λ_0 is the equivalent conductivity of the salt when it is completely dissociated into its ions.

From what has been said it is clear that the value of $\Lambda_0 = l_0^{\cdot} + l_0'$ can only be found when $\alpha = 1$; that is, when all the dissolved molecules are dissociated into their ions. Such solutions, however, do not exist in reality, since the reaction of dissociation is incomplete and proceeds until a state of equilibrium is reached.

Nevertheless the law of the independent wandering of the ions holds for solutions when dissociation is not complete. Dissociation is, in a way, an additive property, and there is a law of independent dissociation of the ions which, while not as exact and of such general application as the other, is still of great use in calculation. It states that the degree of dissociation of a dissolved substance may often be calculated from numbers which are peculiar to each ion. From the two laws it follows that the values of $\alpha l_0^{\cdot}$ and $\alpha l_0'$ are definite for a given concentration. Let $\alpha l_0^{\cdot} = l_c^{\cdot}$ and $\alpha l_0' = l_c'$ be the conductivities of the ions at the concentration c and we obtain for the equivalent conductivity at the concentration c:

$$\Lambda_c = l_c^{\cdot} + l_c';$$

i.e., the equivalent conductivity at the concentration c is equal to the sum of the conductivities of the ions. It must always be kept in mind that the degree of dissociation is always included in the values of $l_c^{\cdot}$ and l_c', but not in the values of $l_0^{\cdot}$ and l_0'. A complete table of the values of l for all ions and for all concentrations is given by Kohlrausch and Holborn.[*] This table is also given in Book II of this series.

The question now arises, how are the values of l_0 and l determined experimentally? On measuring the equivalent conductivity of a n[†] KCl solution we find it to be 98.2, then

$$\Lambda_{KCl}=l_K+l_{Cl}=98.2.$$

Using a n NaCl solution we find

$$\Lambda_{NaCl}=l_{Na}+l_{Cl}=74.4;$$

also

$$\Lambda_{NaNO_3}=l_{Na}+l_{NO_3}=66.0,$$

$$\Lambda_{AgNO_3}=l_{Ag}+l_{NO_3}=67.8.$$

In these four equations there are five unknown quantities, l_K, l_{Na}, l_{Ag}, l_{Cl}, l_{NO_3}, and without further data the single values cannot be found. The fifth necessary equation is furnished by measuring the "transport number," which gives the value of

$$\frac{l'}{l^{\cdot}+l'}=n.$$

For the transport number of KCl,

$$n_{KCl}=\frac{l_{Cl}}{l_K+l_{Cl}}.$$

The value 0.503 has been found by experiment.

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[*] Kohlrausch and Holborn, Leitvermögen des Elektrolyt. Teubner, Leipzig.

[†] The letter n means "normal." 0.1 n is tenth normal; 3 n is three times normal; etc.

From this, and from the conductivity of a normal KCl solution, $\Lambda_{KCl} = l_K + l_{Cl} = 98.2$, the value of l_{Cl} is found to be 49.4.

With the help of this figure we obtain the following values for the conductivities of the five unknown quantities

l_K	l_{Cl}	l_{Na}	l_{NO_3}	l_{Ag}
48.8	49.4	25.0	41.0	26.8

In exactly the same way the values for l may be found for other concentrations, for instance, for 0.01 n they are

61.3 62.0 40.5 56.8 51.9.

It must not be forgotten that these numbers represent not the velocities of the ions alone, but the velocities multiplied by the degree of dissociation.

In order to determine the values of $l_0^{\cdot}$ and l_0' we must know the value of Λ_0. This cannot be measured directly, since dissociation is complete only at an infinite dilution. If we plot the value of Λ in its dependance on the concentration we obtain a curve similar to Fig. 6. In this the abscissæ represent the dilution and the corresponding equivalent conductivities are plotted as ordinates. As

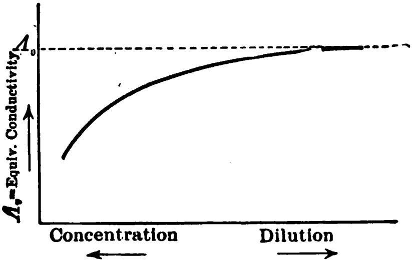

FIG. 6.

the dilution increases the curve approaches asymptotically a maximum which we cannot reach experimentally, but which may be found by extrapolation. In this way it is possible to determine the value of Λ_0. Since the transport number remains essentially the same for all concentrations we may use the value found to calculate l_0,

$$l_0' = n\Lambda_0 \quad \text{and} \quad \Lambda_0 - l_0' = l_0^{\cdot}.$$

Pure substances conduct poorly: the specific conductivity of ordinary distilled water at 18° is about 10^{-6}. But even this low conductivity is not the conductivity of pure water, but is due almost entirely to small amounts of dissolved substances. Although the amount of these dissolved impurities may be so small as to escape any chemical tests, still they have a very marked influence on the conductivity. Glass may be dissolved to a very slight extent by water, also carbon dioxide from the air when dissolved in water furnishes ions which may impart a marked conductivity to the water.

By very careful distillation and other methods, Kohlrausch was able to obtain water so pure that its specific conductivity was only 0.0384×10^{-6}. Probably a part of even this low figure is due to dissolved impurities, but in any case not a very large part, as the following calculation shows: From the specific conductivity κ (= reciprocal of the resistance of a centimetre cube of water) and the values of the velocities of the ions $H^{\cdot}$ and OH',

$$\kappa = m(l_H + l_{OH}) = 0.0384 \times 10^{-6} = m(318 + 174),$$

we obtain as the number (m) of $H^{\cdot}$ and OH' ions in 1 c.c. of this water $m = 0.78 \times 10^{-10}$. In 1 litre, then, the concentration of $H^{\cdot}$ and OH' ions is 0.78×10^{-7} at 18°. The fact that several other methods for determining the value of this concentration have given as an average 0.78×10^{-7} at 18° proves that 0.0384×10^{-6} must be very nearly the actual conductivity of absolutely pure water.

A number of other pure substances behave in a similar way at ordinary temperatures. They have a very low conductivity and consequently can contain very few ions. For instance, pure anhydrous sulphuric acid is very weakly dissociated according to the scheme

$$H_2SO_4 \rightleftarrows 2H^{\cdot} + SO_4''$$

when the two pure substances H_2O and H_2SO_4 are mixed; i.e., if H_2SO_4 is dissolved in water, the resulting solution conducts more or less readily.

According to the views developed in the preceding pages, the reason for this is that the pure substances alone contain very few ions, but mixing or dissolving the two substances in some way gives rise to the formation of a large number of ions.

An instructive example of this general fact is furnished by the conductivity of sulphuric acid of different strengths. The accompanying curve (Fig. 7) shows the relation between the concentration and conductivity of H_2SO_4, conductivity being plotted on the vertical axis and concentration on the horizontal.

At the concentration zero, i.e., in pure water, the conductivity is practically zero. As the concentration of H_2SO_4 increases, the conductivity increases rapidly and at 32% reaches a maximum. It then falls off until at 82% a minimum is reached, the solution at this point having a composition corresponding to the formula $H_2SO_4 \cdot H_2O$.

This monohydrate is to be considered as a comparatively poor conductor. When more sulphuric acid is added the curve rises again (the following solutions may be considered as a solution of H_2SO_4 in the hydrate, $H_2SO_4 \cdot H_2O$), at 92% reaches a maximum and then falls off practically to 0 at 100%. If SO_3 is added to the anhydrous H_2SO_4 a new curve with another maximum is obtained, as shown in the figure above 100%.

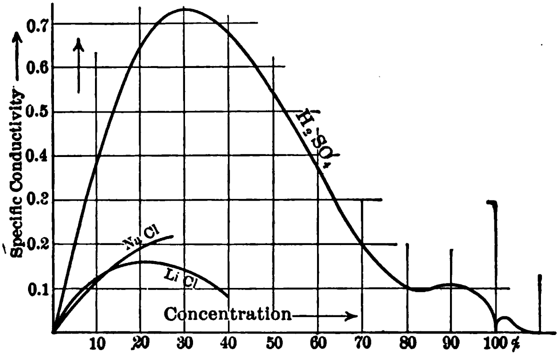

FIG. 7.

Solutions of all other conducting substances behave in a similar way, although frequently the solubility is not high enough to allow the maximum conductivity to be attained, as the curve for NaCl shows (Fig. 7). The more soluble LiCl, however, shows the maximum.

The question now arises, does a conducting solution, i.e., one containing many ions, always result from the mixture of two different substances? This must be answered in the negative. The dissociation depends on the nature of the two components of the solution. Water possesses the property of forming with most of the acids, bases, and salts solutions which conduct very well; i.e., it compels the dissociation of these substances. We say that water has a great "dissociating power"; but all substances dissolved in it are not necessarily dissociated. For instance, sugar, urea, boric acid, and many organic substances when dissolved in water give non-conducting solutions, which therefore contain no ions.

Another class of substances, the alcohols, are good solvents, though by no means as good as water; their solvent power decreases with an increase in molecular weight. Liquid ammonia is almost as good a solvent as water; it dissolves many substances and gives solutions which conduct very well.

In order to compare solvents with respect to their dissociating power two points must be kept in mind. The conductivity of a solution is dependent not only on the degree of dissociation of the dissolved electrolyte but also on the resistance or friction which the ions must overcome in moving through the solution. A solvent of low dissociating power may give a solution of higher conductivity than a second solvent whose dissociating power is greater. If the friction which the ions have to overcome in one solution is low enough, this may more than compensate for the larger number of ions in the other solution. Water and liquid ammonia are two such solvents: the first possesses the higher dissociating power, but the latter presents much less resistance to the movements of the ions, as might be expected from the mobility and volatility of liquid ammonia.

Nernst has proposed the following explanation of the ability of different solvents to dissociate dissolved salts into the ions. The electrostatic attraction of the oppositely charged ions must evidently tend to diminish the dissociation of a given salt, and acts in opposition to that force which strives to dissociate the compound, and whose nature is as yet entirely unknown. The rivalry between these two opposing forces regulates the actual equilibrium of dissociation. The dissociation must therefore increase if the electrostatic attraction is diminished. The study of static electricity has shown that two bodies having opposite charges of electricity attract each other with a force which varies inversely with the dielectric constant of the medium which surrounds the bodies. According to this view those solvents which have the highest dielectric constant must have the highest dissociating power. This rule, which was proposed simultaneously by Thomson and Nernst, holds very well in most cases, as is shown by the following table of Nernst.*

Medium	Dielectric Constant	Electrolytic Dissociation
Gases.	1.0	Immeasurable at ordinary temperature
Benzol.	2.3	Conductivity extremely low, indicating very slight dissociation
Ether.	4.1	Perceptible conductivity of dissolved electrolytes
Alcohol.	25	Moderate dissociation
Formic acid.	62	Strong dissociation
Water.	80	Very strong dissociation

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* The values of the different dielectric constants and a table showing the relation between the dissociating power and a number of the physical properties of the different solvents will be given in Book II.

Apparently most of the physical properties of solvents, such as "association," dissociating power, etc., are in some way connected. Dutoit and Aston have found that solvents with a high dissociating power are in general inclined to polymerization in the liquid state. Polymerization is generally noticed in the case of substances which contain an element of variable valence, such for instance as NH_3, which contains the tri- or pentavalent element N or H_2O, which contains the di- or tetravalent element oxygen. The occurrence of these elements in a compound therefore would seem to be connected with the dissociating power.

Aside from the dissociating power and internal friction there are other influences at work concerning whose nature we are completely in the dark. Formic acid, for instance, has a dielectric constant of 62, and accordingly should have a high dissociating power, nevertheless HCl dissolved in formic acid gives a practically non-conducting solution, although salts like NaCl, KBr, etc., conduct very well in formic acid. In this case the hydrochloric acid probably unites directly with the formic acid and is therefore unavailable for conducting purposes. In general the dissociation depends not only on the solvent but also on the nature of the dissolved substance. The tendency of the different elements and radicals to take up an electric charge—a tendency which makes itself evident in the electromotive force of the elements—and the ease or difficulty with which they may be deposited on an electrode, plays an important part in determining the relative dissociation. The tendency of elements to pass into the ionic condition is closely related to the general chemical properties of the elements, and thus the degree of dissociation becomes an important factor in determining the chemical activity of a dissolved substance. We must therefore consider the relations of dissociation somewhat more fully.

As we have seen on p. 87, the degree of dissociation is calculated according to the equation $\alpha = \frac{\Lambda_c}{\Lambda_0}$. The following table shows how the degree of dissociation of certain typical electrolytes when dissolved in H_2O changes with the concentration.

$c = 1/v$	HCl	KOH	KCl	$KC_2H_3O_2$	$\frac{1}{2}BaCl_2$	$\frac{1}{2}K_2SO_4$	$\frac{1}{2}ZnSO_4$	CH_3COOH	NH_4OH
0.0001	—	—	0.992	0.990	0.992	0.992	0.989	0.308	0.28
0.001	0.992	0.998	0.979	0.973	0.962	0.959	0.890	0.118	0.119
0.01	0.974	0.973	0.941	0.931	0.886	0.873	0.664	0.041	0.041
0.1	0.924	0.860	0.861	0.830	0.759	0.713	0.418	0.013	0.014
1	0.792	0.786	0.755	0.628	0.579	0.534	0.241	—	—

The first vertical column contains the concentration *c* (reciprocal of the dilution), the others contain the degree of dissociation of the different substances at these particular concentrations. HCl is dissociated the most, and the dissociation of the other strong monobasic acids as HNO_3, HClO, HBr, HI, etc., follows that of HCl closely; the bases NaOH. KOH, LiOH, TlOH, etc., are also just as highly dissociated. The 1 : 1 salts are slightly less dissociated; still less the 1 : 2 salts, while the 2 : 2 salts like $ZnSO_4$ are the least dissociated.*

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* By a 1 : 1 salt is meant one derived from a monobasic acid and a

The strength of the acid and base from which the salt is derived has considerable influence on the degree of dissociation. The *K* salt of the weak acetic acid is less dissociated than the corresponding salt of the stronger hydrochloric acid. This fact is still more evident when we compare the acids and bases themselves, for instance, acetic with hydrochloric acid; ammonia with potassium hydroxide; etc. Since the $H^{\cdot}$ ion is common to all acids and always has the same tendency to take up an electric charge the difference in the degrees of dissociation can only be due to the fact that chlorine has a much higher tendency to pass into the ionic condition than the acetic-acid radical, i.e., it has a higher " electro-affinity."

Strength of Acids and Bases.

The degree of dissociation is of the highest importance in determining the chemical activity of an acid or base. The common characteristic of all acids is the formation of $H^{\cdot}$ ions in a water solution, consequently in all reactions which may be brought about by any acid and which therefore depend on the presence of the $H^{\cdot}$ ion, the concentration of the $H^{\cdot}$ ion is of decisive importance. In a similar way the common property of all bases is their ability to form OH' ions in a water solution, consequently the bases will act more vigorously according as their degree of dissociation is high or low.

The strength of a base or acid makes itself felt in the reaction of distribution. If we add to a solution of NH_3

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monacid base; 1:2 are derived from a monobasic acid and diacid base, or vice versa, as $BaCl_2$, or Na_2SO_4, etc. 2:2 are such as $ZnSO_4$, $MgCO_3$, etc.

and KOH an amount of HCl which is less than sufficient to neutralize both bases, this acid will be distributed between the two bases. Both potassium and ammonium chloride will be formed, but more of that salt whose base is the stronger. In the same way a base is distributed between two acids, so that the larger part falls to the lot of the stronger acid. Further, if we add to the salt of a weak base, such as NH_4Cl, the stronger base KOH, a redistribution of the HCl takes place, the KOH takes the acid from the ammonia, the latter is set free and may be driven out of the solution by boiling. Still further, if we add hydrochloric acid to a solution of sodium acetate the HCl displaces the acetic acid. In all these cases, however, the displacement takes place only till a state of equilibrium is reached, and this equilibrium is determined by the value of the dissociation constants of the acids and bases.* It has been found that the ratio of distribution is equal to the ratio of dissociation of the two acids or bases at the dilution in question.

The strength of an acid also makes itself felt in a certain class of reactions which are "catalytically" accelerated by the presence of $H^{\cdot}$ ions. Such a reaction is the inversion of cane-sugar into levulose and dextrose, which causes a good deal of trouble in the refining of sugar, since the two resulting compounds are very hard to crystallize. The reaction

$$C_{12}H_{22}O_{11}+H_2O=2C_6H_{12}O_6$$

proceeds very slowly in a neutral solution, but is greatly accelerated by the presence of acids. This catalytic

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* For the relation between the dissociation constant and the distribution, cf. Nernst, Theoretische Chemie, 1903, p. 506.

acceleration is greater according to the number of $H^{\cdot}$ ions which a given acid can supply; in other words, the acid accelerates this reaction more or less according as it is strongly or weakly dissociated. If the acids are arranged in the order of their conductivity this same order represents also their relative activity in accelerating the inversion of sugar. A similar case is furnished in the decomposition of the ester:

$$CH_3COOC_5H_{11} \rightleftarrows CH_3COOH + C_5H_{10}.$$

This reaction is accelerated to a different degree by strongly and weakly dissociated acids.

The strength of a base regulates the velocity of the reaction of saponification. The higher the dissociation of a base the faster it will saponify the ethereal salts of the fatty acids.

As yet we have considered the connection between the dissociation and strength of an acid or base only in a qualitative way. How can we obtain definite quantitative relations?

The law of mass action applies to the reaction of dissociation, as it does to all reactions. If we write the equation for the dissociation of acetic acid,

$$CH_3COOH \rightleftarrows CH_3COO' + H^{\cdot},$$

and apply to this the mass-action law we have

$$c_s = Kc_i^2.$$

c_s represents the concentration of the undissociated molecules and c_i that of the ions. (In any solution the concentration of the two different kinds of ions must necessarily be equal.) K is the dissociation constant. If the value of K is known for any acid or base the value of the dissociation may be at once calculated for any dilution, and also the conductivity, if the values of l_0 and l_0' are known. van't Hoff and Reiche give the following table for acetic acid:

MOLECULAR CONDUCTIVITY OF ACETIC ACID AT 14.1°.

v	Λ_v	100α Observed	100α Calculated	
0.994	1.27	0.402	0.42	
2.02	1.94	0.614	0.60	
15.9	5.26	1.66	1.67	
18.9	5.63	1.78	1.78	$K=0.0000178$
1500	46.6	14.7	15.0	$\log K=5.25-10$
3010	64.8	20.5	20.2	$\Lambda_0=316$
7480	95.1	30.1	30.5	
15000	129	40.8	40.1	
[∞	316	100	100]	

The first column contains the dilution in litres per mol, the second the observed molecular conductivities Λ_v, the third the value of α calculated from the conductivity measurements by means of the formula $\alpha=\frac{\Lambda_v}{\Lambda_0}$. In the fourth column are the values of α calculated from the equation $Kv(1-\alpha)=\alpha^2$, using 0.0000178 as the value of K. The equation $c_s=Kc_1^2$ is identical with this since $c_s=\frac{1-\alpha}{v}$ and $c_1=\frac{\alpha}{v}$. In regard to the physical significance of K the following may be said: in the case of a binary electrolyte (i.e., one which dissociates into two ions) K is equal to half the concentration at which the electrolyte is 50% dissociated.*

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* This is readily shown by substituting 0.5 for α in the equation.

Strange to say, this law, which was first derived by Ostwald and is known as the Ostwald dilution law, holds only for electrolytes which are weakly dissociated. It does not at all fit the case of highly dissociated salts. A possible reason for this is the following: in calculating the dissociation we tacitly assumed that the mobilities of the ions $l_0^{\cdot}$ and l_0' were independent of the concentration, and that the friction they meet with on the part of the solvent is not affected by the presence of the undissociated molecules and other ions. Since Ostwald's law holds for weak electrolytes where a great many undissociated molecules are present, it has been argued that these must be without effect on the velocity of the ions. In the case of the strongly dissociated salts where very many ions are present some disturbing factor is present, and it seems as if the ions have some mutual influence on each other's velocity. Still it is quite possible that the undissociated molecules have a favorable effect on the mobility of the ions; with a slightly dissociated electrolyte, where the relative number of undissociated molecules is only slightly increased as the concentration increases, this may have an unnoticeable effect on the value of K, but with a strong electrolyte the effect may be very great. The whole matter has not yet been satisfactorily cleared up.

From the law of mass action the following rule has been derived: For a binary electrolyte the ionic concentration, and consequently the conductivity, is proportional to the square root of the total concentration when the electrolyte is not very strongly dissociated.

For highly dissociated electrolytes van't Hoff has found empirically that the following expression holds true:

$$\frac{c_i^3}{c_s^2}=\text{a constant},$$

and from this the conductivity may be calculated. According to this the cube of the concentration of the ions is proportional to the square of the concentration of the undissociated molecules.

The dissociation constants of different electrolytes may have widely differing values, as the following table of " affinities " of a number of acids and bases shows:

	K
Acetic acid, CH_3COOH	0.0000180
Mono-chlor-acetic acid, $CH_2ClCOOH$	0.00155
Tri-chlor-acetic acid, CCl_3COOH	1.21
Ammonia, NH_4OH	0.000023
Methylamine, NH_3CH_3OH	0.00050
Aniline, $NH_3C_6H_5OH$	1.1×10^{-10}
Carbonic acid, HCO_3H	3040×10^{-10}
Hydrogen sulphide, HSH	570×10^{-10}
Boric acid, H_3BO_3	17×10^{-10}
Prussic acid, CNH	13×10^{-10}
Phenol, C_6H_5OH	1.3×10^{-10}

One very important consequence of the law of mass action is the following: the dissociation of acetic acid follows the equation

$$CH_3COOH \rightleftarrows CH_3COO' + H^{\cdot}.$$

The law of mass action requires

$$^{*}K[CH_3COOH]=[CH_3COO'][H^{\cdot}].$$

If an excess of either of the ions is introduced into the solution of acetic acid, for instance CH_3COO', by the

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* The concentration of any compound or radical is indicated by enclosing the symbol in brackets.

addition of CH_3COONa or $H^{\cdot}$ by addition of a strong acid, the equilibrium is disturbed. The right-hand side of the equation becomes too large and in order for K to remain constant the dissociation must decrease.

If two solutions have a common ion and their concentration with respect to this ion are the same, then their solutions may be mixed and no change in the state of dissociation of either of the substances will occur; such solutions are called "isohydric."

Two solutions of acids whose dissociation follows the law of mass action—for instance acetic and propionic acids—are without effect on their mutual dissociation, i.e., are isohydric when their concentrations stand in the inverse ratio of their dissociation constants.

This forcing back of the dissociation by the addition of a solution containing a common ion is of great importance in many analytical operations. The theory of dissociation has explained the mode of action of many empirical chemical receipts. For instance, the dissociation of a normal solution of acetic acid is 0.4%, but this is reduced to 0.0018% if a gram equivalent of sodium acetate is added to the solution. Since the strength of the acid, or the intensity with which it takes part in reactions or accelerates them (cf. the inversion of sugar, p. 98) is determined by the concentration of the $H^{\cdot}$ ions, it is evident that acetic acid is very much weakened by the addition of CH_3COONa. The same is true of other acids and bases. For instance, the precipitation of ZnS by H_2S is prevented by the addition of acid, for the $H^{\cdot}$ ions of the acid cause a great decrease in the dissociation of the H_2S with a consequent decrease in the number of S'' ions. For the same reasons the precipitation of $Mg(OH)_2$ by NH_4OH is prevented by the previous addition of ammonium salts. The forcing back of the dissociation is also of great importance in all reactions of precipitation. If we wish to precipitate $Ag^{\cdot}$ ions by Cl' ions and add an amount of chlorine which is exactly equivalent to the silver, then a quantity of silver corresponding to the solubility of AgCl remains in solution. This is 0.000011 mol., i.e., a saturated solution of AgCl contains $0.000011 \times 108 = 1.2$ mgr. of silver. In washing a silver-chloride precipitate an appreciable error might be introduced owing to the solubility of the precipitate. The law of mass action requires for the reaction of solution

$$K[AgCl_{solid}] = [AgCl_{dissolved}] = 0.000011.$$

In this very dilute solution we may assume that the dissociation is practically complete, so that

$$AgCl_{dissolved} = Ag^{\cdot} + Cl'.$$

Then

$$L = [Ag^{\cdot}][Cl'] = (1.1 \times 10^{-5})^2 = 1.21 \times 10^{-10}.$$

L is the "solubility product" of silver chloride. If we add KCl so that the solution is normal with respect to the chlorine ions, then, since L is a constant, the concentration of the silver ions will be reduced to 1.2×10^{-10}, a value too small to be of any analytical importance. It is customary therefore to add an excess of KCl for the precipitation, and to wash with a solution containing Cl' ions, as dilute HCl. For similar reasons a number of sulphide precipitates are washed with water containing H_2S.

These facts may easily be demonstrated in the case of $PbCl_2$. If a few drops of a strong solution of NaCl are added to a saturated solution of $PbCl_2$, a heavy white precipitate forms; the dissociation is forced back by the addition of the chlorine ions and more undissociated $PbCl_2$ results than corresponds to the solubility, and this excess appears as a precipitate.

The examples cited above of the precipitation of $Mg(OH)_2$ by ammonia and of ZnS by H_2S depend on the reverse process. The addition of an ammonium salt to the ammoniacal magnesium salt solution robs the NH_4OH of a large share of its basic nature; OH' ions and $NH_4^{\cdot}$ ions can only exist in a solution in such amounts as are governed by the dissociation constant of NH_4OH. On adding $NH_4^{\cdot}$ ions in the form of a salt, the concentration of the OH' ions is greatly reduced, and consequently in the mass action equation

$$K[Mg(OH)_2]=[Mg^{\cdot\cdot}][OH']^2$$

the right-hand side becomes too small, and therefore much more $Mg^{\cdot\cdot}$ will go into solution than if no NH_4 salt were present.

The quantitative relations may be obtained when we consider the matter as a question of distribution (p. 97). When a strong base such as NaOH is added to a Mg salt, the anion of the Mg salt is distributed between both the Na and the weaker Mg, consequently a large amount of $Mg(OH)_2$ is formed and appears as a precipitate. The NH_4OH, however, which has been weakened by the addition of NH_4 salt, is no longer able to displace the Mg from its salts.

As yet we have considered only such dissociations as take place according to one equation. But with many salts two stages in the dissociation are possible. The most important example is water, which dissociates according to the two equations

$$(1)\quad H_2O \rightleftarrows H^{\cdot} + OH',$$

and

$$(2)\quad H_2O \rightleftarrows H^{\cdot} + H^{\cdot} + O''.$$

The second dissociation, however, takes place to a very slight extent, or, as we may also put it, the dissociation constant of the second $H^{\cdot}$ ion is very much smaller than that of the first. Similar reactions are possible with many other substances, for instance

$$(1)\quad H_2SO_4 \rightleftarrows H^{\cdot} + HSO_4',$$

$$(2)\quad H^{\cdot} + HSO_4' \rightleftarrows H^{\cdot} + H^{\cdot} + SO_4''.$$

$$(1)\quad BaCl_2 \rightleftarrows BaCl^{\cdot} + Cl',$$

$$(2)\quad BaCl_2 = Ba^{\cdot\cdot} + Cl' + Cl'.$$

It sometimes happens that two molecules unite and then dissociate by "steps." With $CdCl_2$ the following modes of dissociation are possible:

$$CdCl_2 \rightleftarrows CdCl^{\cdot} + Cl',$$

$$CdCl_2 \rightleftarrows Cd^{\cdot\cdot} + Cl' + Cl',$$

$$2CdCl_2 \rightleftarrows Cd_2Cl_3^{\cdot} + Cl',$$

$$2CdCl_2 \rightleftarrows Cd_2Cl_2^{\cdot\cdot} + Cl' + Cl'$$

$$2CdCl_2 \rightleftarrows Cd^{\cdot\cdot} + CdCl_4'',$$

$$2CdCl_2 \rightleftarrows CdCl^{\cdot} + CdCl_3', \text{ etc.}$$

This polymerization of the molecules is the cause of many of the deviations from the laws of solutions.

Conductivity and Temperature.

The temperature has a great effect on the conductivity of the electrolytes, and the temperature coefficient is practically always positive, i.e., the conductivity increases as the temperature rises. Two causes must be distinguished. The dissociation of most salts decreases as the temperature rises, and this decrease though generally small should lower the conductivity. On the other hand, the mobility of the ions is much increased and this tends to increase the conductivity.

The temperature coefficient of most salts in water has such a value that at about $-30°$ the conductivity would be zero. Since the fluidity of water (reciprocal of the internal friction) follows a temperature formula which also gives zero as the value for $-30°$, it seems clear that the influence of temperature on the conductivity is due to the effect of the temperature on the internal friction of water.

At ordinary temperatures the temperature coefficient of dilute solutions of salts is from 0.02 to 0.023, i.e., the conductivity is raised by $2-2.3\%$ for 1 degree rise in temperature. For acids and some acid salts the coefficient is 0.009 to 0.016, for alkalies it is 0.019 to 0.02.

The temperature coefficient depends but little on the concentration. In nearly all cases it decreases slightly as the concentration rises, and then rises again at higher concentrations. With certain salts such as the chlorides and nitrates of K and NH_4 the decrease persists even in the stronger solutions.*

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* A classic work on the conductivity of the electrolytes is the book by Kohlrausch and Holborn, published by Teubner of Leipzig, which

The high temperature coefficient of substances which conduct electrolytically is of especial importance in the case of solid salts. At ordinary temperatures these are practically non-conductors, but at higher temperatures the conductivity increases greatly, and salts in a state of fusion are among the best conductors. Even solid substances when highly heated may show considerable conducting power. A good example is furnished by the "glower" of the Nernst light.

The Transport Number.

We will consider first a binary electrolyte, say NaCl. If we send a unit quantity of electricity through this solution both ions take part in transporting the current, and since the concentrations of the two ions are equal and the pull exerted by the electrodes is the same for both, the part taken by each in the conduction will be proportional to the velocity of the ions. If E' is the quantity of electricity transported by the anion and $E^{\cdot}$ the part transported by the cation, then

$$E' + E^{\cdot} = E \quad \text{and} \quad E' : E^{\cdot} = V : U,$$

where U and V are the velocities of the cation and anion respectively. We then obtain

$$E' : E = V : U + V \quad \text{and} \quad E^{\cdot} : E = U : U + V.$$

The phenomena attending the passage of the current will be better understood from Fig. 8. A tube which is divided into three compartments by two porous diaphragms contains at one end the anode and at the other

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contains the theory of the methods of measurement and extended tables.

the cathode. At first the electrolyte has the same concentration throughout the tube as is indicated by the upper series of ± signs. Every ± sign represents a gram-molecule of salt, the + signs represent the cations, and the − signs the anions. Let us assume that the velocity of the cation is to that of the anion as 5 : 3. We send 16 *F** through the solution, which results in the separation of 16 mols of cations at the cathode and 16 mols of anions at the anode.

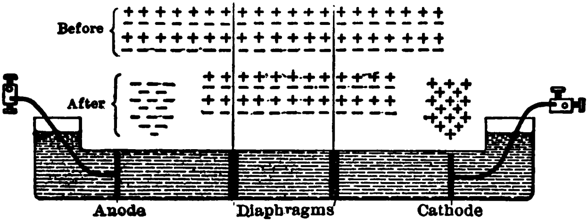

FIG. 8.

In the actual transporting of the current the ions take part in the ratio of their velocities, i.e.,

$$E^{\cdot} : E' = 10\,F : 6\,F$$

$$E^{\cdot} : E = 10\,F : 16\,F$$

$$E' : E = 6\,F : 16\,F.$$

While the + ions all move 5 units of length in one direction the − ions move 3 units in the other. The final distribution is shown by the lower series of ± signs of Fig. 8. It is seen that 16 mols have been set free at each electrode, the concentration in the middle compartment

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* In honor of Faraday the charge on 1 gr. equivalent of ions or 96 540 coulombs is represented by *F*.

remaining unchanged, while that in each electrode compartment has changed to a different degree. The changes in the salt concentration in each of the electrode compartments are to each other as the velocities of the ions which have left those compartments. In this case the change at the cathode is to the change at the anode as the velocity of the anion is to the velocity of the cation or as 3 is to 5.

The value of $\frac{U}{V}$ can therefore be found by sending a known quantity of current through a suitable form of apparatus and determining before and after the concentrations in the electrode compartments. The fact that the concentration in the middle compartment does not change is a proof that diffusion has not influenced the result.*

The above method only applies when the ions are precipitated or otherwise removed from the solutions. If instead of the ion which has transported the current, some other ion is set free, it is necessary to calculate by Faraday's law (p. 52) how much of the first ion should have been removed by the electrolysis and subtract this from the concentration found before we can tell how the concentration has been affected by the wandering of this ion.

If the original concentration is c, and the concentrations after electrolysis are $c^{\cdot}$ at the cathode and c' at the anode. so that the losses at the electrodes are $c-c^{\cdot}$ and $c-c'$ respectively, then

$$V:U=c-c^{\cdot}:c-c'.$$

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* For more detailed information concerning the methods of measurement and calculation of results cf. Book II.

$U:V$ is the ratio between the velocities of the two ions. Hittorf (1856), who was the first to investigate this subject, called the fraction $\frac{V}{U+V}=n$ the "transport number of the anion." Since $\frac{V}{U+V}$ and $\frac{U}{U+V}$ together are equal to one, $\frac{U}{U+V}=1-n$ is the transport number of the cation.

With the help of this new term we may now summarize the most important formulæ concerning the conductivity of an electrolyte. If η represents the concentration in mols per c.c., α the degree of dissociation, then $\alpha\eta$ is the concentration of the ions and the specific conductivity κ is

$$\kappa=\alpha\eta F(U+V).$$

Putting $l_0^{\cdot}=FU$ and $l_0'=FV$ (cf. p. 84), then

$$\kappa=\alpha\eta(l_0^{\cdot}+l_0').$$

Now the molecular conductivity is $\Lambda=\frac{\kappa}{\eta}$ and we obtain $\Lambda=\alpha(l_0^{\cdot}+l_0')$. At very great dilutions $\alpha=1$, consequently if we represent by Λ_0 the molecular conductivity at extreme dilutions then $\Lambda_0=l_0^{\cdot}+l_0'$.

$$l_0'=n\Lambda_0 \quad \text{and} \quad l_0^{\cdot}=(1-n)\Lambda_0.$$

These last equations are the mathematical expression of Kohlrausch's law of the independent wandering of the ions.

Absolute Velocity of the Ions.

The velocities or mobilities $l^{\cdot}$ and l' are based on the ohm as the unit of resistance (cf. p. 79). In order to obtain U and V, the acutal velocities in centimetres per second with which the ions move in a field where the fall of potential is 1 volt per centimetre, we must remember that each gram equivalent of ions carries with it 96 540 coulombs, and since the conductivities $l_0^{\cdot}$ and l_0' represent velocity×charge we have

$$96\,540(U+V)=l_0^{\cdot}+l_0'.$$

Accordingly we obtain the actual velocities U and V in centimetres per second by dividing the mobilities l by 96 540. For infinite dilution the following are the calculated absolute velocities of some of the ions at 18°.

U of $K^{\cdot}$ = 0.000669 cm.
U " $NH_4^{\cdot}$ = 0.000667 "
U " $Na^{\cdot}$ = 0.000450 "
U " $Li^{\cdot}$ = 0.000346 "
U " $Ag^{\cdot}$ = 0.000559 "
U " $H^{\cdot}$ = 0.003415 "
V " Cl' = 0.000667 "
V " NO_3' = 0.000640 "
V " ClO_3' = 0.000570 "
V " OH' = 0.001802 "

It is possible to calculate the force which must be exerted on an ion to give it a velocity of 1 centimetre per second. This force is about 10^{10}, i.e., a force represented by the weight of 10 000 000 000 kilograms. We may easily see that such a force is necessary when we remember that a finely divided precipitate often requires many hours to settle, on account of the friction against the solvent which the particles must overcome. It is not surprising therefore that the ions, which are very many times smaller than the finest particle of a precipitate, meet with such an enormous friction. The actual velocities of the ions are capable of direct measurement by a method first worked out by Whetham and Masson, and later improved by Abegg and Steele. The observed and calculated results are in perfect agreement.*

Dielectric Constants.

Two bodies carrying an opposite charge of electricity attract each other, and the force of this attraction varies with the nature of the medium surrounding the two bodies. If k is the attraction when the bodies are placed in a vacuum and k' the attraction in some other medium, then the dielectric constant DC of this medium is given by $DC = \frac{k}{k'}$. For the vacuum $DC = 1$ and is but slightly greater than 1 for the different gases. In water the attraction is $\frac{1}{80}$ of that in a vacuum, i.e., the dielectric constant of water is 80.

The capacity of a condenser, i.e., the quantity of electricity which it is necessary to add in order to give the two plates a difference of potential of 1 volt, varies directly with the dielectric constant of the medium which occupies the space between the two plates of the condenser. If c is the capacity when air is used, the capacity is cDC

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* For details cf. Book II.

when a substance whose dielectric constant is DC is used.

According to the theory of electric vibrations the velocity with which electric waves travel along wires varies inversely as the square root of the dielectric constant of the surrounding medium.

The methods of measuring the dielectric constant are founded on these two laws. The quantity of electricity is measured which is necessary to charge a given condenser; this is best done by the use of the Wheatstone bridge. Or the deflection of the needle of a quadrant electrometer is observed once in air and again in the medium in question, and thus the difference in the force of attraction between the needle and the quadrants is directly determined for the two media. Another method, worked out by Drude, depends on the determination of the length of electric waves along wires surrounded by different media. A table of the values of the dielectric constants of a number of substances which can be used as solvents for electrolytes will be given in Book II, and also a more complete description of the methods of measurement.

CHAPTER V.

ELECTROMOTIVE FORCE AND THE GALVANIC CURRENT.

To aid in forming a clear idea of the relations between current and voltage we will make use of an illustration, although this illustration, like all comparisons, does not hold at all points. Suppose we have an air-tight ring-shaped tube filled with air. At a point *A* in Fig. 9 we place a pumping arrangement which draws in air on one side and expels it on the other. As a result a partial vacuum is created to the right of the pump and the pressure of the air on the other side is raised. The air seeks to equalize this difference in pressure by flowing around through the tube from left to right, and the pump strives to keep up the difference in pressure. As a result a stationary condition is arrived

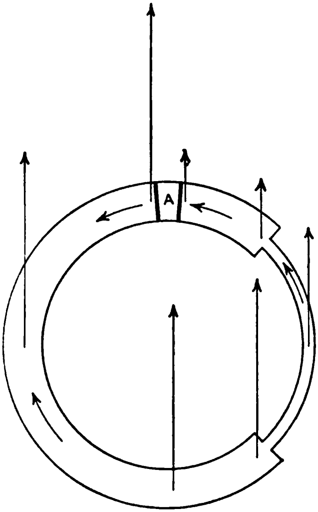

FIG. 9.

at when the quantity of air flowing around through the tube from left to right is the same as that brought over by the pump from right to left. From right to left along the tube the difference in pressure gradually falls off, as is indicated in the figure by the different lengths of the arrows. In the narrow part of the tube where the air finds the greatest resistance the pressure falls off most rapidly. If the tube is closed at any point the pump continues working for a short time and forces air over till the difference in pressure between the ends of the tube is the same as the pressure which the pump can exert.

Let us now take, in place of the tube, a wire through which electricity can flow, and replace the air-pump by an electricity pump which takes in positive electricity on one side and gives it out on the other (or what amounts to the same thing, gives out positive electricity on one side and negative on the other). For this purpose we may use a battery or a dynamo. In the first illustration the air pressure on the left was raised and on the right lowered; in this case also the electric pressure, or "potential," is raised on the left and lowered on the right.

The electricity seeks to equalize this difference of potential by flowing around through the wire, while the battery strives to maintain the constant difference of potential. The potential falls off along the wire from the left pole around to the right, and it decreases most rapidly at those points where the electricity finds the greatest friction, i.e., where the resistance of the circuit is highest. If we cut the wire at any point so that electricity can no longer flow, the battery still continues to work for an instant, but only until the difference of potential between the ends of the wire is the same as the electromotive force of the battery. The amount of electricity which is necessary to bring the ends of the wire up to this potential is known as the capacity of the wire; the capacity is equal to one, when 1 coulomb is required to give a difference of potential of 1 volt.

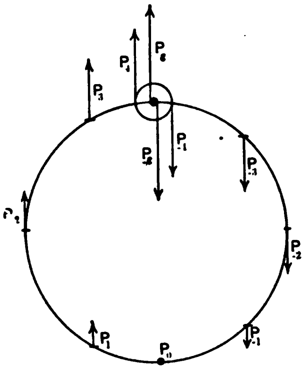

FIG. 10.

If the circuit is closed so that a current can pass, Ohm's law applies to every portion of the circuit (cf. p. 78). If ϵ is the difference of potential between any two points, w the resistance, and i the quantity of electricity passing per second, then $\epsilon = iw$. If, in Fig. 10, P_ϵ and $P_{-\epsilon}$ represent the potentials on the left- and right-hand sides of the battery when the circuit is open, so that $P_\epsilon - P_{-\epsilon}$ represents the electromotive force of the battery, then the potential will gradually fall off along the wire from P_ϵ to $P_{-\epsilon}$ when the circuit is closed. Let the potential at different points along the wire be

$$P_\epsilon P_4 P_3 P_2 P_1 P_0 P_{-1} P_{-2} P_{-3} P_{-4} P_{-\epsilon},$$

and let the value of each be indicated by the length of the arrow. P_0 represents the original potential of the wire before the battery was attached and the direction of the arrows shows whether the potential at any point is higher(↑) or lower (↓) than at P_0.

If the electromotive force at the terminals of the battery (represented by P_4 and P_{-4} in Fig. 10) is measured while the battery is in action we no longer obtain the true electromotive force of the cell $P_{\epsilon}-P_{-\epsilon}$, since part of the voltage is used in sending current through the cell itself. This loss of voltage in the battery is given by $\epsilon_1 = iw_1$, where w_1 is the internal resistance. If the measurement is made when the circuit is open, when $i=0$ then ϵ_1 is also zero and we obtain the true electromotive force $P_{\epsilon}-P_{-\epsilon}$ of the battery. In measuring the electromotive force of a cell, then, we obtain the true value only when no current is flowing. A value slightly smaller is obtained when the current is very low, and for this reason all voltmeters are made with a high resistance. If any appreciable current is taken from the cell the voltage measured at the terminals may be much lower than the true voltage of the cell, and the error will be larger the greater the internal resistance of the cell.

Contact Electricity.

A difference of potential is always present when two different substances are brought in contact and the surface of contact is the seat of the electromotive force. Positive electricity is taken from one substance and collected on the other, or, what amounts to the same thing, one substance becomes charged positively, the other negatively. Chemical reactions are undoubtedly the cause of this contact electricity, but their nature has not been determined in all cases. The amounts of substance which enter into chemical reactions under these circumstances are so excessively small that the quantity of electricity produced is also very small.

It is a well-known fact that when one substance is rubbed with another, both become electrified (frictional electricity). When sealing-wax is rubbed with a piece of wool the wool becomes positively electrified ; when glass is rubbed with silk, the silk becomes negatively charged.

No simple law without any exceptions has yet been discovered with regard to contact electricity. Substances may, however, be arranged in a series so that a body rubbed with any of those following it in the series becomes positively charged; the charges so produced are larger the farther apart the substances stand. Such a series is the following: glass, wool, silk, wood, metal, amber, hard rubber, sulphur, shellac, sealing-wax. Coehn has discovered a law which seems to have pretty general application: When two substances are brought in contact, the one whose dielectric constant is higher becomes positively electrified.

Since contact and frictional electricity are of very little importance in chemistry on account of the very small amounts of electricity concerned, we will only mention one fact in this connection, which has lately become of technical importance. If we suspend in water some very finely divided material such as powdered glass, precipitates, dyes, peat, etc., and introduce two electrodes which are connected with a source of electricity, we find that the particles which become negatively charged are attracted to the cathode and deposited there. This movement of the suspended particles is called " Endosmosis " or " Cataphosesis." If an electric current is sent through peat mud, the positively charged water moves to the negative pole, and this fact may be used for expelling water from peat. On the other hand, water when pressed through a porous diaphragm carries positive electricity with it, and so gives rise to a current.

Galvanic Production of Current.

If we wish to obtain larger quantities of electricity (without using a dynamo) we must use some arrangement in which the chemical energy of large quantities of material is converted into electric energy. This can be done by using a galvanic cell.

The early experiments of Galvani on the twitching of a frog's nerve under the influence of electric-spark discharges showed that those same movements also occurred when two metals touched each other and also the nerve. Galvani wrongly attributed this to an electric force in the nerve itself. Volta found, however, that the twitching did not occur when the same metal touched the nerve at two points, but that two different metals were necessary. His classic experiments showed further that two metals and a simple salt solution are sufficient to produce a current. He believed that the force producing the current lay at the junction of the two metals, but found further that a series of metals connected one with another could give no current in the absence of moisture, although they became electrically charged. On the basis of his discoeriev s

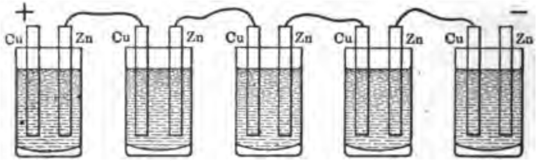

FIG. 11.

Volta built his well-known Voltaic Pile, which consisted of a number of pairs of Zn and Cu plates having between each pair a pad soaked in ordinary salt solution. One end of this arrangement he found was strongly charged with positive electricity and the other end with an equal amount of negative. The production of electricity is due to a reaction between the solution and the zinc, which becomes oxidized. This "pile," like the battery shown in Fig. 11, rapidly loses its electromotive force when current is taken from it.

Volta placed in each of a number of beakers a strip of copper and one of zinc, filled the beakers with dilute sulphuric acid and connected each copper with a zinc pole as shown in Fig. 11. The electromotive force of this battery falls off rapidly, since hydrogen is evolved on the copper. The reaction which furnished the current is

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

In order to avoid the evolution of hydrogen Daniell used a combination of two metals and two solutions, forming the well-known Daniell element. A porous porcelain cell is filled with a solution of copper sulphate and in this is placed a rod of copper; this cell is then placed in a solution of $ZnSO_4$ contained in a glass jar and a zinc rod is

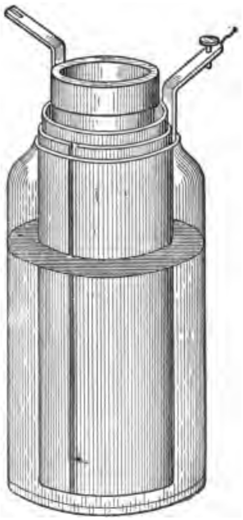

FIG. 12.

placed in the $ZnSO_4$.* When the two metals are connected by a wire electricity flows through the wire from the copper to the zinc.

The reaction which occurs in the Daniell cell is

$$Zn + CuSO_4 = ZnSO_4 + Cu,$$

or written in the ionic form,

$$Zn + Cu^{\cdot\cdot} \rightarrow Cu + Zn^{\cdot\cdot}.$$

Copper is displaced from its salt by zinc; the zinc passes over from the metallic state into the state of ions, and copper passes from ions into the metallic state.

The arrangement of the above cell

$$Zn/ZnSO_4 - CuSO_4/Cu$$

shows that at the left position ions go into solution and at the right position ions are precipitated, and thereby just as much positive electricity is taken away from the zinc electrode as is given up to the copper electrode. This process goes on, before the circuit is closed, until the electrostatic attraction or repulsion between the electrodes and ions prevents any more ions from entering or leaving the solution. The process therefore stops as soon as the electromotive force between the electrodes corresponds to the energy of the reaction. In the case of the Daniell cell the difference of potential between the electrodes is about 1.1 volts.

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* In Fig. 12 is shown the arrangement of a Bunsen cell, which is similar to the Daniell except that in place of copper in copper sulphate a carbon rod in HNO_3 is used. A number of other cells, with the reactions taking place in them, will be given in Book II.

As soon as the electrodes are connected by a wire, the two kinds of electricity flow through the wire and unite. The chemical reaction seeks to maintain the two electrodes at a difference of potential of 1.1 volts, so that an uninterrupted current flows through the wire from copper to zinc.

Calculation of Electromotive Forces.

The electromotive force of a chemical reaction can only be calculated in such cases where the process is a reversible one (see p. 12); that is, when the chemical energy is converted entirely and without loss into electrical energy.

The various formulæ no longer hold when insulation is faulty, or when unknown secondary chemical reactions are involved.

A chemical reaction is reversible when it can be made to go backward and the system be restored to its original condition by the exact quantity of electrical work which the reaction has furnished. The process at an electrode of Cu in $CuSO_4$ is reversible. If we send current through the electrode in one direction, copper is dissolved according to the scheme $Cu \rightarrow Cu^{\cdot\cdot}$. If current is sent in the opposite direction copper is precipitated: $Cu^{\cdot\cdot} \rightarrow Cu$.

The reaction at an aluminium electrode, $Al \rightarrow Al^{\cdot\cdot\cdot}$, is not reversible, because the reverse reaction, $Al^{\cdot\cdot\cdot} \rightarrow Al$, does not take place in a water solution. Aluminium cannot be deposited on an electrode by the electrolysis of a water solution of an Al salt. The $H^{\cdot}$ ions are discharged instead.

We saw on p. 10 that there is a relation between the heat of a reaction and its electromotive force. If the formula which was derived,

$$A = q + T\frac{dA}{dT},$$

is true of any given reaction, then we may be sure that our experimental arrangement fulfils the condition of reversibility. In order to use this equation in electrical calculations it must be remembered that the transformation of 1 gram equivalent of any metal into ions results in the production of 96 540 coulombs of electricity. In the case of the Daniell cell, where the elements Cu and Zn are divalent, 2 ×96 540 coulombs are produced for every atomic weight in grams of zinc which is dissolved. When 2 ×96 540 coulombs pass through the cell 65.6 grs. of Zn are dissolved and 63.6 grs. of Cu are deposited. The work done by the cell is therefore coulombs × voltage E (cf. p. 6), and

$$A = 96\,540\,nE,$$

where n is the valence.

Consequently
$$E = \frac{q}{96540n} + T\frac{dE}{dT}.$$

This is the well-known Gibbs-Helmholtz equation.

Another method of calculating the electromotive force of chemical reactions is furnished by van't Hoff's energy equation (p. 31). Copper is precipitated from the solution until equilibrium is reached. If c_1 represents the concentration of the Zn ions, c_2 that of the Cu ions in the cell at the start, and if the concentrations of $Zn^{\cdot\cdot}$ and $Cu^{\cdot\cdot}$ are c_{o_1} and c_{o_2} after equilibrium is reached when practically all the Cu has been removed from solution, then van't Hoff's equation gives

$$A = RTln\frac{c_{o_1}c_2}{c_{o_2}c_1}.$$

If n is the valence of the reaction (in this case 2) we obtain

$$n96\ 540E = RTln\frac{c_{o_1}c_2}{c_{o_2}c_1}.$$

Substituting the value of R in watt-seconds, $=8.3167$ (cf. p. 5), and changing the natural to the Briggs logarithm by multiplying by 2·3026 we have

$$n\ 96\ 540E = 8.3167 \times 2.3026T \log \frac{c_{o_1}c_2}{c_{o_2}c_1},$$

or

$$E = \frac{0.0001983}{n}T \log \frac{c_{o_1}c_2}{c_{o_2}c_1}.$$

For the ordinary temperature of 18° ($T = 273 + 18$) we have

$$E = \frac{0.0577}{n} \log \frac{c_{o_1}c_2}{c_{o_2}c_1}.$$

The values of c_{o_1} and c_{o_2} are called the equilibrium concentrations of the ions. They may be determined if we allow the reaction to continue till it stops of itself, and then measure the different concentrations. In most cases, however, our chemical methods are not delicate enough, for many reactions go on until one of the substances seems to entirely disappear.

The ratio of the two concentrations $\frac{c_{o1}}{c_{o2}}$, however, may often be determined by electrical methods; for example, by measuring the electromotive force when the concentrations c_1 and c_2 are known.

Illustration: If the concentrations of Zn and Cu ions are made equal to 1, or if they are simply made equal whatever their values, then c_1 and c_2 cancel in the equation and we have

$$E=\frac{0.0577}{n}\log\frac{c_{o1}}{c_{o2}}.$$

E has been found to be 1.1 volts, so that $\log\frac{c_{o1}}{c_{o2}}=38$ or $\frac{c_{o1}}{c_{o2}}=10^{38}$; that is, when we put zinc into a solution of $CuSO_4$ the copper will be precipitated until the concentration of the zinc ion is 10^{38} times that of the remaining copper ions. For all analytical purposes this precipitation is absolutely quantitative; but theoretically this small remainder is of very great importance, since otherwise the energy of this reaction would be infinite.

As a second example we will calculate the electromotive force of a Daniell cell in which $c_1=1$ and $c_2=0.001$; then we have

$$E=0.029\log 10^{38}\frac{c_2}{c_1},$$

or

$$E=1.1+0.029\log 0.001=1.013 \text{ volts}.$$

In a similar way, if we know the electromotive force for some particular concentration we can calculate it for any concentration.

Nernst has given the name "electrolytic solution pressure" to the values c_{o_1} and c_{o_2}. The meaning of this term will be considered in the next section.

Nernst's Formula.

Every substance has a certain tendency to change over from the condition in which it happens to be to some other. This tendency has been given the name of "fugacity." For instance, liquid water has a tendency to pass over into water vapor, and water vapor, on the other hand, strives to condense and reform liquid water. If the first tendency prevails evaporation actually takes place. The fugacity is dependent on the temperature, but at constant temperature is higher the higher the concentration, or in the case of condensation, the higher the vapor density.

When a solid soluble salt is brought in contact with water it strives to pass over into the dissolved condition. The concentration of the solid salt is constant and consequently the fugacity of a solid salt is constant. On the other hand the salt which has already dissolved has a tendency to leave the solution and go back to the solid state, and this tendency is greater the higher the concentration of the solution is. The actual force which causes the salt to dissolve is equal to the difference between the two fugacities and is therefore smaller the more concentrated the solution is. Finally the concentration of the solution reaches a value where the two fugacities balance, then no more salt dissolves and the solution is saturated. If the concentration is too high, i.e., if the solution is supersaturated, the tendency to take the solid form overcomes the tendency to dissolve and the reaction goes in the reverse direction.

Very similar relations hold for the metals. They all have a tendency to pass over into the form of ions, and this tendency is constant as long as solid metal is present, for the active mass of a metal is constant. On the other hand, the ions strive to pass back into the metallic condition, and their tendency to do so varies according to their concentration. We represent the first value by P, the *solution pressure*, as P_{Zn}, P_{Cu}, P_{Ag}, etc.; the deionizing tendency will be represented by p, and is nothing less than the osmotic pressure of the ions. The osmotic pressure and deionizing tendency both strive to make the solution more dilute.

As in the reaction of a salt going into solution, a precipitation of the metals actually takes place, according as P or p has the higher value, but the one essential point of difference lies in the fact that the metals can only go into solution in the form of positively charged ions and thus carry positive electricity with them. Consequently the passage of the metal from the solid to the dissolved state leaves the remaining metal negatively charged (or if $p > P$, the resulting solid metal is positively charged) and the electrostatic attraction (or repulsion) thus produced soon puts a stop to any further solution (or deposition).

The following three cases are possible, illustrated by Figs. 13, 14, and 15. If $P > p$ traces of metal will go into solution and the metal takes on a negative charge. If $P < p$ a few ions separate out on the metal and give it a positive charge, leaving the solution negative. If $P = p$ no changes occur.

If we can arrange so as to conduct the electricity away from the solution and the electrode, the influence of the electrostatic charge disappears and considerable quantities of metal may go into solution or be deposited, according as the conditions are those represented by Fig. 13 or Fig. 15.

These two processes can furnish a certain amount of work. When a substance changes its pressure from P to p the work to be obtained is

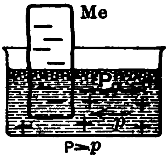

FIG. 13.

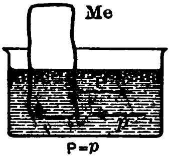

FIG. 14.

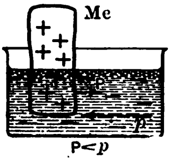

FIG. 15.

$$A = RTln\frac{P}{p} \text{ (cf. p. 21).}$$

Since the solution or deposition of 1 equivalent of any metal is accompanied by the passage of 96 540 coulombs, and that of a mol of any metal by 96 540*n*, where *n* is the valence, and since, further, the work obtainable is measured by the electromotive force × the number of coulombs, we have

$$n96\,540E = RTln\frac{P}{p}.$$

If we simplify this expression in the same way as the corresponding one on p. 121 we obtain

$$E=\frac{0.0577}{n}\log\frac{P}{p}.$$

Now it is possible to find a concentration, c_o, at which the osmotic pressure of the ions just balances the solution pressure of the metal, and the condition of things is as represented in Fig. 14. c_o corresponds to the solution pressure P, and if c represents the concentration at which the osmotic pressure of the ions is p, then

$$c_o:c=P:p \quad\text{and}\quad E=\frac{0.0577}{n}\log\frac{c_o}{c}.$$

E is the electromotive force with which the metal seeks to go into solution when the concentration of the ions is c, and

$$E_1=\frac{0.0577}{n}\log c_o$$

is the electromotive force in a solution when the ions have a concentration of one, i.e., 1 mol per litre. E_1 is called the *electrolytic potential* of the metal.

If the concentration of the ions of a metal is changed by a power of 10, the potential changes by $\frac{0.058}{n}$ *volts at ordinary temperature.*

We will now combine two systems, each consisting of a metal dipping in a solution of one of its salts, the two solutions being separated by a porous diaphragm which hinders the two solutions from mixing, but does not prevent the passage of the current. The condition of the system is as follows (Fig. 16): metal I becomes charged negatively, since its solution pressure P_1 is greater than the osmotic pressure p, of the metallic ions in the solution; metal II becomes positively charged, since p_2 is greater than P_2. There will therefore be a certain difference of potential between the two metals. If the metals are connected for an instant by a wire, the charges on the two electrodes unite. The electrostatic repulsion and attraction at the electrodes disappears, and traces of metal I again go into solution and traces of metal II are precipitated until the electrostatic forces again stop the process. If we allow the electrodes to remain connected a continuous current will flow through the wire, metal I will continue to be dissolved and metal II to be precipitated. The Daniell cell is an arrangement of this sort.

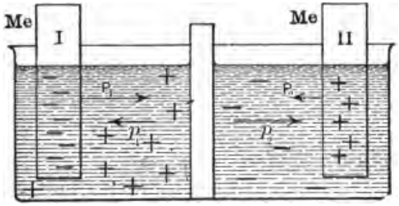

FIG. 16.

How much work can such an element do, and what is its electromotive force? Evidently

$$E=E_1-E_2=\frac{0.0577}{n_1}\log\frac{P_1}{p_1}+\frac{0.0577}{n_2}\log\frac{p_2}{P_2}.$$

If the two metals have the same valence ($n_1=n_2=n$) as in the Daniell cell, then, if we put $c_o:c=P:p$,

$$E=\frac{0.0577}{n}\log\frac{c_{o_1}c_2}{c_{o_2}c_1},$$

which is identical with van't Hoff's equation on p. 125. If P_2 is also greater than p_2 for the second metal, then

$$E = E_1 - E_2 = \frac{0.0577}{n_1} \log \frac{P_1}{p_1} - \frac{0.0577}{n} \log \frac{P_2}{p_2},$$

or, since $\log \frac{P_2}{p_2} = -\log \frac{p_2}{P_2}$, this equation is identical with the one first given. In this case the two metals are both negatively charged before the circuit is closed, but to a different degree, and this difference causes the current to flow on completing the circuit. The positive current flows through the wire from the metal having the lower value of $\frac{P}{p}$ to the other; this latter therefore dissolves and the first is deposited.

When the concentration of the ions is the same in both compartments of the cell, $\frac{c_1}{c_2} = 1$ and we have

$$E = \frac{0.0577}{n} \log \frac{P_1}{P_2}.$$

The electromotive force E of such a cell furnishes a means of calculating the ratio of $\frac{P_1}{P_2}$.

In order to determine the actual separate values of P_1 and P_2 we must use some combination of metal and solution where $P = p$. Unfortunately no such combination is known with certainty, and we are obliged to resort to the same principle which is used in deciding on the atomic weights, i.e., we must fix an arbitrary unit. We do not know the actual weight of the atoms; what we measure is the relative weight. We arbitrarily take 16 as the atomic weight of oxygen and use this as the standard.

Following a suggestion of Nernst's, we arbitrarily take *the solution pressure of hydrogen as one*, so that

$$0.0577 \log 1 = 0.$$

To determine the electrolytic solution pressure of the other metals we measure the electromotive force of cells built up in this way:

$$\mathrm{Pt}_{\mathrm{H}_2} | n\mathrm{H}^{\cdot} \text{ solution} - n\mathrm{Metal}^{\cdot} \text{ solution} | \mathrm{Metal}.$$

A platinum electrode over which bubbles of hydrogen gas are passed, dipping in an acid solution whose $\mathrm{H}^{\cdot}$ ion concentration is 1 (normal), is combined with a metal dipping into a solution of one of its salts of such strength that the ionic concentration is one and the electromotive force of the whole combination is measured. A platinum electrode saturated with hydrogen gas behaves as regards its electromotive force as if made of the metal hydrogen (cf. p. 136). If we find that the combination

$$\mathrm{Pt}_{\mathrm{H}_2} \left| \underset{\longrightarrow}{n\mathrm{H}^{\cdot} - n\mathrm{Ag}^{\cdot}} \right| \mathrm{Ag}$$

has an electromotive force of −0.771 volt, then the electrolytic potential of silver is −0.771. The minus sign is used because hydrogen has a higher solution pressure than silver, and the current flows in the connecting wire from the silver to platinum. In the combination

$$\mathrm{Pt}_{\mathrm{H}_2} \left| \underset{\longleftarrow}{n\mathrm{H}^{\cdot} - n\mathrm{Zn}^{\cdot\cdot}} \right| \mathrm{Zn}$$

the voltage is +0.770; here the current flows in the opposite direction. From these two values we find the electromotive force of the combination

$$Zn|nZn^{\cdot\cdot}-nAg^{\cdot}|Ag$$

to be 0.770−(−0.771)=1.541 volts. The positive sign is given to the potential of those metals whose solution pressure is higher than that of hydrogen, since they have a greater power for taking on a positive charge; metals whose solution pressure is less than that of hydrogen, and also elements or radicals which take on a negative charge, have a negative potential. The same thing is meant when we speak of the "nobility" of the metals; silver is more noble than zinc, and zinc is less noble than hydrogen, etc.

Now the hydrogen electrode is not so easily reproducible as certain other electrodes which are known, and which would naturally be chosen as standards in determining the exact values of the different potentials. The easiest electrode to make, and one which always has the same potential is the "normal calomel electrode,"

$$Hg|HgCl+n\ KCl.*$$

The calomel electrode has a potential of −0.283 against the hydrogen electrode, i.e., an element of the form

$$Pt_{H_2}|nH \text{ solution}-nKCl+HgCl|Hg$$

has an electromotive force of −0.283 volt, and in it the

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* (Cf. p. 18 and the chapter on Methods of Measurement in Book II for details concerning the calomel electrode and certain other normal electrodes.)

positive current goes through the solution from the hydrogen to the mercury electrode.

The numbers in the following table have been obtained with the help of such normal electrodes. Column 1 contains the electrolytic potentials of the different elements; the second column contains the same values all shifted 0.277 volt in order to refer them to another standard proposed by Ostwald.*

	Calomel Electrode = −0.283 Hydrogen Electrode = 0.0	Calomel Electrode = −0.56 'Absolute" Potentials
Mn.	+1.075	+0.798
Zn.	+0.770	+0.493
Cd.	+0.420	+0.143
Fe.	+0.344	+0.067
Tl.	+0.322	+0.045
Co.	+0.232	−0.045
Ni.	+0.228	−0.049
Pb.	+0.151	−0.132
H.	±0.0	−0.277
Cu.	−0.329	−0.606
Hg.	−0.753	−1.030
Ag.	−0.771	−1.048
Cl.	−1.353	−1.636
Br.	−0.993	−1.270
I.	−0.520	−0.797

We can obtain from this table the electromotive force of any cell of the Daniell type. For instance, a copper-nickel element, in which the concentration of the metallic

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* According to a theory of Helmholtz, the surface tension of polarized mercury has a maximum value when there is no difference between its potential and that of the solution. This theory, however, has not been satisfactorily proven; it appears that the surface-tension phenomena of polarized mercury are more complicated than Helmholtz supposed.

ions of each salt is equal, has an electromotive force of $+0.288-(-0.329)=0.557$ volt. A Zn−Pb cell has a voltage of 0.619, Zn−Cu, i.e., the Daniell cell, has 1.099 volts, Cu−Ag 0.442 volt, etc.

Gas Electrodes.—If we take an electrode of platinum which has had deposited on it a coating of finely divided platinum and allow bubbles of hydrogen to pass up over it, some of the gas dissolves in the platinum and the electrode behaves electrochemically as if it were composed of the metal hydrogen. Every chemist knows that most gases, hydrogen particularly, are chemically much more active in the presence of finely divided platinum (Pt "sponge"). This is probably due to the fact that hydrogen dissolved in Pt is partially dissociated into atoms, $H_2=H+H$, and the atoms enter into reaction much more readily than the H_2 molecules. The quantity of hydrogen which dissolves in the Pt, i.e., its concentration or active mass, is dependent on the pressure which is exerted on the hydrogen above the solution. This follows from Henry's absorption law, which states that the solubility of a gas in a liquid or solid is proportional to the concentration of the gas, and this in turn, according to Boyle's law, is directly proportional to the pressure on the gas.

To calculate the electromotive force of gas electrodes we again make use of van't Hoff's equation, but we must remember that in previous cases the active mass of the metals were constants and therefore cancelled out in the fraction after the log. In the case of gases, however, the active masses do not thus disappear; they are not constants, but are dependent on the pressure.

Let us consider two hydrogen electrodes at atmospheric pressure in a solution whose $H^{\cdot}$ ion concentration is c_1, then

$$E = \frac{RT}{2} ln \frac{C_A}{c_1} - \frac{RT}{2} ln \frac{C_A}{c_1} = 0.$$

C_A is the active mass of the hydrogen dissolved in the Pt at atmospheric pressure P. The 2 in the denominator is due to the fact that H_2 has a valence of 2. If we combine an electrode under atmospheric pressure with another under the pressure p, in which the active mass of the hydrogen is C_p, we have

$$E = \frac{RT}{2} ln \frac{C_p}{c_1} - \frac{RT}{2} ln \frac{C_A}{c_1},$$

or since $C_p : C_A = p : P$,

$$E = \frac{RT}{2} ln \frac{p}{P}.$$

If $p > P$ the current in the solution goes from the p electrode to the P electrode; if $p < P$ it goes in the opposite direction, that is, the electrode which has less hydrogen gets more from the passage of the current, and this will continue till the pressure at both electrodes becomes the same. If the pressures p and P are kept constant the cell

Pt with H_2 under pressure P|solution|Pt with H_2 under pressure p

will furnish a steady current. The reactions at the electrodes are

$$H_2 \rightarrow 2H^{\cdot} \quad \text{or} \quad 2H^{\cdot} \rightarrow H_2$$

according to the direction of the current. This is a "concentration cell" in which the current is due to a difference in concentration of the substances forming the electrodes. If the pressure is changed by a power of 10 the potential is changed $\frac{0.058}{2} = 0.029$ volt.

Other gases when dissolved in Pt act similarly to hydrogen in their electrochemical relations. A platinum electrode saturated with chlorine behaves like an electrode of the element chlorine, and its potential, which is -1.35 at atmospheric pressure, changes with the pressure in the same way as that of the hydrogen electrode. The oxygen electrode also changes its potential with the pressure, but we must remember that in this case the molecule O_2 has a valence of four.

From the values for the potentials of the metalloids as given in the table on p. 135 we can derive the electromotive force of any cell; for instance, the cell

$$Zn|ZnCl_2|Pt_{Cl_2}$$

has an electromotive force of 2.12 volts; the voltage with which chlorine displaces iodine from a solution of an iodide is $1.35 - 0.52 = 0.83$ volt when the concentration of chlorine and iodine ions is normal.

The Grove gas-cell,

$$O_2|\text{solution}|H_2,$$

has a voltage of 1.12. This value for the potential of O_2 refers to a solution when the concentration of $H^{\cdot}$ ions is normal. We cannot calculate the true potential of oxygen in a solution which is normal with respect the O'' ions, for at present we do not know the concentration of the O'' ions in any solution with any degree of certainty.

Potential of Alloys.—The dependence of the electromotive force on the concentration of the substances forming the electrodes is also seen in the case of metals which form alloys. Suppose we have a cell whose electrodes are composed of dilute zinc amalgams whose zinc concentrations are different, and in which the electrolyte is a solution of $ZnSO_4$; the electromotive force of such a cell is, as above,

$$E=\frac{RT}{2}ln\frac{P_2}{P_1}.$$

Here P_2 and P_1 are the solution pressures of the zinc in the amalgams, and since, as in the case of Pt and H_2, we may consider zinc as the dissolved substance and mercury as the solvent, we have $P_2:P_1=c_2:c_1$, where c_2 and c_1 are the zinc concentrations in the amalgams. We have therefore

$$E=\frac{0.0577}{2}\log\frac{c_2}{c_1}.$$

This formula has been verified experimentally. We have assumed in the above formula that the molecules of the dissolved zinc are composed of single atoms. If this were not the case, and the molecules were composed, say, of two zinc atoms, Zn_2, then we would have to divide RT by 4 to get the electromotive force. But since the formula as written represents the experimental facts, this in itself furnishes a proof that the zinc molecules when dissolved in mercury are composed of single atoms.

The amalgams, or in general the alloys, may be divided into three classes:

1. The metals form a mechanical mixture. Such mixtures have the potential of the "less noble" metal. For instance a mixture of Zn and Fe has the potential of pure zinc.

2. The metals form a solution (amalgam or alloy). A metal solution is always "nobler," i.e., has a potential nearer that of oxygen, than its least noble component, and the greater the amount of work which results from the formation of the alloy the nearer will its potential approach that of oxygen.

3. The metals form a chemical compound. In this case the electrode has its own particular solution pressure, and the ions it sends into solution are formed in the same proportion as the elements exist in the electrodes.

These various conditions have to be considered in the electrolytic solution of impure metals; for instance, in the refining of crude copper, silver, and gold. Details concerning the solution of alloys and the refining of the metals will be given in Books II and III.

Potential of Compounds.—Case 3, mentioned above, has a very general application. Every element when entering a compound attains an entirely different potential. For instance, chlorine has a very different potential, according as it is present as the free element, or a as solution in platinum, or as a chloride, and its potential is changed to a larger degree according to the amount of free energy developed in the formation of the compound.

As may be seen from the table on p. 135, AgCl has a lower potential of formation than CuCl, i.e., its chlorine potential is higher than that of CuCl. This will be clearer when we remember that the reaction

$$2Ag + Cl_2 \rightleftarrows 2AgCl,$$

like all reactions, goes on only till a certain state of equilibrium is reached. All the chlorine does not enter into combination, but an excessively small quantity of Ag and Cl_2 remains free. This small remainder may react like chlorine at an exceedingly low concentration, and silver chloride will have a chlorine potential corresponding to this concentration of Cl_2, i.e., its electromotive force will be that of a chlorine electrode at very low pressures. The more stable a compound is, i.e., the higher the voltage of the cell

Metal | solution of the chloride of the metal | chlorine

is, the more complete is the reaction and the lower the chlorine pressure and chlorine potential.

An electrode made of a metal covered with its solid chloride has a perfectly definite potential and is reversible with respect to chlorine. For instance, the electrode

$$Hg/HgCl + nKCl$$

has a potential of −0.283 volt. If current passes from left to right HgCl is formed; if in the reverse direction, chlorine goes into solution and HgCl disappears. Electrodes like this which are reversible with respect to the anion are called electrodes of the second kind, while those reversible with respect to the metal are called electrodes of the first kind. Electrodes of the second kind are very often employed in potential measurements on account of their constancy. The calomel electrode is the one most used. The potential varies with the concentration of the Cl′ ions in the solution according to the same formula as for the metals,

$$E=\frac{0.058}{n}\log\frac{P}{c},$$

where $\frac{0.058}{n}\log P$ is the potential of the electrode when the concentration of the Cl′ ions in the solution is 1. Reversible electrodes for other metalloids or radicals can be made in the same way; for instance,

$$Ag/AgI+KI \quad \text{or} \quad Hg/Hg_2SO_4+H_2SO_4, \text{ etc.}$$

Salts which are the least soluble in water are naturally chosen for use in normal electrodes. The following table gives the potentials of some electrodes of this sort:

	Hydrogen Electrode $=0$	Calomel Electrode $=-0.56$
$Pb/PbSO_4 + 1.04nH_2SO_4$	0.284	0.007
$Hg/Hg_2SO_4 + 1.0nK_2SO_4$	−0.644	−0.921
$Hg/Hg_2Cl_2 + 1.0nKCl$	−0.283	−0.560
$Hg/Hg_2Cl_2 + 0.1nKCl$	−0.338	−0.614
$Ag/AgCl + 1.0nKCl$	−0.209	−0.483
$Ag/AgCl + 0.1nKCl$	−0.263	−0.540

The values given in this table are to be used in the same way as those given on p. 135, so that a cell consisting of Zn in $ZnSO_4$ combined with a mercurous sulphate electrode will have a voltage of $0.77+0.644=1.414$ volts.

The so-called oxidation and reduction potentials are to be considered in a similar way. A Pt electrode covered with potassium chlorate ($KClO_3$) has a perfectly definite potential, for the chlorate has a definite oxygen pressure, due to the incompleteness of the reaction which has produced the chlorate. The Pt electrode becomes charged with oxygen at this pressure and thus becomes an oxygen electrode, which can bring about reactions of oxidation. The potential of such a secondary oxygen electrode corresponds to the pressure with which the oxidizing agent tends to give up oxygen. The potential of a Pt electrode in a solution of an oxidizing agent, therefore, is due simply to a charge of gaseous oxygen furnished by the oxidizing agent, as Nernst has proven experimentally.

The reduction potential of reducing agents is due to exactly similar causes. Reducing agents give up H_2 to a Pt electrode, or, what amounts to the same thing, they abstract oxygen, until the gas concentration, and consequently the potential, reaches a value corresponding to the reducing power of the substance. If we bring together on a Pt electrode an oxidizing agent, such as $KMnO_4$ and a reducing agent, such as $FeCl_2$, the permanganate gives up oxygen to the electrode and the $FeCl_2$ takes it away; that is, the second substance becomes oxidized by the first. The potential with which this reaction takes place is simply the difference between the oxidation potentials of the two substances. These potentials are dependent on the concentrations of the oxidizing and reducing agents and may be calculated by Nernst's equation. Data and information concerning the use of a number of oxidation and reduction electrodes will be given in Book II. The Grove gas-cell, for instance, is an oxidation-reduction cell, consisting of the oxidizing agent oxygen and the reducing agent hydrogen.

Concentration Cells. — A kind of concentration cell differing from that on p. 139 is the following:

$$\mathrm{Ag}|\underset{c_1}{\mathrm{AgNO_3}}-\underset{c_2}{\mathrm{AgNO_3}}|\mathrm{Ag},$$

i.e., electrodes of the same metal dipping into solutions of a salt of the metal having different concentrations. The current through the solution flows from the less concentrated to the more concentrated solution. On one side silver is dissolved, on the other precipitated, until the concentration on both sides is the same. If we neglect on account of its smallness the difference of potential at the point of contact of the two solutions—as we have always done hitherto—the electromotive force at 18° is given by

$$E=RTln\frac{c_1}{c_2}=0.0577 \log \frac{c_1}{c_2}.$$

The solution pressure of the metal, being the same at each electrode, does not appear in the formula.

In many cases the electromotive force at the junction of the two solutions may be neglected, but not always. The following consideration will show the cause of this electromotive force and how to calculate it. Two solutions of different concentration always strive to diffuse into each other till the concentration is the same at all points. When a dissolved salt diffuses the ion having the highest velocity tends to move on ahead of the other. In the case of acids this is the hydrogen ion which has the highest velocity of any of the ions. This partial separation of the ions can only take place to an immeasurable extent, for since the more dilute solution has an excess of $H^{\cdot}$ ions, the electrostatic attraction of the ions gives rise to a force which compels the two kinds of ions to remain together. As a result, in the diffusion of a salt the more rapid ion is held back and the slower is accelerated. This tendency of one ion to hurry on ahead of the other gives rise to an electromotive force which, as Nernst has shown, can be calculated from the velocity of the ions. If u represents the velocity of the cation and v that of the anion, then

$$e = RT\frac{u-v}{u+v}ln\frac{c_1}{c_2},$$

e being the difference of potential at the junction of two solutions whose concentrations are c_1 and c_2; the salt in each solution is supposed to be completely dissociated and the ions all univalent. This formula holds only for 1:1 salts (cf. p. 96); the formulæ for others are more complicated, and most of them have not been derived.*

From the theory of the diffusion of electrolytes it follows that this electromotive force at the junction of two solutions of different concentration practically disappears when each solution contains equal amounts of another salt whose concentration is much higher. To avoid this somewhat uncertain contact-electromotive

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* For further particulars see the list of text-books named at the close of this volume: in particular Nernst, Theoretische Chemie, 4th edition, p. 699.

force a large excess of some indifferent salt is often added.

Applications of Nernst's Formula.—The formula on p. 144 has been experimentally verified in a great number of cases, and may be used to determine the solubility of certain difficultly soluble salts in cases where the solubility is too small to be measured by chemical means. We find, for instance, that the electromotive force of the cell $Ag|0.001\ n\ AgNO_3+1.0\ n\ KNO_3-1.0\ n\ KNO_3+AgI|Ag$ is 0.22 volt. The concentration of the silver ions on the left is 0.001; let that on the right be c where c is the value sought. From the formula

$$0.22=0.0577 \log \frac{0.001}{c}$$

we find that $c=1.6\times10^{-8}$, i.e., a litre of a saturated AgI solution contains 1.6×10^{-8} mols of AgI = 0.0000035 gr. AgI. This agrees very well with the value 1.5×10^{-8} obtained from conductivity measurements.

Another very important application of the measurement of concentration cells is in determining the dissociation constant of water, a method already mentioned on p. 72.

The cell

$$Pt_{H_2}|NaOH-HCl|Pt_{H_2}$$

is called the "neutralization cell" because the reaction of neutralization is the one which furnishes the current

$$NaOH+HCl=NaCl+H_2O,$$

or more correctly, as we saw on p. 66,

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

The voltage of this cell with 0.1 *n* solutions is 0.6460 at 25°. To this 0.0468 volt must be added, because at the contact of the two solutions there is an opposing electromotive force of this value. The voltage of the cell without this "diffusion" voltage would therefore be 0.6928. The concentration of the $H^{\cdot}$ ions in a 0.1 *n* solution of HCl is 0.0924, that of the OH' ions in a 0.1 *n* solution of NaOH is 0.0847, as found from conductivity measurements.

The cell is to be considered as a concentration cell with respect to the $H^{\cdot}$ ions, and therefore follows the formula on p. 144. Introducing the different values we have

$$0.6928 = 0.05898 \log \frac{0.0924}{c},$$

where c is the concentration of the $H^{\cdot}$ ions in the NaOH solution. c is found to be 1.66×10^{-13}. Therefore

$$[H^{\cdot}][OH'] = 1.406 \times 10^{-14} \quad \text{and} \quad c_0 = 1.187 \times 10^{-7},$$

which is in excellent agreement with the values obtained by other methods (cf. p. 65 and also p. 91).

Secondary Elements and the Accumulator.

The secondary elements do not differ in principle nor in the calculation of their electromotive forces from the primary elements which we have just studied. They are nominally distinguished from the first, however, because after they are once used up they may be revived or recharged by sending a reverse current of electricity through them, and it is not necessary to rebuild them of fresh material as in the case of primary cells. The oxygen-hydrogen cell

$$Pt_{O_2}|\text{solution}|Pt_{H_2}$$

may be considered as a secondary cell if the gases resulting from the electrolysis are collected at the electrodes and then used to produce a current.

The most important of the secondary elements is the lead accumulator or storage battery. If we put two lead electrodes in a solution of sulphuric acid a small amount of $PbSO_4$ is formed by chemical action on the surface of the electrodes. If we pass a current through the solution, the $PbSO_4$ on the cathode becomes reduced to metallic lead, and at the anode is oxidized to lead peroxide (PbO_2), so that we now have a polarization element (cf. p. 152) of the form

$$Pb|H_2SO_4|PbO_2.$$

This can furnish a current and has an electromotive force of about 2 volts. Since the formation of $PbSO_4$ was very slight, very little Pb and PbO_2 was formed and the cell can only furnish a small amount of electricity. To increase the capacity, i.e., to allow of the formation of large amounts of PbO_2, the electrodes should expose as large a surface as possible. This may be accomplished, according to Planté, by electrolyzing first in one direction and then in the other, which causes the electrodes to become somewhat porous; or, according to Faure, a paste of lead oxide and red lead is spread on a grating of lead and when this is electrolyzed we obtain spongy lead at the cathode and lead peroxide at the anode. When such an element furnishes a current $PbSO_4$ is formed at both electrodes.

In "Charging," the $PbSO_4$ on the cathode, or "negative pole," is reduced to Pb, and the following reaction occurs:*

$$PbSO_4 + 2\ominus = Pb + SO_4''.$$

This is an electrode of the second kind, which sends SO_4'' ions into solution (cf. p. 141). At the anode or "positive pole" SO_4'' ions are set free, which through the agency of water act on the $PbSO_4$, forming PbO_2 and H_2SO_4:

$$PbSO_4 + 2H_2O + SO_4'' + 2\oplus = PbO_2 + 4H^{\cdot} + 2SO_4''.$$

In "Discharging," SO_4'' is liberated at the anode (now the lead pole):

$$Pb + SO_4'' + 2\oplus = PbSO_4.$$

At the cathode (now the PbO_2 pole) $H^{\cdot}$ ions are discharged and with the help of the H_2SO_4 act on the PbO_2 and convert it into $PbSO_4$:

$$PbO_2 + 2H^{\cdot} + H_2SO_4 + 2\ominus = PbSO_4 + 2H_2O.$$

Summing up these equations we obtain as the chemical process which produces the current the equation

$$PbO_2 + Pb + 2H_2SO_4 \rightleftarrows 2PbSO_4 + 2H_2O.$$

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* In equations the symbol $\oplus$ represents 96 540 coulombs of positive electricity, $\ominus$ the same quantity of negative

Read from right to left this represents the reaction on charging, from left to right the reaction on discharging. In charging $2PbSO_4$ and $2H_2O$ disappear and PbO_2, Pb, and $2H_2SO_4$ are formed; the reverse is true on discharging.*

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* On the application of the different thermodynamical and electrochemical theories to the lead accumulator, see Book II, and also the excellent work of F. Dolezalek, "The Theory of the Lead Accumulaor," Wiley & Sons.

CHAPTER VI.

POLARIZATION AND ELECTROLYSIS.

In this chapter we will discuss briefly a number of facts which are of the greatest importance to the experimental and technical side of electrochemistry and which will be easily understood from what has been said in the previous chapters. The way in which a current is conducted through a solution and the part played by the different ions has been discussed in the chapter on conductivity.

On arriving at the electrodes the ions give up their charges, and are either precipitated as neutral substances, where they remain in a solid state as in the case of the metals, or, as in the case of the gases, escape into the atmosphere or dissolve in the solution; on the other hand, they may react at once with the surrounding solution as soon as they are set free, and thus give rise to oxidizing or reducing effects. As a result of electrolysis either the electrode or the solution around the electrode is changed, and conditions are produced which result in an electromotive force opposed to that which is sending the current through the solution; in other words, the electrolytic cell becomes " polarized."

Polarization.

If we electrolyze a solution of HCl with an electromotive force of 0.7 volt, a very small quantity of hydrogen is deposited at the cathode, and a very small quantity of chlorine at the anode, and current will flow until the concentrations of the gases in the cell $Pt_{H_2}|HCl|Pt_{Cl_2}$ is high enough to produce a counter electromotive force just equal to the applied 0.7 volt. A hydrogen-chlorine cell in which the gases have a pressure of 1 atmosphere has, according to the table on p. 135, a voltage of 1.35. At 0.7 volt we therefore have a H_2-Cl_2 cell in which the concentration of the gases and therefore their solution pressure is much smaller than at atmospheric pressure (cf. p. 136). These concentrations only become high enough to just balance the applied voltage.

In order to produce this formation of H_2 and Cl_2 current must flow on applying an electromotive force, but this soon stops on account of the counter electromotive force of the H_2-Cl_2 cell which is thus formed. If we now increase the applied voltage to 1 volt a new current appears, the electrodes become charged with more gas, and the chlorine hydrogen cell also soon attains an electromotive force of 1 volt. This goes on until we come to 1.35 volts. At this voltage the electrodes are charged with gas at atmospheric pressure.

This counter electromotive force is called "polarization."

If we now increase the voltage to 1.5 the polarization is no longer able to bring the current down to zero, and above 1.35 volts we have a perceptible, continuous current. 1.35 is called the decomposition voltage of HCl. Above 1.35 volts the current follows the law,

$$E - \varepsilon = iw,$$

where E is the applied voltage, ε the counter electromotive force of polarization, and w the resistance of the solution. The polarization increases very slightly above 1.35 as the voltage and current rise, since the gases are evolved under a pressure greater than that of the atmosphere, but since they are able to escape in gaseous form the polarization will never be as great as the applied electromotive force.

Similar conditions also prevail when solid substances are precipitated. For instance when we electrolyze a solution of $CuCl_2$ between Pt electrodes, chlorine is formed at the anode under a certain pressure, and at the cathode a Cu coating of such a density that the resulting cell

$$\mathrm{Pt_{Cu}|CuCl_2|Pt_{Cl_2}}$$

has the same electromotive force as the applied voltage.

The small amount of electricity which is necessary to bring the electrode into the polarized condition is known as the "polarization capacity" of the electrode. This capacity is naturally dependent on the surface of the electrode and further depends on the nature of the metal of which the electrode is made. For equal surfaces palladium has a higher polarization capacity when hydrogen is discharged on it than platinum, and platinum a higher capacity than iron; for the solubility of hydrogen is the greatest in palladium, and consequently a larger amount of hydrogen and therefore a larger amount of current is required to bring the hydrogen dissolved in palladium up to the same pressure as that dissolved in platinum or iron.

If for any reason the substances which cause polarization are removed, either by dissolving in the solution and diffusing away, or by chemical actions, we say that "depolarization" occurs. This is the case when we electrolyze a substance which gives soluble gases. Further, polarization is prevented when we have a reducing agent, as $FeCl_2$ at the anode, for this prevents the oxygen polarization by combining with oxygen to form a ferric salt (cf. p. 143). Such substances are called "depolarizers." $FeCl_3$ is a cathodic depolarizer, since it prevents the hydrogen polarization and is reduced to $FeCl_2$.

The electrolysis of water furnishes a good illustration of these facts. If we apply 1 volt to two platinum electrodes in water, the cathode becomes charged with hydrogen and the anode with oxygen until the electromotive force of this gas-cell is 1 volt, when the current should stop. The two gases O_2 and H_2, however, are soluble in water, and they consequently diffuse away from their electrodes and either escape into the air or recombine at the electrodes to form water. The electrodes therefore are continually losing gas, and in order to make good this loss and keep up the electromotive force of 1 volt a small current must continue to flow. This small current is known as the residual current (Reststrom). Such substances as are easily oxidized at the anode and reduced at the cathode may maintain a much larger residual current. For instance if an iron salt gets into the storage battery, it is reduced to ferrous salt at the cathode, diffuses to the anode, and is there oxidized to ferric salt, diffuses back to the cathode, and is again reduced, etc. Iron salts in the storage battery therefore maintain a residual current which is useless for charging purposes and causes a considerable loss.

If oxygen or air is passed over the cathode during the electrolysis of water, this removes the hydrogen polarization, and such an electrode is called "unpolarizable." Those anodes are unpolarizable which are electrolytically dissolved, such as Cu. In general an electrode is unpolarizable when no new substance is formed on it during electrolysis.

In order to determine the decomposition voltage of a salt, we put two Pt electrodes in the solution and connect them with a source of electricity whose voltage may be varied at will. We then gradually increase the voltage and observe the current at each voltage. The current first rises and then decreases almost to zero every time the voltage is raised, until the decomposition voltage ε is reached. From this point on the current follows Ohm's law (cf. p. 78):

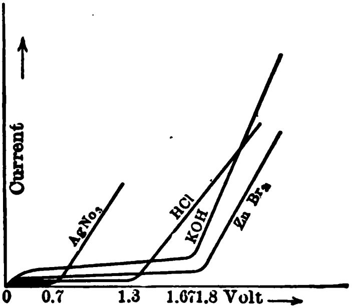

FIG. 17.

$$E-\varepsilon=iw.$$

If the voltage is plotted as abscissa and the current as ordinate we obtain the curves shown in Fig. 17. In the case of $AgNO_3$ the current below 0.7 volt is practically zero, above this it increases regularly. 0.7 volt is therefore the decomposition voltage of silver nitrate.

The values in the following table were obtained by Le Blanc and his students.

DECOMPOSITION VOLTAGES.

Acids	
Sulphuric acid, H_2SO_4	1.67
Nitric acid, HNO_3	1.69
Phosphoric acid, H_3PO_4	1.72
Malonic acid, $CH_2(COOH)_2$	1.69
Perchloric acid, $HClO_4$	1.65
Hydrochloric acid, HCl	1.31
Oxalic acid	0.95
Hydrobromic acid	0.94
Hydriodic acid	0.52

Bases	
Sodium hydroxide, $NaOH$	1.69
Potassium hydroxide, KOH	1.67
Ammo'm hydroxide, NH_4OH	1.74

Salts	
Zinc sulphate, $ZnSO_4$	2.35
Zinc bromide, $ZnBr_2$	1.80
Nickel sulphate, $NiSO_4$	2.09
Nickel chloride, $NiCl_2$	1.85
Lead nitrate, $Pb(NO_3)_2$	1.52
Silver nitrate, $AgNO_3$	0.70
Cadmium nitrate, $Cd(NO_3)_2$	1.98
Cadmium sulphate, $CdSO_4$	2.03
Cadmium chloride, $CdCl_2$	1.88
Cobalt sulphate, $CoSO_4$	1.92
Cobalt chloride, $CoCl_2$	1.78

Since the polarization is nothing less than a galvanic cell resulting from electrolysis, it will follow the same laws and formulæ as these cells. Just as the electromotive force of a galvanic cell is made up of two separate potentials (cf. p. 132) so the decomposition voltage of an electrolyte is composed of the two voltages necessary to discharge the ions. Furthermore these "deposition voltages" must be exactly the same as the single potentials of the metals which are being deposited. They also follow Nernst's formula, i.e., the deposition voltage is lower, and precipitation takes place easier when the concentration of the ions which are to be precipitated is high. The decomposition voltage of zinc chloride, 2.1 volts, is composed of the potential of zinc, 0.77, and that of chlorine, 1.35 (cf. table on p. 135). The deposition voltages may be measured by combining the electrode in question with one whose potential is constant and of known value. If a current is passed through the combination

$$Pt|CuSO_4—H_2SO_4+Hg_2SO_4|Hg$$

so that Cu is precipitated, it is found that the electromotive force of the resulting cell,

$$Cu|CuSO_4—H_2SO_4+Hg_2SO_4|Hg,$$

is 0.315 volt. Knowing that the single potential of the mercurous sulphate electrode is -0.644 (cf. p. 140) we find that the deposition voltage of Cu is -0.329, which is just the same as the single potential of Cu.

There is still another kind of polarization, in which the electrodes are not changed. If we have two silver electrodes in a solution of $AgNO_3$, and pass a current, a displacement of the concentration occurs, due to the different velocities with which the anion and cation move (cf. p. 108). Consequently a concentration cell is formed whose electromotive force acts in opposition to the applied voltage. This cell also, like all concentration cells, must follow Nernst's formula.

Deposition and solution do not necessarily accompany electrolysis. Other reactions, as oxidation and reduction, may take place, and these obey the laws which have been discussed in the preceding pages. Every reaction taking place at an electrode has its own particular voltage. For instance, it requires a definite potential to reduce $FeCl_3$ to $FeCl_2$.

In certain cases the gases do not act in accordance with Nernst's formula. When a gas is evolved at an electrode two separate reactions are to be distinguished: first, the discharge of the ions to form atoms, as

$$H^{\cdot} \rightarrow H,$$

and secondly, the union of the atoms to form the molecules of the gas, as

$$H + H = H_2.$$

This reaction meets with a different resistance from the different metals used as electrodes, or, more correctly, this reaction has a great chemical resistance which is removed catalytically to a different extent by the different metals. Platinized platinum is the most effective catalyzer for this purpose; hydrogen is evolved on platinized platinum at the potential 0.0 volt. Iron is less effective as a catalyzer and Hg, Pb, and Zn are the least. This phenomenon is called "overvoltage," and we say that hydrogen is evolved on zinc with an overvoltage of 0.7 volt. The following table shows the overvoltages necessary to evolve hydrogen and oxygen on the different metals.

OVERVOLTAGE.

Hydrogen Deposition		Oxygen Deposition	
Metal	Potential	Metal	Potential
Pt platinized.......	0.00	Au................	1.75
Au................	0.01	Pt polished........	1.67
Fe in NaOH.......	0.08	Pd............	1.65
Pt polished........	0.09	Cd................	1.65
Ag................	0.15	Ag..............	1.63
Ni................	0.21	Pb..............	1.53
Cu................	0.23	Cu................	1.48
Pd................	0.46	Fe..............	1.47
Sn................	0.53	Pt platinized....	1.47
Pb................	0.64	Co..............	1.36
Zn................	0.70	Ni polished........	1.35
Hg................	0.78	Ni spongy.......	1.28

The recognition of these facts was extremely important, for it explained a number of experimental discoveries which could not be theoretically accounted for.

In nearly all solutions there are several different ions which may be discharged, and consequently several different reactions are possible at the electrodes. The general rule is that *that process actually takes place which requires the least expenditure of energy.* For instance, if we have a solution containing $ZnCl_2$, $CuCl_2$, and HCl no electrolysis will be effected by any electromotive force less than 1 volt, for the decomposition voltage of $CuCl_2$ is 1 volt. Between 1 and 1.35 volts the only reaction at the cathode will be the deposition of Cu, since the decomposition voltage of HCl is 1.35. Above 1.35 volts both Cu and H may be deposited, but in reality that process will take place which requires the lowest voltage, and only Cu will be deposited as long as it is present in sufficient quantity. If the solution is electrolyzed with a high current, however, the Cu in the immediate neighborhood of the cathode soon becomes nearly all used up, its deposition voltage is raised in accordance with Nernst's formula, and finally a condition is reached where hydrogen is more easily discharged than copper. Finally, if the voltage is raised above 2.2 zinc may also be deposited, and this may be brought about by using a high-current density so that the solution around the cathode contains very little copper. By using a high-current density brass may be deposited on the cathode on electrolyzing a mixture of copper and zinc salts.

Now, hydrogen ions are always present in some quantity, and the fact that zinc may be deposited from a solution containing hydrogen ions can only be explained by the phenomenon of overvoltage. If there were no overvoltage we could no more deposit zinc from a water solution than we can aluminium or sodium. As it is zinc can only be precipitated from a neutral or alkaline solution, and not from one containing acids. The deposition voltage of zinc is 0.77, that of hydrogen from an acid solution, on account of the overvoltage, is raised from 0.0 to 0.70 as soon as the slightest trace of zinc is deposited. In an acid solution the hydrogen will therefore be deposited before the zinc. In a neutral solution, however, when the concentration of the $H^{\cdot}$ ions is about 10^{-7} the deposition voltage of hydrogen is raised, and is $0.0577 \log 10^{-7} = 0.404$ volt higher than in an acid solution; it is raised still further in an alkaline solution where the $H^{\cdot}$ ion concentration is very much lower. From a neutral solution, therefore, hydrogen can be discharged electrolytically on zinc only at a potential of $0.4 + 0.7 = 1.1$ volts, and consequently from such a solution the zinc will be deposited before the hydrogen.

What is true of the deposition of ions is true of certain other reactions: that one occurs first which requires the lowest potential. If we have a solution of potassium permanganate and chloric acid, that one of these substances will be first reduced which has the highest oxidizing potential, for oxidizing potential is nothing less than the effort of the substance to give up oxygen and become reduced. Such processes are really nothing less than a change of the charges on the ions. For instance, the reduction of $FeCl_3$ to $FeCl_2$ simply consists in $Fe^{\cdot\cdot\cdot} \rightarrow Fe^{\cdot\cdot}$. The reduction of MnO_4 to a manganese salt consists in $MnO_4{}' \rightarrow Mn^{\cdot\cdot}$. If we keep in mind this transfer of charges, we can derive a formula similar to Nernst's for all such reactions.

Using the method explained on p. 155 we can often obtain the deposition voltages of every kind of ion in the solution (Fig. 18). In the anodic curve for H_2SO_4 a slight bend is noticed at 1.12 volts where the oxygen ions are discharged. The change in direction of the curve is slight, as Fig. 18 shows, because the concentration of the O'' ions is excessively small, and when used up they are not immediately replaced by a further dissociation of the water. On further raising the voltage another bend is noticed at 1.67 volts which probably corresponds to the discharge of the OH' ions. Under suitable conditions two other points are obtained with H_2SO_4, at 1.9 where the SO_4'' ions are discharged and at 2.6 where the HSO_4' ions are discharged.

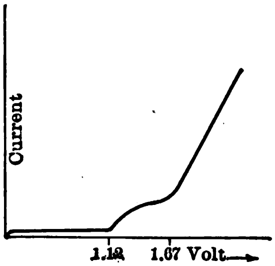

FIG. 18.

The following deposition voltages not contained in the other table have been obtained by Nernst and his students:

Mg	+1.482	SO_4	−1.9
Al	+1.276	HSO_4	−2.6
* O	−1.12	NO_3	−1.88
* OH	−1.67		

* These figures refer to solutions normal with respect to the H˙ ion; 1.12 and 1.67 are the deposition voltages of O'' and OH' from a normal acid solution.

To discharge OH' or O'' ions from a normal alkaline solution requires 0.8 volt less than to discharge them from a normal acid solution; to discharge H from a normal alkaline solution requires 0.8 volt more than from a normal acid solution.

Faraday's Law.

As we have already shown (pp. 52, 82), equivalent quantities of the ions of different substances are always combined with the same amount of electricity, and this charge is 96 540 coulombs for every equivalent in grams. This amount of electricity is carried by 39.15 grams of the positively charged univalent potassium ion, or by 35.5 grams of negatively charged univalent chlorine ion. In general the ions of any substance carry 96 540 coulombs for every valence.

If one equivalent of any substance passes through the cross-section of an electrolytic cell, it carries with it 96 540 coulombs and the current strength is 96 540 ampere-seconds. When 108 grams of silver are deposited on the cathode, 96 540 coulombs of positive electricity pass from the solution to the electrode. If 1 coulomb, i.e., 1 ampere for 1 second, is passed through an electrolytic cell 0.01036 mg. equivalents are deposited. Faraday's law may therefore be stated: *The amount of electricity required to deposit, dissolve, or otherwise bring into chemical action 1 gram equivalent of any element or compound is always 96 540 coulombs.* The weight in grams of the substance which is produced or destroyed may therefore be obtained by dividing the molecular weight (in the case of elements the atomic weight) by the valence, multiplying by the number of ampere-seconds and then by 0.00001036. The following table contains in the first column the elements, in the second the atomic weights, in the third the milligrams per ampere-second, and in the fourth the grams per ampere-hour. All the values except those for $H^{\cdot}$, $Ag^{\cdot}$, and $Cu^{\cdot\cdot}$ are approximate.

Elements	Symbol and Valence	Atomic Weight	Milligrams per Ampere-second	Grams per Ampere-hour
Aluminium	$Al^{\cdot\cdot\cdot}$	27.1	0.0935	0.337
Antimony	$Sb^{\cdot\cdot\cdot}$	120.2	0.415	1.494
“	$Sb^{\cdot\cdot\cdot\cdot\cdot}$	120.2	0.25	0.90
Barium	$Ba^{\cdot\cdot}$	137.4	0.712	2.56
Bismuth	$Bi^{\cdot\cdot\cdot}$	208.5	1.08	3.89
Bromine	Br'	79.96	0.8	2.94
Cadmium	$Cd^{\cdot\cdot}$	112.4	0.583	2.10
Calcium	$Ca^{\cdot\cdot}$	40.1	0.2075	0.75
Carbon	$C^{\cdot\cdot\cdot\cdot}$	12.00	0.031	0.1115
Chlorine	Cl'	35.45	0.3677	1.322
Cobalt	$Co^{\cdot\cdot}$	59.0	0.306	1.10
Copper (cuprous)	$Cu^{\cdot}$	63.6	0.66	0.237
“ (cupric)	$Cu^{\cdot\cdot}$	63.6	0.3294	1.186
Gold (aurous)	$Au^{\cdot}$	197.2	2.043	7.36
“ (auric)	$Au^{\cdot\cdot\cdot}$	197.2	0.68	2.45
Hydrogen	$H^{\cdot}$	1.008	0.0104	0.03762
Iodine	I'	126.85	1.314	4.725
Iron (ferrous)	$Fe^{\cdot\cdot}$	55.9	0.290	1.04
“ (ferric)	$Fe^{\cdot\cdot\cdot}$	55.9	0.193	0.694
Lead	$Pb^{\cdot\cdot}$	206.9	1.072	3.86
Magnesium	$Mg^{\cdot\cdot}$	24.36	0.126	0.453
Manganese (manganous)	$Mn^{\cdot\cdot}$	55.0	0.285	1.025
“ (manganic)	$Mn^{\cdot\cdot\cdot}$	55.0	0.19	0.88
“ (permanganate)	$Mn^{\cdot\cdot\cdot\cdot\cdot\cdot\cdot}$	55.0	0.08	0.29
Mercury (mercurous)	$Hg^{\cdot}$	200.0	2.072	7.45
“ (mercuric)	$Hg^{\cdot\cdot}$	200.0	1.036	3.73
Nickel	$Ni^{\cdot\cdot}$	58.7	0.304	1.093
Oxygen	O''	16.00	0.083	0.2985
Platinum	Pt	194.8	——	——
Potassium	$K^{\cdot}$	39.15	0.406	1.46
Silver	$Ag^{\cdot}$	107.93	1.118	4.025
Sodium	$Na^{\cdot}$	23.05	0.24	0.86
Strontium	$Sr^{\cdot\cdot}$	87.6	0.454	1.635
Sulphur	S''	32.06	0.166	0.598
“	$S^{\cdot\cdot\cdot\cdot}$	32.06	0.083	0.298
Tin (stannous)	$Sn^{\cdot\cdot}$	119.0	0.62	2.23
“ (stannic)	$Sn^{\cdot\cdot\cdot\cdot}$	119.0	0.31	1.11
Zinc	$Zn^{\cdot\cdot}$	65.4	0.34	1.222

The quantity of any substance formed or destroyed is easily obtained with the help of this table. For instance, in the electrolysis of Na_2SO_4, H_2SO_4 is formed at the anode and NaOH at the cathode. The equivalent of the first is $\frac{1}{2}(1+1+32+64)=49=0.507$ mg. of H_2SO_4 per ampere-second; the equivalent of NaOH is $23+16+1=40$, so that 0.414 mgr. NaOH are formed per ampere-second. At the same time $8\times0.01036=0.0834$ mgr. of oxygen is liberated at the anode and $1.01\times0.01036=0.0105$ mgr. of hydrogen at the cathode.

Electrolysis.

We will now discuss briefly a few of the most important reactions which occur at the electrodes.

Acids, and the salts of all metals which are discharged less easily than hydrogen, give off hydrogen at the cathode on electrolysis, and in the case of these salts the hydroxide of the metal is also formed. In a solution of NaCl the current is transported by the ions $Na^\cdot$ and Cl', since these are present in far greater quantities than the ions of water, $H^\cdot$ and OH'. The passage of electricity from the solution to the cathode, however, is taken care of, not by the $Na^\cdot$ ions, but by the $H^\cdot$ ions, since these have a much lower deposition voltage. At the cathode, therefore, $H^\cdot$ ions disappear and pass off as gaseous H_2, OH' ions remain, and $Na^\cdot$ ions are brought up by the current, so that the result of electrolysis is the formation of NaOH and gaseous H_2 at the cathode.

The concentration of the ions must always be considered as on p. 156. The deposition of nickel from an acid solution is impossible, since from such a solution $H^\cdot$ ions are more easily discharged than the $Ni^{\cdot\cdot}$ ions, but Ni can easily be deposited from a neutral or alkaline solution.

The deposition of zinc is only made possible by the high overvoltage of H on zinc. If the zinc solution contains another metal such as iron which is easily deposited and on which the overvoltage of hydrogen is not so high, the least trace of this metal on the cathode gives the hydrogen an opportunity to be discharged, and no zinc can be deposited; on the contrary, if any zinc has been precipitated it redissolves at once with the evolution of hydrogen.

For similar reasons the presence of foreign metals in a storage battery is very injurious. The reduction of $PbSO_4$ at the cathode would be impossible if lead showed no overvoltage. As a matter of fact, when we try to reduce $PbSO_4$ on a Pt electrode no lead is formed, and we have simply an evolution of hydrogen. The same thing happens when a foreign metal such as copper gets into the storage battery. It is deposited on the cathode, and when we attempt to charge the battery, hydrogen is evolved on the traces of copper and no $PbSO_4$ is reduced.

These facts are important in the analytical determination of the metals by electrolysis (cf. Book II). The metals can only be deposited when their deposition voltage is below that of hydrogen, and we must give the solution such a composition that this will be the case. In determining nickel, for instance, we use an ammoniacal solution.

What has been said also applies to the reaction at the anode. An anion will only be discharged when this reaction takes place easier than the discharge of the O'' or OH' ions which are always present. We can never obtain fluorine by electrolyzing a water solution, but we *can* obtain bromine and iodine. When we electrolyze a solution of Na_2SO_4, the SO_4'' ions are not discharged, but rather the oxygen ions, and gaseous oxygen is evolved. As the oxygen ions disappear hydrogen ions remain in the solution, and since SO_4'' ions are brought up by the current, this results in the formation of sulphuric acid at the anode.*

Another class of reactions may occur when the ions which have been brought up to the anode find an opportunity to enter into a reaction which requires a potential lower than that necessary for their discharge. In a strongly acid solution of Na_2SO_4 which contains very few O'' ions, the reaction $SO_4+SO_4=S_2O_8$ can be more easily brought about than the evolution of oxygen, consequently $H_2S_2O_8$ is formed and little or no oxygen is produced. In an acid solution of Na_2SO_4, however, OH' and HSO_4' ions are also present, and it is very probable that the formation of persulphuric acid is due to the direct union of two discharged HSO_4 ions.

We have still to consider the presence of OH' ions. When we electrolyze a solution with a voltage of about 1.12 or a little higher, O'' ions are discharged, but they soon become so largely removed in the vicinity of the

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* It should be noticed that many text-books explain these facts in a somewhat different way, by assuming that the SO_4'' ions are actually discharged and then react with water according to the equation

$$SO_4+H_2O=H_2SO_4+O.$$

The formation of NaOH at the cathode is similarly explained on the assumption that Na ions are first discharged and then immediately react with the water, forming H and NaOH. It is evidently unnecessary to explain the facts in this roundabout way.

electrode that their deposition voltage is raised above that of the OH′ ions. Therefore in the electrolysis of a NaOH solution we have only a very weak current between 1.12 and 1.67 volts. Above this last voltage, which is the deposition potential of the OH′ ions, we obtain a much stronger current. The reaction which takes place at the electrodes is

$$OH + OH = H_2O + O.$$

A reaction of this sort in which the ions are destroyed is evidently not reversible (cf. p. 12 and 123), for the OH ions cannot be restored to the solution by reversing the current.

A chemical reaction may be brought about more easily than by direct deposition if the ions have an opportunity to form a compound or alloy. For instance, if we electrolyze a sodium-chloride solution, using a mercury cathode, two causes unite to lower the deposition voltage of the $Na^{\cdot}$ ions below that of hydrogen: first, the discharge of Na is facilitated because it may unite with mercury to form an amalgam, and secondly, the discharge of H on mercury requires a high overvoltage. In this case $Na^{\cdot}$ ions can be discharged before $H^{\cdot}$ ions, and this fact forms the basis of a very important industry: the manufacture of sodium amalgam and its subsequent conversion into pure sodium hydroxide.

These primary reactions of deposition are to be distinguished (Book III) from secondary reactions into which the deposited substances may enter. In the electrolysis of sodium chloride the chlorine set free at the anode dissolves in the solution, diffuses away, and reacts with the NaOH which is formed at the cathode, thus:

$$2NaOH + Cl_2 = NaOCl + NaCl + H_2O;$$

i.e., the hypochlorite is a secondary product of electrolysis. This reaction also has great technical importance, for the electrolytic hypochlorite solutions are largely employed for bleaching purposes. If these bleaching solutions are again electrolyzed the hypochlorite is oxidized to chlorate.

CHAPTER VII.

THE ELECTRON THEORY.

Recent researches on the chemical effect of the silent electric discharge, on the cathode and X-rays, and especially the discoveries in connection with radioactivity have caused the revival of an old theory, according to which electricity is an actual chemical substance (formerly called the " electric fluid "). We must confine ourselves to a very brief outline of the development of the " electron theory " and its application to electrochemical questions.

The cathode rays discovered by Hittorf are rays sent out from the cathode of a vacuum tube under the influence of very high voltages. They consist of negative electricity which is ejected from the cathode at a very high velocity. These particles of electricity must possess a certain weight, since they are capable of exerting a force when in motion. At discharge potentials of 3000 to 14 000 volts their velocity ranges from 0.3 to 0.7×10^{10} centimetres per second, i.e., is from $\frac{1}{10}$ to $\frac{1}{4}$ of the velocity of light. When the rays enter an electric or magnetic field, their path becomes changed. From this deviation and from the velocity it has been calculated that the weight of the electric atom or " electron " is about $\frac{1}{2000}$ that of the hydrogen atom.

The Becquerel rays emitted by radium and other radioactive substances are very similar to the cathode rays, only their velocity (and consequently their penetrating power) is greater, being from 2.5 to 2.8×10^{10} cms. per second, or nearly as high as the velocity of light. If the cathode rays consist of negative electrons, we must assume that the same is true of the radium rays. It therefore follows that negative electrons are capable of existing in a free state and not combined with matter. The same should be true of the positive electrons, although it is doubtful whether they have yet been isolated.

When electrons pass through air, they attach themselves to the gas molecules and form air ions, and the gas becomes a conductor of electricity. The velocities of these ions have been measured, and it has also been found that they obey the ordinary laws of diffusion. The diffusion coefficients of the gas ions have been calculated on the assumption that they are electrically univalent, i.e., contain only one positive or negative electron, and the calculated and experimental values agree very well. The conductivity imparted to air by the electrons, and also their effect in causing the condensation of supersaturated vapors (which last may also be brought about by dust particles), forms an important test for the presence of electrons.

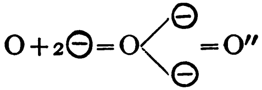
When an electron moving at a high velocity collides with a "neutron," the latter is broken up and new positive and negative electrons are formed. These may later on recombine and again form neutrons, according to the equation

$$\oplus + \ominus = \oplus\ominus.$$

We must assume the existence of these neutrons if we accept the electron theory. Neutrons must be present everywhere like the ether, and are without mass, non-conducting but capable of being polarized.*

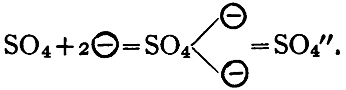
The following electrochemical definitions would follow from the theory. The electron acts chemically like an element. It combines with other elements to form saturated compounds, which are the ions. 96 540 coulombs correspond to 1 mol of a univalent element; the $\ominus$ unites with negative elements or radicals to form saturated compounds, as

$$Cl + \ominus = Cl\ominus = Cl'$$



$$O + 2\ominus = O\Big\langle\begin{matrix}\ominus\\ \ominus\end{matrix} = O''$$

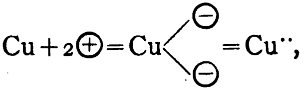
$$NO_3 + \ominus = NO_3\ominus = NO_3'$$



$$SO_4 + 2\ominus = SO_4\Big\langle\begin{matrix}\ominus\\ \ominus\end{matrix} = SO_4''.$$

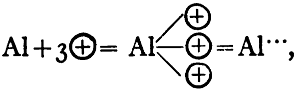
$\ominus$ can replace the metallic element in compounds, while $\oplus$ combines with the positive elements and radicals and is capable of replacing the negative elements and radicals:

$$H + \oplus = H\oplus = H^{\cdot},$$



$$Cu + 2\oplus = Cu\Big\langle\begin{matrix}\ominus\\ \ominus\end{matrix} = Cu^{\cdot\cdot},$$

$$NH_4 + \oplus = NH_4\oplus = NH_4^{\cdot},$$



$$Al + 3\oplus = Al\Big\langle\begin{matrix}\oplus\\ \oplus\\ \oplus\end{matrix} = Al^{\cdot\cdot\cdot},$$

etc.

If an electron can spring from one atom to another as in the reaction

$$Zn + Cu^{\cdot\cdot} = Zn^{\cdot\cdot} + Cu,$$

---

* For further details see Nernst, Theoretische Chemie, 4th edition, p. 389 ff.

it must be capable of existing in a free state for a certain length of time, a conclusion which we have already drawn from the conduct of the cathode rays.

The electrons have a different affinity for the different elements, just as the elements have a different affinity for one another. The positive electrons have a greater affinity for the metals, and the order of this affinity is shown in the table of potentials (p. 135); the negative electrons have an affinity for the metalloids and negative radicals. The affinity of the positive electron ⊕ for any element or radical increases as the affinity of the negative electron decreases, as in the following list:

$$F, SO_4, Cl, O, Br, I, Ag, Hg, Cu, Fe, Zn, Al, Na, Cs.$$

When two ions unite, as $H^{\cdot} + Cl' = HCl$, the molecule HCl is to be considered as a double salt of the form $H\oplus\ominus Cl$, which decomposes into its components on being dissolved in H_2O:

$$H\oplus\ominus Cl \rightleftarrows H\oplus + Cl\ominus = H^{\cdot} + Cl';$$

i.e., it dissociates just as the alums do when dissolved:

$$K_2Al_2(SO_4)_4 \rightleftarrows K_2SO_4 + Al_2(SO_4)_3.$$

These "neutron double salts" in no way resemble their components, while the alloys, and compounds like PCl_3, $BrCl$, etc., which are not neutron double salts, retain some of the characteristics of the elements from which they are made.

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