viations are of such a nature that K' increases with increasing ion concentration.

This result, when examined from the standpoint of activity, as defined by Lewis, furnishes another illustration of the apparently general rule that when the concentration of an ion is based on conductance measurements the ratio of its activity to its concentration decreases somewhat with increasing ion concentration. An important consequence of this rule is that the solubility product of a salt will not be exactly constant but will increase with increasing ion concentration.

Values were also calculated for another equilibrium function $K = (I^-)(I_2)/(I_3^-)$. The results confirm the conclusion reached in an earlier paper that K decreases with increasing concentration of iodide, but show that other salts do not produce a similar effect.

Conductance measurements were also made with a number of the equilibrium solutions. These show that cupric iodide and cupric tri-iodide are ionized to the same extent as magnesium chloride, and that cupric nitrate is ionized to a somewhat less extent.

BOSTON, July, 1910.

THE POTENTIAL OF IRON CALCULATED FROM EQUILIBRIA MEASUREMENTS.[1]

BY ARTHUR B. LAMB.

Knowing the dissociation pressure of a metallic oxide, its heat of formation, the change of its heat of formation with the temperature, the solubility of its oxide in water, and finally, knowing the single potential of the oxygen electrode, it is possible to calculate on the basis of the fundamental laws of energetics and the concentration law the potential of the metal against a normal solution of its ions.[2]

Many metals give fairly definite and easily measurable potentials, especially when an amalgamated electrode can be employed.[3] When this is the case, an indirect calculation, such as the one just outlined, depending upon measurements of such difficulty as the dissociation pressures of metallic oxides at high temperatures, would be disadvantageous. The reverse calculation, that is, the calculation of dissociation pressures from electromotive forces, would be more rational, and indeed, has most often been made. This is not, however, always the case. Many solid metals give rather variable potentials, and certain

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[1] Presented in preliminary form before the New York Section, Dec. 11, 1908.

[2] van't Hoff, Ostwald's Klassiker No. 110, pp. 76 and 103 (1885); also Lewis, THIS JOURNAL, 28, 162 (1906). *Z. physik. Chem.*, 55, 470 (1906).

[3] Lewis, THIS JOURNAL, 32, 732 (1910).

metals, such as iron, have yielded widely differing values of the potential. Thus Richards and Behr[1] found that the true potential of iron was apparently as high as 0.18 volt, for the porous form, and 0.15 volt for the massive, if the calomel electrode is taken as —0.56, while other investigators had obtained values about a tenth of a volt lower. It is evident that in such a case as this a calculation of the potential from equilibria measurements might well be of interest.

Unfortunately, measurements of the equilibrium between iron, ferrous oxide and oxygen have not been made. It is certain, too, that such measurements would be very difficult of execution, for the temperature necessary to produce a measurable dissociation of the ferrous oxide would be very high. However, equilibrium measurements upon the system iron, ferrous oxide, carbon monoxide and carbon dioxide can be used for the desired calculation, just as well as the direct measurement of the dissociation pressure of the ferrous oxide; for our knowledge of the carbon monoxide, carbon dioxide and oxygen equilibrium is relatively very satisfactory. By combining the equations for these two equilibria we can easily calculate the dissociation equilibrium of ferrous oxide.

Baur and Glaessner[2] have made the necessary measurements of the equilibrium between iron, ferrous oxide and mixtures of carbon monoxide and dioxide. They found that at 1000° absolute, a mixture containing 40 per cent. carbon dioxide and 59 per cent. carbon monoxide was in equilibrium with a mixture of iron and ferrous oxide at atmospheric pressure. We can now calculate from the results of Nernst and v. Wartenberg[3] what the partial pressure of the oxygen must have been in this mixture of carbon monoxide and dioxide at this temperature. They found that at 1000° absolute and at atmospheric pressure carbon dioxide is 1.58×10^{-5} per cent. dissociated. Since

$$K_p = \frac{p_{CO_2}}{P_{CO} \times p_{O_2}^{1/2}}$$

where K_p represents the equilibrium constant expressed in units of pressure, and p_{CO_2}, p_{CO}, p_{O_2} the respective partial pressures, it follows that

$$K_p = \frac{1}{(1.58 \times 10^{-7})(\frac{1.58 \times 10^{-7}}{2})^{1/2}}, \text{ or } = 2.25 \times 10^{10}.$$

Substituting the values of Baur and Glaessner in this equation,

$$\frac{0.41}{(0.59)(p_{O_2})^{1/2}} = 2.25 \times 10^{10}$$

and therefore, $P_{O_2} = 0.95 \times 10^{-5}$ atmospheres, at 1000° abs.

[1] *Publication of the Carnegie Institution*, No. 61; *Z. physik. Chem.*, **58**, 334 (1907).

[2] *Z. physik. Chem.*, **43**, 358 (1903).

[3] *Ibid.*, **56**, 556 (1906).

It is also evident that equilibrium measurements similar to the above, but with carbon present as an additional solid phase, would be equally useful for evaluating the partial pressure of oxygen over ferrous oxide. Such measurements have been carefully made by Schenck, Similler and Falcke.[1]   Marked differences in the total pressures were found when different varieties of carbon were used, but the relative amounts of carbon monoxide and dioxide were found to be independent of this factor, as would be expected. Since only these relative amounts of carbon monoxide and dioxide concern us in the present calculation, we can select those measurements made in the immediate vicinity of 1000° abs., which happen to be those where amorphous carbon was used.   Interpolating for 1000° we find that the equilibrium mixture contained 61 per cent. carbon monoxide and 39 per cent. carbon dioxide.   Substituting these values in the above equation derived from the results of Nernst and v. Wartenberg, we obtain for the partial pressure of oxygen at 1000° abs.

$$P_{O_2} = 0.81 \times 10^{-21}.$$

This agrees excellently with the value 0.95×10^{-21} obtained from the results of Baur and Glaessner.   The mean of both results is

$$P_{O_2} = 0.88 \times 10^{-21}.$$

The dissociation pressure of oxygen over the oxide at 25° can be calculated from this value by means of the van't Hoff equation, knowing the heat of formation.   We cannot, however, assume that the heat of formation is constant over so long a range, and a modified form of the van't Hoff equation must therefore be used.   Such an equation has been deduced by Lewis[2] and applied to a similar problem.   It is

$$\ln \frac{p_1}{p_2} = -\frac{U_0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \frac{R - C}{R}\ln\frac{T_1}{T_2},$$

where

U_0 = twice the heat of formation of ferrous oxide at absolute zero;
T_1 = 1000° absolute;
T_2 = 298°;
p_1 = the partial pressure of the oxygen at $T_1 = 0.88 \times 10^{-21}$ atm.;
p_2 = the partial pressure of the oxygen at T_2;
C = the decrease in the heat capacity of the system $2FeO = 2Fe + O_2$, when a molecular weight of oxygen is liberated;
R = the gas constant = 1.985 cal./T.

The value of C at 25° can be computed with some accuracy.   According to Pionchon's[3] formula, representing his observations below 700°, the specific heat of iron at 25° would be 0.1116 cal./T.   Taking Nernst

[1] *Ber.*, 40, 1708 (1907).
[2] *Loc. cit.*
[3] *Ann. chim. phys.*, [6] 11, 72 (1887).

and v. Wartenberg's[1] formula for the molecular heat of permanent gases, based on Holborn and Austin's[2] measurements, the molecular heat of oxygen at constant volume would be 4.76 cal./T. The author and Mr. Barmeyer, in some unpublished measurements of the specific heat of ferrous oxide, found the specific heat of this substance to be 0.1660 cal./T at 25° to 100°, or 0.1627 at 25°, assuming that its specific heat changes at the same rate as does that of iron. Referring these values to equivalent molecular quantities, we find that

$$C_{25} = 2 \times (11.65) - 4.76 - 2 \times (6.23)$$
$$= 6.08 \text{ cals.}$$

The *mean* value of C over the temperature interval of 25° to 727°, which we require, can not be computed with as much accuracy, for the temperature coefficient of the specific heat of ferrous oxide is not known. An approximate value for C_{mean} can be obtained by assuming that this coefficient has the same relative value as that of metallic iron. Taking Pionchon's measurements at 710° as a basis, we find that 116.9 cal. is required to heat one gram of iron from 25° to 727°, or 13056 cals. for two-gram atoms. A gram molecule of oxygen would require 3400 cals. to be heated through the same interval. Assuming that ferrous oxide has the same temperature coefficient as iron below the recalescent point, two gram molecules of it would require 22,770 cals. It follows then that

$$C_{mean} = \frac{22770 - 3400 - 13056}{702} = \frac{6317}{702} = 9.0 \frac{\text{cal.}}{T}.$$

The uncertainty in the assumption regarding the temperature coefficient of the specific heat of ferrous oxide is so great that this value might be in error by as much as one or two calories. This inaccuracy has but a negligible effect on the final result.

The heat of formation of ferrous oxide has been measured directly by Le Chatelier,[3] using a calorimetric bomb. He found it to be 64,600 cal. at 17° and constant volume (for *one* gram molecule). The heat of formation at absolute zero may be found from the expression

$$U_o = U + CT.$$

Therefore, $U_o = 2 \times (64,600) + 6 (17 + 273) \text{ cal.}$
$$= 130,940 \text{ cal.}$$

Substituting these values in the above equation, we obtain

$$p_2 = P_{O_2} = 4.4 \times 10^{-90} \text{ atmospheres at } 25°.$$

A cell at 25°, consisting of an oxygen electrode and an iron electrode, plunged in a saturated solution of ferrous hydroxide, would then give zero electromotive force when the pressure of the oxygen over the oxygen electrode equaled 4.4×10^{-90} atmospheres.
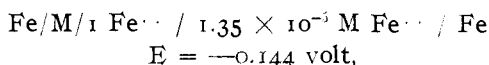
[1] *Loc. cit.*

[2] *Sitzungsber d. kgl. preuss. Akad.*, **1905**, p. 175.

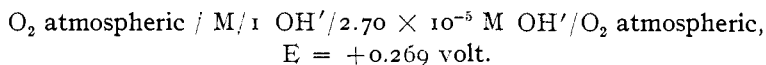[3] *Compt. rend.*, **120**, 623 (1895).

One can now calculate from the familiar equation of Nernst what electromotive force such a cell would have if the pressure of the oxygen were increased to atmospheric, and, knowing the solubility of ferrous hydroxide or ferrous oxide, what the electromotive force would be were the iron and hydroxyl ions present in normal concentration. Thus, were the oxygen at atmospheric pressure, the electromotive force would equal

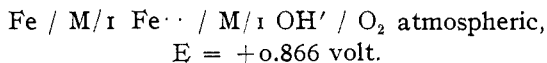$$E = \frac{0.059}{4} \log \frac{1}{8 \times 10^{-88}} = +1.279 \text{ volts.}$$

The solubility of ferrous hydroxide in water has been determined by Mr. Bridges and the author to be 1.35×10^{-5} mols. at $25°$. Then, for the cell

$$Fe/M/1 \; Fe\cdot\cdot \; / \; 1.35 \times 10^{-5} \; M \; Fe\cdot\cdot \; / \; Fe$$
$$E = -0.144 \text{ volt,}$$

and for the cell

$$O_2 \text{ atmospheric } / \; M/1 \; OH'/2.70 \times 10^{-5} \; M \; OH'/O_2 \text{ atmospheric,}$$
$$E = +0.269 \text{ volt.}$$

Combining these cells we obtain for the cell

$$Fe \; / \; M/1 \; Fe\cdot\cdot \; / \; M/1 \; OH' \; / \; O_2 \text{ atmospheric,}$$
$$E = +0.866 \text{ volt.}$$

Taking the normal calomel electrode as -0.564 at $25°$, the potential of oxygen against normal hydroxyl ions is -0.674, according to the recent investigations of Lewis[1] and others.[2] Hence the single potential of iron against a molecular normal solution of ferrous ion would be

$$E = 0.192 \text{ volt.}$$

This value agrees excellently with the value 0.19 volt obtained by Richards and Behr.

The significance of this agreement can be determined only by an examination of the experimental data as regards their probable errors, and the effect of these errors upon the final result.

Of these data the one requiring the most careful scrutiny from this point of view is the heat of formation of ferrous oxide. The value 64,600 cal., used in the above calculation for this quantity, was obtained by Le Chatelier from an experiment with a calorimetric bomb. The heat of formation of HYDRATED ferrous oxide calculated from three independent series of experiments[3] has an identical value in each case of 68,300 cal. at room temperature and constant pressure, or 68,000 cal. at room temperature and constant volume. This roughly confirms the value found by Le Chatelier for

[1] Z. physik. Chem., 55, 465 (1906); THIS JOURNAL, 28, 130 (1906).

[2] Z. physik. Chem., 56, 513 (1906); Ibid., 59, 313 (1907).

[3] Andrews, Pogg. Ann., 59, 439 (1843); Thomsen, J. prakt. Chem., [2] 11, 419 (1875); Berthelot, Ann. chim. phys., [5] 23, 118 (1881); see Ostwald, Lehrbuch II², 295.

dry ferrous oxide, as we should expect a higher value for the hydrated form. The difference, however, is greater than the probable heat of hydration, and would indicate that Le Chatelier's value was too low rather than too high.[1]

It appears improbable from these considerations that LeChatelier's value is in error (probably low) by more than three per cent. This error would give rise to an error in the potential of iron of about 25 millivolts, and in the sense that a higher value of the heat of formation would give a higher value for the potential.

The other data involved in the calculation afford less probability of error. Thus any considerable error in the value for the partial pressure is unlikely. The partial pressure was calculated from two independent series of observations and the resulting values agreed to within a few per cent. Data on the dissociation of carbon dioxide were involved in both calculations, but their accuracy is well established. It would seem highly improbable that the mean value for the partial pressure could be in error by 100 per cent., but even then the potential of iron would be altered only by seven millivolts.

The solubility measurements were made by the Kohlrausch method and the value employed was the mean of several concordant results. It is improbable that this value is in error by more than ten per cent. An error of this magnitude would only affect the final potential by about three millivolts, and in the sense that an increase in the solubility of the hydroxide would raise the calculated potential.[2]

[1] This heat of formation can be roughly calculated directly from the measurements of Baur and Glaessner, for their experiments extended over nearly two hundred degrees. Applying the above combination of van't Hoff's and Kirchhoff's theorems to the experimental values at $727°$ and $880°$, inserting the corresponding values for the dissociation as calculated from the observations of Nernst and v. Wartenberg, and using the same values for the specific heats, we obtain $U_0/2 = 72,000$ cal. or $U_{17}/2 = 72,870$ cal. Or, starting from the fact that the Fe, FeO, CO, CO_2, O_2 equilibrium curve, obtained by Baur and Glaessner, shows a minimum at $680°$, and that hence the heat of reaction must be zero at this temperature, we know that there the heat of formation of carbon dioxide from carbon monoxide must equal the heat of formation of ferrous oxide. Using the data collected by Haber (Thermodynamics of Technical Gas Reactions, p. 317), we find this to be $67,490$ cal. Correcting this to $17°$, using the same specific heat as above, we obtain $U_{17}/2 = 70,470$ cal. The accuracy of Baur and Glaessner's measurements is not, however, sufficient for calculations of this sort—and the values here given may well be in error on that account by 10 per cent. They can do no more than roughly indicate that the heat of formation of ferrous oxide at high temperatures is the same as that at low temperatures, and that LeChatelier's value for the heat of formation is perhaps too small.

[2] The uncertainty regarding the specific heat of ferrous oxide is of very slight importance in the calculation of the potential. An error of 50 per cent. in it would only affect the potential by about three millivolts. There is a slight error involved in taking the solubility of the ferrous hydroxide instead of that of ferrous oxide. The

Summarizing this calculation of the potential of iron and this discussion of the effect of the probable experimental errors on the final result, we may say:

(1) That the calculated potential of iron against a molecular normal solution of ferrous ions, taking the calomel electrode as —0.564 volt, is **0.192**, in excellent agreement with the experimental results of Richards and Behr;

(2) That, in so far as errors in the experimental data involved are concerned, this result can scarcely be in error by more than three centivolts, and that it is probably too low, rather than too high.

UNIVERSITY HEIGHTS, NEW YORK CITY,
June 20, 1910.

THE INVERSION OF CANE SUGAR BY INVERTASE. VI. A THEORY OF THE INFLUENCE OF ACIDS AND ALKALIS ON THE ACTIVITY OF INVERTASE.
BY C. S. HUDSON.

In alkaline solutions invertase shows no activity, in weakly acid solutions its enzymotic power reaches a maximum from which it decreases with increasing acidity. The simplest theoretical interpretation of this striking fact is that acids and alkalis combine with invertase by the principles of the law of mass action and prevent it from inverting cane sugar. In the following calculations this hypothesis will be tested. If invertase combines with both acids and alkalis it is an amphoteric electrolyte and may be assumed to dissociate as follows:

(1)   Invertase $\rightleftarrows \dot{H}$ + anion (acidic dissociation).

(2)   Invertase $\rightleftarrows OH'$ + cation (basic dissociation).

If a units of invertase are dissolved in a unit volume of a solution containing hydrogen and hydroxyl ions in the fixed concentrations $(\dot{H})$ and (OH), it will form x units of anion and y units of cation, leaving $a - x - y$ units of undissociated invertase. The mass-action law requires the fulfilment of the following conditions when equilibrium is attained:

$$(3)\ \frac{(x)\,(\dot{H})}{(a-x-y)} = K_1, \text{ and } (4)\ \frac{(y)\,(OH')}{(a-x-y)} = K_2$$

The quantity $a - x - y$ is the concentration of uncombined or undissociated invertase, and it is here assumed that the enzymotic activity is caused by this substance and is proportional to its concentration.

difference, however, must be small, since, from the properties of ferrous oxide, we know that the heat of hydration is probably very small. Since the solubility of ferrous oxide, could it be measured, would be greater than that of ferrous hydroxide, this inaccuracy also tends to make the true potential higher.