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EQUILIBRIUM IN THE DEACON PROCESS.

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IN THE well-known process for making chlorine, invented by Deacon, a mixture of air and hydrochloric acid gas is led over a rough surface impregnated with cupric chloride, kept at a temperature of about 400°. The cupric chloride acts only as catalyzer and may be replaced by the chloride of iron, nickel or cerium. The reaction is simply,

$$4HCl + O_2 = 2H_2O + 2Cl_2.$$

This reaction never runs completely to an end, but approaches a state of equilibrium which, according to the conditions of temperature and concentration, fixes a definite limit to the yield of chlorine which it is possible to attain.

Reliable data concerning this equilibrium have not been obtained hitherto. A number of investigations have been made to determine the yield of chlorine in the Deacon process under actual working conditions, in which ordinarily the gases are sent past the catalyzer too rapidly for the establishment of equilibrium. The most extensive research of this kind is one by Lunge and Marmier.[1] It seems not unlikely that at the highest temperatures at which they worked equilibrium was frequently reached. We shall return later to a consideration of their results.

The present investigation of this equilibrium was undertaken partly on account of the technical significance of the process, but more especially because a knowledge of this equilibrium enables us to find at any temperature the difference between the free energy of formation of hydrochloric acid and that of water, two data of fundamental importance in chemistry. In particular, this study will permit a new calculation of the potential of the oxygen electrode, for which I have recently found a value differing by more than one-tenth of a volt from the one commonly accepted.[2]

EXPERIMENTAL METHOD.

The thermostat used in the following experiments was a modification of one that I have previously described.[3] It consisted

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[1] Z. angew. Chem. 1897, p. 105.

[2] This Journal, 28, 158 (1906); Z. physik. Chem. 55, 465 (1906).

[3] P. Am. Acad. 40, 719 (1905); Z. physik. Chem. 52, 310 (1905).

in a fused mixture of sodium and potassium nitrates, in nearly equal proportions, contained in a vessel of enameled iron.[1] This vessel was surrounded by asbestos cloth upon which an electric heating coil of nickel steel wire was wound. The whole was packed in loose asbestos in order to avoid too great loss of heat. A current passed continuously through this outer coil, sufficient to heat the thermostat nearly to the desired temperature. The remainder of the heating was done by another electric heater[2] which was directly immersed in the bath and connected with the thermal regulator.

This regulator consisted of a hollow steel cylinder, holding about 300 cc., from which a steel tube of small bore led out of the thermostat to a height of nearly two meters; at the upper end it was joined to a glass capillary. The whole was filled with mercury, which on expanding made contact with a platinum wire in the glass capillary and thus operated a relay which broke the current in the inner heating coil. On account of the height of the mercury column, the thermostat could be used at temperatures far above the boiling-point of mercury.

The thermostat was well stirred and gave entire satisfaction. Without any readjustment it would run night and day for weeks without changing in temperature as much as a degree.

The temperatures were measured with a mercury thermometer. In order to eliminate the correction for the exposed stem, the thermometer was surrounded by a glass tube, about 4 cm. in diameter, in which the liquid of the bath could be drawn up nearly to the top of the mercury column. The liquid was thus raised and lowered several times until the thermometer gave a constant reading. Under the same conditions the thermometer was standardized by comparison with an accurately calibrated thermocouple which was kindly placed at my disposal by Mr. R. D. Mailey.

The apparatus in which the experiments were carried on is sketched in Fig. 1. Inside the thermostat (dotted lines) was situated the chamber *E* in which the reaction occurred. It was a

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[1] The ware known as agateware is the only one which I have found satisfactory for this purpose.

[2] This heater was made by the Simplex Electric Co., of Cambridge, Mass., and proved very serviceable. It was simply a resistance wire, wound with asbestos, and enclosed in a spiral tube of copper.

glass cylinder of about 200 cc. capacity, half filled with the catalyzer and then drawn out at both ends and sealed to stout capillaries, which led out of the thermostat. One of these tubes, *D*, connected with the reservoir *B*, which contained the mixture of oxygen and hydrochloric acid. This reservoir was a 10-liter bottle joined by a siphon to a similar bottle, *A*. The gaseous mixture was kept over strong sulphuric acid.

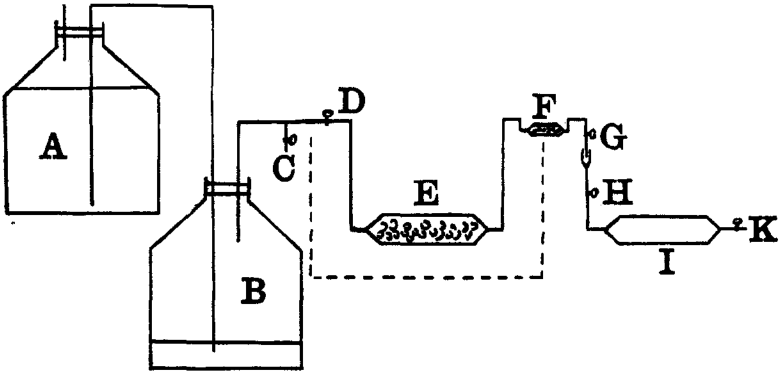

Fig. 1.

The hydrochloric acid was made from strong sulphuric acid and a solution of chemically pure hydrochloric acid. The oxygen was prepared by heating potassium permanganate. In the desired amounts these gases were introduced into *B* through *C*, forcing the sulphuric acid through the siphon into *A*, whence it later flowed back into *B* as the gas was drawn off. The hydrochloric acid dissolved somewhat in the strong sulphuric acid, and diffused through it, thus causing a slight change in the composition of the mixture from day to day.

The gas was introduced into the catalyzing chamber through *D* and after remaining there a suitable time was withdrawn for analysis through *F G*. As the gases were being removed the water vapor which was produced during the reaction showed a tendency to deposit on the colder part of the exit tube. Water thus condensed would dissolve considerable quantities of hydrochloric acid and thus vitiate the analysis. To avoid this difficulty, the tube *F*, containing glass beads saturated with strong sulphuric acid, was inserted in the exit tube. It was placed outside the thermostat, but near enough to be kept warm by it. The sulphuric acid soon became saturated with oxygen, chlorine and hydrochloric acid, after which it allowed these gases to pass through in unchanged proportions, removing only the water vapor.

The bulb *HI* was so made that its end fitted over the end of the exit tube and could be made tight by a rubber connection. The gases from *E* were drawn into this bulb, after which it was removed and the gases analyzed, as will be described below.

The catalyzer was pumice stone, broken into pieces about the size of a pea, cleaned by boiling with hydrochloric acid, and then saturated with a 10 per cent. solution of cupric chloride. It was then dried in a current of dry hydrochloric acid gas at 250°, until it ceased to give off water. This frequently took several days. The last part of the drying was done inside the catalyzing chamber.

That part of the glass apparatus which came in contact with the fused nitrates of the bath proved very fragile and the work was much delayed by breakages. For very generous aid in the construction of several of the catalyzing cylinders I wish to express my thanks to Mr. C. A. Kraus.

The method of carrying out the experiments was as follows: The tube *I* was exhausted, stop-cocks *K* and *H* being open, *G* and *D* closed. *K* was then closed, and *G* opened for an instant, during which a certain amount of gas passed from *E* into *I*. After *G* was closed *D* was opened, allowing the gas from *B* to pass into *E*, where it was left for half an hour or more. The process was then repeated over and over in order to establish constant conditions in the catalyzing chamber and the drying tube *F*. When finally these constant conditions were reached the tube *I* was removed after each filling (stop-cocks *G H* and *K* being closed) and the contents analyzed for oxygen, chlorine and hydrochloric acid, in the manner described below.

Each time when the gas had been left in the catalyzing chamber for the desired time, and just before the tube *I* was attached for drawing off the gas, a manometer was joined to the end of the exit tube and the stop-cock *G* turned for an instant. This gave the pressure in E. A rough measurement sufficed, for a change in pressure affects the equilibrium but little.

The analysis of the mixture in *I* was made in the following way: The stop-cock *K* was opened under a solution of pure potassium iodide, about one-fifth normal, prepared from water freshly boiled and cooled. The bulb was then shaken until all the chlorine and hydrochloric acid were dissolved. The gas remaining was nearly pure oxygen. It was measured in a gas burette, and then absorbed in pyrogallol in order to determine the amount of impurity.

The iodide solution was titrated with thiosulphate, about one-tenth normal, and when the iodine, which had been set free by the chlorine, was just neutralized, phenolphthalein was added and the same solution titrated with one-twentieth normal alkali (potassium hydroxide, with a little barium hydroxide). This method of successive titration with thiosulphate and alkali has been used by Lind.[1]

In this way the oxygen, chlorine and hydrochloric acid could all be separately determined. However, in all the later experiments, since it was found that the amount of oxygen present could be calculated with sufficient accuracy from the composition of the original mixture, only the ratio of chlorine to hydrochloric acid in the final mixture was determined. The procedure was then much simplified. It was no longer necessary to take pains to produce a thorough vacuum in the tube *I* before the gas was let in. Furthermore, it was no longer necessary to use a large volume of iodide solution and the titrations could therefore be made with greater precision.

The composition of the original mixture was determined as follows: The bulb *I* was attached to *C* and filled with gas from the reservoir at a pressure slightly above that of the atmosphere. One of the stop-cocks was then opened for a moment and the gas allowed to come to atmospheric pressure. Water was then allowed to run in until the hydrochloric acid was completely absorbed and the pressure was again that of the atmosphere.

During the whole process the bulb was kept at a known constant temperature. It was then weighed. From this weight, together with the weights of the bulb empty and full of water, the proportion of hydrochloric acid and oxygen could be readily determined, allowance being made for the pressure of aqueous vapor. In order to make sure that the gas left in the bulb was pure oxygen it was absorbed in pyrogallol. The volume of the residue never amounted to more than a small fraction of a per cent. of that of the original mixture and was corrected for.

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[1] Dissert. Leipzig, 1905.

EXPERIMENTAL RESULTS.

For some time no concordant results could be obtained. This proved to be due to slow changes in the catalyzer. The method adopted does not permit the direct determination of the amount of water produced in the reaction. We assume that it is equivalent to the quantity of chlorine produced, but if the catalyzer gives up either water or chlorine this will not be true. It was found necessary, therefore, to pass a mixture of given composition over the catalyzer until the latter reached such a condition that it suffered no further change. At 352°, the lowest temperature at which experiments were made, several days were required, and frequently a week, before this stationary condition was reached

Just what the change in the catalyzer is I am unable to say, but the experiments showed that in the presence of a mixture containing a large excess of oxygen, considerable quantities of oxygen were taken up by the catalyzer. If later a mixture with an excess of hydrochloric acid was passed through, the oxygen was set free once more in the form of water. Probably in the first case the oxygen set free chlorine, forming an oxide or oxychloride of copper. In the second case this oxide or oxychloride united with the hydrochloric acid to form normal chloride again and water.

If the oxide (or oxychloride) and the chloride formed separate phases, there would be only one composition of the mixture of oxygen and hydrochloric acid which would permit the permanent co-existence of both phases. If, however, the oxide (or oxychloride) formed a solid solution, the catalyzer would have a different composition corresponding to every mixture of the gases.

We will make no assumption as to the composition of the catalyzer, nor as to its mode of action. We need only assume that when the measurements become concordant and remain so for some time the catalyzer has reached a condition of constant composition.

The first experiments at 352° were made with a mixture containing 92.7 mols. of oxygen to 100 mols. hydrochloric acid. After several days preliminary experiments showed that the catalyzer had reached constancy, ten consecutive measurements were made, the results of which are given in Table I. The extent to which the reaction runs may be expressed in various ways. Previous writers have denoted by x the fraction of the hydrochloric acid decomposed, or, in other words, the ratio of free chlorine to total chlorine in the final mixture. We will adopt this nomenclature. The values of x are given in the third column. The second column shows how long the gas was left in the catalyzing chamber.

TABLE I.

No.	Time in hours.	x.
1	1½	0.870
2	16	0.872
3	1½	0.871
4	1½	0.870
5	12	0.870
6	1½	0.868
7	1½	0.867
8	5	0.869
9	4	0.867
10	12	0.871
	Average,	0.8695

The preliminary experiments had shown that half an hour was not quite sufficient to establish equilibrium. It will be noticed that Expts. 1, 3, 4, 6 and 7 lasted one and one-half hours each, while the five others lasted from four to sixteen hours each. The average value of x for the first set is 0.8692, for the second, 0.8698. The close agreement of the two averages indicates that true equilibrium[1] had been reached in every case.

This experiment shows that at 352° this mixture containing 92.7 mols. of oxygen and 100 mols. of hydrochloric acid reacts until 86.95 per cent. of the hydrochloric acid is decomposed, when equilibrium is reached. In the final mixture there would therefore be $100 - 86.95$ or 13.05 mols. of hydrochloric acid; $\frac{1}{2} \times 86.95$ or 43.47 mols. of chlorine; also 43.47 mols. of water vapor; and $92.7 - \frac{1}{4} \times 86.95$ or 71.0 mols. of oxygen.

The average pressure in the experiments was very close to one atmosphere. The partial pressures of the four gases must be proportional to the above figures and their sum must equal unity. They are therefore, HCl, 0.0763; Cl_2, 0.2542; H_2O, 0.2542; O_2, 0.4152.

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[1] In an experiment of this kind the fact that after a certain time a constant state is reached does not prove beyond question that equilibrium is reached. But this fact and the consistency of the results obtained at different temperatures and concentrations together show pretty conclusively that this is the case.

According to the mass law,

$$\frac{p^{\frac{1}{2}}_{Cl_2}\, p^{\frac{1}{2}}_{H_2O}}{p_{HCl}\, p^{\frac{1}{4}}_{O_2}} = K,$$

where K is a constant at any one temperature. Substituting the above values in this equation we obtain for K, the equilibrium constant at 352°, the value 4.15.

Another series of experiments at 352° was made in a new apparatus with fresh catalyzer. In this case the mixture contained 29.7 mols. of oxygen to 100 mols. hydrochloric acid. After the gas had passed through the apparatus for several days the measurements were begun. It was at once apparent that a longer time was required for the establishment of equilibrium than in the preceding case. Later experiments showed that in general the reaction progresses more slowly the greater the percentage of hydrochloric acid in the original mixture. This fact has also been inferred by Haber[1] from the experiments of Lunge and Marmier.[2]

With this mixture at least four hours was allowed for each experiment. Twenty-four experiments lasting, altogether, seven days gave concordant results. The last ten of these may be regarded as the best. They are recorded in Table II.

TABLE II.

No.	Time in hours.	x.
1	5	0.810
2	12	0.810
3	6	0.806
4	6	0.802
5	5	0.813
6	4	0.801
7	4	0.816
8	10	0.815
9	6	0.802
10	5	0.808
	Average,	0.808

The average pressure in these experiments was 0.93 atmosphere. Calculating as in the preceding case we find, $K = 3.95$.

The ratio of hydrochloric acid to oxygen in the final mixture was eleven times as great in this case as in the preceding. A small error in x is considerably magnified in K. Considering this fact and the slowness whith which equilibrium is attained at this temperature, the agreement between the two values of K at 352° may be regarded as satisfactory.

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[1] Haber: Thermodynamik technischer Gasreaktionen.

[2] Loc. cit.

In better agreement were the two series at 386° recorded in Tables III and IV. Table V contains the results of a single series at 419°. At these temperatures, it will be noted, a shorter time was necessary for establishing equilibrium. In each series the catalyzer had reached a constant state for at least twenty-four hours before the experiments were begun.

TABLE III.

No.	Time in minutes.	x.
1	20	0.844
2	20	0.844
3	30	0.843
4	115	0.848
5	185	0.845
	Average,	0.845

Temperature 386°
Average pressure, 0.98 atmosphere.
Original composition, 327 mols. O_2 to 100 mols. HCl.

TABLE IV.

No.	Time in minutes.	x.
1	60	0.803
2	840	0.808
3	30	0.809
4	20	0.809
5	30	0.801
6	60	0.801
7	60	0.797
8	60	0.805
9	240	0.797
10	120	0.806
	Average,	0.804

Temperature 386°.
Average pressure, 0.96 atmosphere.
Original composition, 48.8 mols. O_2 to 100 mols. HCl.

TABLE V.

No.	Time in minutes.	x.
1	35	0.819
2	55	0.817
3	60	0.816
4	30	0.824
5	30	0.824
6	30	0.818
7	40	0.824
8	10	0.823
9	20	0.819
10	20	0.820
	Average,	0.820

Temperature 419°.
Average pressure 1.08 atmospheres.
Original composition, 327 mols. O_2 to 100 mols. HCl.

The results of all five series are collected in Table VI. The ratio of oxygen to hydrochloric acid in the final mixtures, given in the fifth column, is not used in the calculations but is given to show the range of the experiments.

TABLE VI.

No. of series.	Temp. Degrees.	Average pressure in atmospheres.	Mols. O_2 to 100 mols. HCl in original gas.	Mols. O_2 to 100 mols. HCl in final gas.	x.	K.
1	352	1.00	92.7	544.0	0.869	4.15
2	352	0.93	29.7	49.5	0.808	3.95
3	386	0.98	327.0	1970.0	0.845	2.94
4	386	0.96	48.8	146.0	0.804	3.01
5	419	1.08	327.0	1700.0	0.820	2.40

THERMODYNAMIC CONSIDERATION OF THE RESULTS.

It is evident from the preceding tables that the equilibrium constant, and, for a mixture of given composition, the yield of chlorine, are higher, the lower the temperature. This fact is in accordance both with the observations of previous experimenters and with the demands of thermodynamics, for the decomposition of hydrochloric acid by oxygen is accompanied by an evolution of heat. The amount of heat evolved in the reaction may be found from the heats of formation of hydrochloric acid and water.

The various determinations of the heat of formation of liquid water are reviewed in Ostwald's Lehrbuch. The three most reliable seem to be those of Schuller and Wartha,[1] of Than,[2] and of Thomsen.[3]

Schuller and Wartha burned hydrogen at atmospheric pressure in an ice calorimeter and obtained for the heat of formation of one mol. of water 68420 small calories.[4]

Than exploded oxygen and hydrogen in a bomb in the ice calorimeter. For 2 grams of hydrogen, 838.6 grams of ice melted. Taking 2.015 grams hydrogen as 1 mol. and using Smith's[5] value for the latent heat of fusion of ice, 79.9 cal., and adding the correction of 970 cal. calculated by Ostwald, we have 68480 cal.

Thomsen in a water calorimeter found 68360 cal. at 18°. This corresponds to 68500 cal. at 0°.

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[1] Wied. Ann. 2, 359 (1877).

[2] Ibid. 13, 84 (1881).

[3] Pogg. Ann. 148, 368 (1873).

[4] This value and all the following include the external work.

[5] Phys. Rev. 17, 193 (1903).

The mean of these three determinations at 0° is 68470 cal. In order to find the heat of formation of water vapor the heat of vaporization must be subtracted from this quantity. The mean of the three values for the heat of vaporization of 1 mol. of water at 0° given in the tables of Landolt and Börnstein is 10750 cal. From the mean of five determinations of the heat of vaporization at 100°, and from the specific heats of water and water vapor we may calculate the latent heat at 0°. This gives the value 10680 cal. These two values are sufficiently concordant. Subtracting their mean from the heat of formation of liquid water at 0° and then dividing by two we find,

$$H + \tfrac{1}{2}O = \tfrac{1}{2}H_2O \text{ (vapor)} + 28900 \text{ cal.}$$

For the heat of formation of hydrochloric acid Thomsen[1] found,

$$H + Cl = HCl + 22000 \text{ cal.}$$

This value is also used by Berthelot, but whether or not he determined it independently I am unable to learn. This value is nearly independent of the temperature.

Subtracting the second of these equations from the first, we have

$$HCl + \tfrac{1}{2}O = \tfrac{1}{2}H_2O + Cl + 6900 \text{ cal.}$$

From the best determinations of the specific heats of these four gases it appears that the change in heat capacity during this reaction is zero, within the limits of accuracy of the experimental data. The heat of reaction is therefore independent of the temperature.

The change of the equilibrium constant with the temperature is given by the van't Hoff equation,

$$\frac{d\ln K}{dT} = \frac{-Q}{RT^2}, \qquad (1)$$

where K is the equilibrium constant in terms of partial pressures, T is the absolute temperature, R is the gas constant and Q is the total heat evolved when the reaction occurs at constant pressure. If Q is expressed in calories, $R = 1.985$.

When Q is independent of the temperature, as in the present case, equation (1) is, in its integrated form,

$$\ln K = \frac{Q}{RT} + C'$$

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[1] Pogg. Ann. 148, 177 (1873).

where C' is the integration constant. Substituting the numerical values for Q and R and changing from natural to common logarithms, we have,

$$\log K = \frac{1509}{T} + C;$$

C is another constant which can be determined when K is known for any one temperature. It may therefore be found from each of the five results recorded in Table VI. The average of the five values of C thus obtained is —1.811. We have then finally,

$$\log K = \frac{1509}{T} - 1.811 \qquad (2)$$

This simple equation permits the calculation of the equilibrium constant of the Deacon reaction at any temperature. In order to show how well the experimental values of K contained in Table VI agree with theory, I have repeated them in Table VII by the side of the values calculated from equation (2).

TABLE VII.

Temperature. Degrees.	K (obs.)	K (calc.)
352	4.15	4.02
352	3.95	4.02
386	2.94	3.02
386	3.01	3.02
419	2.40	2.35

COMPARISON WITH OTHER DETERMINATIONS.

Haber,[1] in his excellent review of the work of Lunge and Marmier, concludes that true equilibrium was established in these experiments at the highest temperature at which they worked, 480°, and from their data he calculates, $K = 2.0$. Equation (2) gives 1.56 for this temperature. The discrepancy is doubtless due to the fact that in Lunge and Marmier's experiments at 480° the cupric chloride sublimed from the hot to the cooler part of the tube through which the gases were passing. Therefore the gases came in contact last with catalyzer considerably cooler than 480° and hence gave a larger yield of chlorine than corresponds to equilibrium at that temperature.

Another independent value of K at a very high temperature may be calculated from the experiments of Löwenstein[2] upon

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[1] Loc. cit. p. 168.

[2] Z. physik. Chem. 54, 715 (1906).

the dissociation of water vapor and hydrochloric acid. Thus the dissociation constant of water is,

$$K' = \frac{p^{\frac{1}{2}}_{H_2} p^{\frac{1}{4}}_{O_2}}{p^{\frac{1}{2}}_{H_2O}}$$

and that of hydrochloric acid is,

$$K'' = \frac{p^{\frac{1}{2}}_{H_2} p^{\frac{1}{2}}_{Cl_2}}{p_{HCl}}.$$

Hence K, the equilibrium constant of the Deacon process, is equal to $\frac{K''}{K'}$.

Löwenstein finds at 1537° that hydrochloric acid is 0.274 per cent. dissociated into chlorine and hydrogen. From this we find, $K'' = 0.00137$. For water we find from Löwenstein's results, $K' = 0.0074$ at 1510° and $K' = 0.0122$ at 1590°. From these, interpolations by means of the van't Hoff equation give for 1537°, $K' = 0.0103$. Dividing this by the above value of K'' we get, for the equilibrium constant of the Deacon process at 1537°, $K = 0.133$.

From equation (2) we find $K = 0.106$.

This is a very surprising agreement when we consider that the latter result was obtained by an extrapolation through more than 1100°.

THE ELECTROMOTIVE FORCE OF THE HYDROGEN-OXYGEN CELL.

From equation (2) we find for 25°, $K = 1800$. We are now able to calculate the free energy of the Deacon process at 25°.

By a familiar theorem,

$$A = RT \ln K,$$

where A is the free energy (exclusive of this work done by the atmosphere) of the reaction,

$$HCl + \tfrac{1}{4}O_2 = \tfrac{1}{2}Cl_2 + \tfrac{1}{2}H_2O,$$

when the gases consumed and those produced are all at atmospheric pressure.

Substituting numerically for R, T and K, we find $A = 4430$ cal. We may express this result in the form of an equation similar to those of thermochemistry.

HCl(1 atmos.) + $\tfrac{1}{4}O_2$ (1 atmos.) =
$\tfrac{1}{2}Cl_2$ (1 atmos.) + $\tfrac{1}{2}H_2O$ (1 atmos.) + 4430 cal. (free energy).

The free energy of formation of hydrochloric acid may be calculated from the work of Dolazalek,[1] who measured the electromotive force between a hydrogen and a chlorine electrode immersed in a hydrochloric acid solution in which the vapor-pressure of hydrochloric acid was determined. The solutions ranged from five to twelve times normal. From Dolazalek's data Haber has calculated the free energy and found

$$\tfrac{1}{2}H_2(1\ \text{atmos.}) + \tfrac{1}{2}Cl_2(1\ \text{atmos.}) = HCl(1\ \text{atmos.}) + 22428 \pm 118\ \text{cal. (free energy).}$$

This value is for 30°, but the free energy and the heat of formation (22,000) are so nearly identical that the change of the former with 5° change of temperature is negligible. The same equation is true, therefore, at 25°.

Such free energy equations may be added and subtracted just like those of thermochemistry. Adding the two above equations, we have,

$$\tfrac{1}{2}H_2(1\ \text{atmos.}) + \tfrac{1}{4}O_2(1\ \text{atmos.}) = \tfrac{1}{2}H_2O(\text{vapor, } 1\ \text{atmos.}) + 26860\ \text{cal. (free energy).}$$

From the free energy of a reaction it is easy to calculate the electromotive force of a cell in which this reaction occurs. In order to change from calories to volts we will use the same factor that Haber used in changing Dolazalek's data from volts to calories, namely 23110. Dividing 26860 by this number we obtain 1.162 volts as the electromotive force which a cell would have if its reaction consisted in the formation from oxygen and hydrogen at atmospheric pressure of water vapor at atmospheric pressure (assuming that it could exist at this pressure at 25°). Now the vapor-pressure of liquid water at 25° is 23.6 mm. of mercury. A cell converting hydrogen and oxygen into liquid water would have an electromotive force higher by $\frac{RT}{2}\ ln\ \frac{760}{23.6}$, or, 0.045 volt. We therefore find for the electromotive force of the ordinary hydrogen-oxygen cell, 1.207 volts.

The accuracy of this value depends chiefly upon the accuracy of two data which we have used in the calculation. Error in the experimental determination of the equilibrium in the Deacon process could hardly lead to an error of more than a small fraction of a millivolt in this final result. On the other hand, an error of 200 calories in the value we have chosen for the heat of reaction in the

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[1] Z. physik. Chem. **26**, 334 (1898).

Deacon process seems quite possible and would produce an error of about 5 millivolts. It is possible too that Dolazalek's results may be far enough from the truth to give a similar error. On the whole, perhaps, we may regard the present determination as entitled to a little less weight than the value obtained in my previous paper,[1] namely, 1.217 ± 0.010 volts.

The agreement between these two values, obtained in absolutely different ways, without a single datum in common, proves conclusively that the generally accepted value is about one-tenth of a volt too low.

At present we may take as the most probable value of the electromotive force of the hydrogen-oxygen cell, 1.212 volts, the average of the two determinations. I intend soon to review both these determinations with the aid of some new data and to compare them with the experiments of Nernst on the dissociation of water vapor and with those of Haber on the oxygen-hydrogen cell at high temperatures.

In conclusion I wish to express my deep obligation to Professor A. A. Noyes for generously placing at my disposal the means of carrying out this investigation in the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology.

SUMMARY.

Apparatus and method are described by which at the desired temperatures the conditions of equilibrium were obtained for the reaction, $4HCl + O_2 = 2H_2O + 2Cl_2$.

The catalyzer, cupric chloride, in each series of experiments required several days to reach a constant state, after which concordant results were obtained.

The time necessary to bring the gases to equilibrium was greater the lower the temperature and the smaller the percentage of oxygen present.

Experiments were made at three temperatures, 352°, 386° and 419°, and over a considerable range of concentration, the ratio of oxygen to hydrochloric acid in the final mixture being forty times as great in one case as in another.

At constant temperature the results are in accordance with the mass law.

The yield of chlorine from a given mixture is greater the lower the temperature, and the change of equilibrium constant with the

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[1] This Journal, 28, 158 (1906); Z. physik. Chem. 55, 465.

temperature is in good agreement with the equation of van't Hoff.

A simple equation is given from which the equilibrium constant at any temperature may be calculated.

The value thus calculated for 1537° agrees with the results of Löwenstein on the dissociation of water and hydrochloric acid at that temperature.

From the equilibrium constant of the Deacon reaction at 25°, and the experiments of Dolazalek, the electromotive force of the hydrogen-oxygen cell at 25° is calculated to be 1.207 volts, while the value obtained by an entirely different method in a previous paper was 1.217±0.010 volts.

The conclusion of the previous paper, that the value at present accepted for the electromotive force is one-tenth of a volt too low, is thus fully corroborated.

LIQUID METHYLAMINE AS A SOLVENT, AND A STUDY OF ITS CHEMICAL REACTIVITY.

BY H. D. GIBBS.

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SINCE Franklin[1] and his co-workers have shown, in an extended series of investigations, that liquid ammonia shows many analogies to water, both as a solvent and in its reactions, liquid methylamine would naturally be expected to show the same analogies to methyl alcohol. As $H.NH_2$ is to $H.OH$ so is CH_3NH_2 to $CH_3.OH$. Owing to its intermediate position in the group $H.NH_2$, $H.OH$, $CH_3.NH_2$, $CH_3.OH$, one would expect methylamine to possess the property of existing in compounds as methylamine of crystallization to a degree corresponding to that of the other members of the group. The compounds in which water is known to be a constituent as water of crystallization are too numerous for mention; ammonia is a constituent of a large number of known compounds as ammonia of crystallization, and methyl alcohol possesses the property of uniting with many compounds as alcohol of crystallization. Among the latter which are mentioned in the literature are:

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[1] Franklin and Kraus: Am. Ch. J. **20**, 820 and 836; **21**, 1 and 8; **23**, 277; **24**, 83; Franklin and Stafford: Ibid. **28**, 83; Franklin and Cady: This Journal, **26**, 499; Franklin and Kraus: Ibid. **27**, 191; Franklin: Ibid. **27**, 802.