

quinone and pyrocatechol. For while resorcinol dissolves readily to give good conducting solutions, pyrocatechol and hydroquinone apparently do not dissolve at all, and certainly do not give conducting solutions.

(3) That in the paraffin series, the simpler the alcohol—the lower it comes in the series—the greater the conducting power of its solutions. While in the benzene series, the greater the number of carbon atoms in the molecule, the better conductor will the solution of the alcohol be.

(4) That in a very few cases, for two or three of the more dilute solutions, the molecular conductivity increases slightly, or remains practically constant as the dilution increases. But for a majority of the cases examined, and for all the more concentrated solutions, the molecular conductivity decreases rapidly as the dilution increases.

(5) That if we calculate the value of the molecular conductivity from the expression, $\kappa \nu^n$, where n is the number of molecules of solute uniting with one molecule of the solvent to form the electrolytic compounds instead of from the expression $\kappa \nu$, we obtain values which, in the case of the alcohols of the benzene series, vary with the dilution in the same manner as the values for the molecular conductivity of solutions of inorganic salts in water. In the case, however, of the paraffin alcohols, this expression will apply only over a narrow range of dilution.

(6) That the temperature coefficients of conductivity are in some cases positive, in some cases negative, and not infrequently change sign in passing from a concentrated to a dilute solution.

In conclusion, I wish to express my thanks to the trustees of the Elizabeth Thompson Science Research Fund, for a grant which helped to defray the expenses incurred in carrying on this work.

CHEMICAL LABORATORY,
SYRACUSE UNIVERSITY, SYRACUSE, N. Y.

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THE CALCULATION OF SOME CHEMICAL EQUILIBRIA

BY K. GEORGE FALK.

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While assisting Professor W. Nernst in preparing the Silliman lectures which were delivered at Yale University in October, 1906, the writer had occasion to become familiar with the new theory¹ developed by Professor Nernst, which permits the calculation of chemical equilibria from thermal

¹ This theory was published for the first time in the "Nachrichten der K. Gesellschaft der Wissenschaften zu Göttingen, Mathematisch-physikalische Klasse, 1906. Heft 1" under the title "Ueber die Berechnung chemischer Gleichgewichte aus thermischen Messungen." The complete theory so far as it has been developed to the present time has just appeared in book form "Experimental and Theoretical Applications of Thermodynamics to Chemistry" by W. Nernst.

magnitudes only. In this paper, in which the subject is not discussed critically, are presented the equations deduced for this purpose, together with the method of applying them, as well as calculations for several reactions showing the relation between the values obtained experimentally and those calculated by means of the theoretical formulas.

The cases to be dealt with in this article are exclusively reactions in homogeneous gaseous systems, and only the final equations to be used directly in these calculations will be here given. For the fundamental hypotheses on which these equations are based, for their derivation from those hypotheses, and for the significance of the numerical constants and of the so-called *chemical constants* (mentioned below) reference must be made to Nernst's complete treatment.

The notation used in the Silliman lectures will be adhered to here.

The equations, in question, with the general numerical constants already introduced, are as follows:—

$$(1) \quad \log K' = -\frac{Q'_0}{4.571 T} + \Sigma \nu \cdot 1.75 \log T + \frac{\Sigma \nu \beta}{4.571 T} + \Sigma \nu C$$

in which K' represents the equilibrium constant expressed in terms of the partial pressures of the substances present; Q'_0 the heat of reaction near absolute zero (at absolute zero, of course, the gases would no longer exist as such); T the absolute temperature at which the reaction takes place; and $\Sigma \nu C$ the algebraic sum of the chemical constants of the substances taking part in the reaction. $\Sigma \nu$ in the second term denotes the increase or decrease in the number of molecules taking part in the reaction, depending upon which $1.75 \log T$ is to be subtracted or added one or more times. If there is no change in the number of molecules taking part, this term drops out.

$$(2) \quad \Sigma \nu \beta = \frac{\Sigma \nu H_p - \Sigma \nu 3.5}{2T}$$

$\Sigma \nu H_p$ represents the algebraic sum of the molecular heats at the absolute temperature T of the substances taking part in the reaction, and $\Sigma \nu$ in the second term of the numerator of the fraction the change in the number of molecules in the reaction, similar to the above, upon which depends the number of times 3.5 is taken.

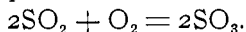
$$(3) \quad Q_p' = Q'_0 + \Sigma \nu 3.5 T + \Sigma \nu \beta T^2$$

Q_p' represents the heat of reaction at constant pressure at the absolute temperature T ; Q'_0 the heat of reaction, calculated, near absolute zero; the second term as before depending upon the change in the number of molecules taking part in the reaction; while $\Sigma \nu \beta$ can be calculated as shown.

By means of these three equations, a chemical equilibrium in a homogeneous gaseous system can be calculated from the heat of reaction at the temperature T , the molecular heats of the reacting substances, and the

chemical constants of these substances. The case of a heterogeneous system will not be gone into here. The chemical constants for a large number of substances have been calculated by Professor Nernst and certain regularities have been observed, so that it is possible to extrapolate for some substances for which the data are not at hand for a direct calculation.

In carrying out the calculations it has been found best to calculate the temperature which corresponds to a given dissociation or given value for the equilibrium constant and compare it with the temperature found experimentally for this equilibrium. The first example to be taken up here will be the formation of sulphur trioxide from sulphur dioxide and oxygen according to the equation



The molecular heat at constant pressure of O_2 is 6.9 and of SO_2 9.8 (Regnault), both at $T = 430$. The molecular heat of SO_3 is not known, but it may safely be put equal to 11.0, somewhat higher than that of SO_2 . Equation (2) gives then

$$\Sigma \nu \beta = \frac{4.5 - 3.5}{860} = 0.0011$$

The value of the molecular heat of SO_3 has only a slight influence on the final calculation. If 11.5 is taken instead of 11.0, $\Sigma \nu \beta = 0$, and the calculated temperatures would all be increased about 20° . Further

$$Q_p' = 45200 \text{ for } T = 290 \text{ (Berthelot)}$$

and therefore $Q_p' = 44100 + 3.5T + 0.0011 T^2$.

Substituting in equation (1)

$$\log K' = -\frac{9500}{T} + 1.75 \log T + 0.00024 T + 3.2.$$

$\Sigma \nu C = 6.6 + 2.8 - 6.2 = 3.2$, the chemical constant for SO_2 being 3.3, for O_2 2.8, and for SO_3 put equal to 3.1, the true value for the latter not being known, in which case the general rule has been found to hold that this constant can be put equal to about 3.0. For SO_3 it has been put at 3.1, as the constants increase slightly with the boiling points of the substances.

The formation of SO_3 from SO_2 and O_2 has been carefully studied by Bodenstein¹ and the equilibria determined experimentally for different temperatures. His results for the equilibrium constants are given in the form

$$K_p = \frac{[\text{SO}_3]}{[\text{SO}_2] [\text{O}_2]^{-\frac{1}{2}}}$$

In this paper the results are given

$$K' = \frac{[\text{SO}_2]^2 [\text{O}_2]}{[\text{SO}_3]^2}$$

¹ Quoted by Haber "Thermodynamik technischer Gasreaktionen" page 178.

and therefore

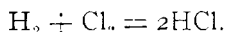
$$K' = \frac{1}{K_p^2}$$

The following table shows the temperatures observed and calculated, which correspond to the equilibrium constants given under K' .

K'	T (obs.)	T (calc.)
0.0010	801	834
0.0053	852	885
0.033	900	949
0.095	953	990
0.29	1000	1035
1.09	1062	1098
2.54	1105	1140
7.81	1170	1202

As can be seen there is a very good agreement between the calculated and the observed values.

The other examples which will be taken up are the equilibria of the halogen hydrides with hydrogen and the halogens at elevated temperatures. Hydrochloric acid will first be considered.



The molecular heats of the hydrochloric acid and the hydrogen are practically equal to each other, that of Cl_2 is uncertain, but since the partial pressure of the chlorine is very small in the final mixture, $\sum \nu H_f$ will equal zero. Since the number of molecules does not change in the reaction, $\sum \nu 3.5 = 0$, and therefore $\sum \nu \beta = 0$. Further $Q_p' = 44000$ for $T = 290$ (Berthelot and Thomseu) and also $Q_0' = 44000$. Substituting in (1)

$$\log K' = -\frac{9626}{T} - 0.8$$

$\sum \nu C = 2.2 + 3.0 - 6.0 = -0.8$, the chemical constant for hydrogen being 2.2, and for both chlorine and hydrochloric acid 3.0. If x denotes the degree of dissociation at the pressure of one atmosphere and $100x$ therefore the percentage dissociation,

$$K' = x^2$$

and

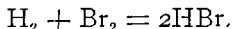
$$\log x = -\frac{4813}{T} - 0.4$$

The only quantitative measurement of the dissociation of hydrochloric acid is given by Loewenstein¹, who obtained 0.274 per cent. dissociation at $T = 1810$. The calculated temperature corresponding to this dissociation is $T = 2220$. The agreement in this case is very poor, but the experimental value is not at all certain, being only a single determination.

¹ Z. physik. Chem., 54, 715.

It may be of some interest to note the temperatures (calculated) which would be required to dissociate hydrochloric acid to different degrees.

100x	T(calc.)
0.01	1340
0.10	1850
1.00	3010



The sum of the molecular heats of Br_2 and H_2 exceeds the molecular heat of 2HBr by 2. at the ordinary temperature.¹ Letting x denote the

$$\Sigma\nu\beta = \frac{2}{580} = 0.0034$$

$$Q_p' = 24400 \text{ for } T = 303 \text{ (Berthelot 24600, Thomsen 24200)}$$

$$Q_p' = 24100 + 0.0034T^2$$

$$\log K' = -\frac{5270}{T} + 0.00074T - 0.5$$

$$\Sigma\nu C = 2.2 + 3.5 - 6.2 = -0.5$$

$\text{H}_2 \quad \text{Br}_2 \quad 2\text{HBr (approx.)}$

degree of the dissociation as before,

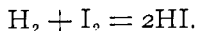
$$\log x = -\frac{2635}{T} + 0.00037T - 0.25.$$

Reichenbach and Bodenstein² observed a dissociation of 0.3 per cent. to 0.9 per cent. at the temperature of 923° to 1023° absolute. For 0.3 per cent. dissociation ($x = 0.003$) the calculated temperature is $T = 1000^\circ$, and for 0.9 per cent. ($x = 0.009$) T (calculated = 1176°). Bodenstein and Geiger³ state that this dissociation is probably too great; that is to say, would correspond to a higher temperature. The same fact is shown by the calculations.

Finally the temperatures required for certain degrees of dissociation are given.

100x	T(calc.)
0.01	660
0.10	858
1.00	1200

The temperatures necessary to produce the same percentage dissociation as with hydrochloric acid are very much lower than with the latter, as was to have been expected.



The molecular heat of H_2 is 6.8, of I_2 8.5 and of HI 7.0; all at $T = 570$.

$$\Sigma\nu\beta = \frac{1.3}{1140} = 0.0011$$

$$\log K' = -\frac{Q_0'}{4.571T} + 0.00024T - 0.2$$

$$\Sigma\nu C = 2.2 + 4.0 - 6.4 = -0.2$$

$\text{H}_2 \quad \text{I}_2 \quad 2\text{HI (approx.)}$

¹Haber, l. c. page 96.

²Z. physik. Chem., 49, 61.

³Ibid., 49, 78.

Q_r ' the heat effect of this reaction is not known with any certainty, due primarily to the dissociation of the iodine molecule into atoms at even moderate temperatures.¹ Since the heat of reaction at all events is small, in order to calculate K' with some degree of accuracy, it would probably be necessary here to take into account higher terms than T^2 in the original deduction. It can, however, be seen qualitatively in the equation by using a small value for the heat of reaction, that there is marked dissociation at comparatively low temperatures, but its change with increasing temperature cannot be followed.

LABORATORY OF PHYSICAL CHEMISTRY.

[CONTRIBUTIONS FROM THE LABORATORY OF THE MALLINCKRODT
CHEMICAL WORKS].

ON THE DENSITY CURVE OF MIXTURES OF BROMINE AND CHLORINE.²

BY LAUNCELOT W. ANDREWS AND HENRY A. CARLTON.

Received February 23, 1907.

The fullest determinations of the densities of bromine at various temperatures appear to be those of Thorpe³ and of Pierre⁴. The former determined the density at 0° to be 3.187, while Pierre found at the same temperature 3.188. At 35° Thorpe found 3.10104 and Pierre 3.10472.⁵ We shall bring forward evidence in the present paper going to show that the results of Thorpe are too low by an amount which can be accounted for on the assumption that his bromine contained about 0.039 per cent. of chlorine. The density of liquid chlorine at 25°, as calculated from the formula of Knietzsch⁶, is 1.39778. The existence of a monochloride of bromine is generally assumed, on the basis of the investigations of Bornemann⁷. There seems to be but little evidence to support this assumption, except the existence at low temperatures of hydrates, said⁸ to have the formulas, $\text{BrCl} \cdot 5\text{H}_2\text{O}$ and $\text{BrCl} \cdot 10\text{H}_2\text{O}$. Obviously the existence of such hydrates, even if fully demonstrated, would constitute no sufficient proof of the existence of the compound BrCl in the absence of water. Proof or disproof of the existence of compounds of chlorine and of bromine with one another must be sought for in the physical properties and behavior of mixtures of these elements at ordinary or at low temper-

¹ See the discussion by Haber, l. c. page 100.

² Read at the New York Meeting of the American Chemical Society.

³ J. Chem. Soc., 37, 172 (1880).

⁴ Moissan, *Traité de chimie minérale*, Tome 1, 133; *Ann. chim. phys.* (3) 20, 45 (1847).

⁵ Interpolated.

⁶ *Ann.*, 259, 100 (1890).

⁷ *Ann.*, 189, 206 (1877).

⁸ Loewig, *Das Brom*, Heidelberg (1829) 64.