Harold Whiting and others, ascribing polymerization to water, is empha-sized.

It is a pleasure to express our thanks to the Carnegie Institution of Washington for the pecuniary support in this investigation.

THE THERMAL DISSOCIATION OF SULFUR DIOXIDE.

BY J. B. FERGUSON.

Carbon dioxide may be decomposed by heat to form carbon monoxide and oxygen, and the degree of this dissociation has been determined both by direct measurements and indirectly from considerations of the so-called water-gas reaction and the dissociation of water vapor. In an analogous fashion sulfur dioxide would be expected to dissociate into sulfur and oxygen, and theoretically the degree of this dissociation could be de-termined in a similar manner. However, in practice, Lewis, Randall and Bichowsky[1] even at $1500°$ were unable to study this reaction quanti-tatively because of the slight extent of the dissociation, and my own ob-servations at temperatures ranging from $1000°$ to $1200°$ are confirmatory of their experiences with this reaction. The indirect methods would therefore appear to be the only ones available for this determination. In the present paper the mode of arriving at results by one indirect method and the results themselves are presented.

The equation for the dissociation of sulfur dioxide may be written $1/2\ S_2 + O_2 \rightleftarrows SO_2$, if the temperature range considered is that in which the density of sulfur vapor corresponds to a formula S_2, and the recent work of Randall and Bichowsky[2] on the dissociation of hydrogen sulfide indicates that no great error is involved in the assumption of the formula S_2 for sulfur vapor at $1500°$.

By a method similar to that employed in calculating the carbon dioxide dissociation from the water-gas equilibrium the sulfur dioxide dissocia-tion may be calculated from equilibrium measurements of either the re-duction of sulfur dioxide by hydrogen[2] or the reduction of sulfur dioxide by carbon monoxide.[3] The latter data were, however, obtained in a more direct manner than the former and will therefore be used. If the equi-librium constant for the reaction

$$CO + 1/2SO_2 \rightleftarrows CO_2 + 1/4S_2$$
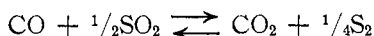
[1] G. N. Lewis, Merle Randall and F. Russell v. Bichowsky, THIS JOURNAL, 40, 356 (1918).

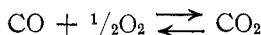[2] Merle Randall and F. Russell v. Bichowsky, Ibid., 40, 368 (1918).

[3] J. B. Ferguson, Ibid., 40, 1626 (1918).

is written

$$K_1 = \frac{P_{CO_2} \cdot P_{S_2}^{\frac{1}{4}}}{P_{CO} \cdot P_{SO_2}^{\frac{1}{2}}} \quad (1)$$

and if the equilibrium constant for the reaction

$$CO + \tfrac{1}{2}O_2 \rightleftarrows CO_2$$

is written

$$K_2 = \frac{P_{CO_2}}{P_{CO} \cdot P_{O_2}^{\frac{1}{2}}} \quad (2)$$

then, by dividing (2) by (1) and squaring:

$$\left(\frac{K_2}{K_1}\right)^2 = \frac{P_{SO_2}}{P_{S_2}^{\frac{1}{2}} \cdot P_{O_2}} = K \quad (3)$$

we get the equilibrium constant K for the sulfur dioxide dissociation.

The actual determination of K in this manner is, however, a somewhat laborious task and the work may be materially lessened if instead of determining the actual values of K_1 and K_2, use is made of the equations in which the logarithms of these values are represented as functions of the absolute temperature. The simple subtraction of two such equations is equivalent to the division of K_2 by K_1 and yields a new equation in which the logarithm of $\sqrt{K}$ is represented as a function of the absolute temperature and by means of which K may be calculated for any temperature at which the original equations would hold. The free energy equation, that is, the equation representing the thermodynamical potential at constant temperature and pressure, is an equation of the desired type, since the free energy is defined by the equations[1]

$$\Delta F = \Delta H_0 - \Delta \Gamma_1 T \, ln \, T - \tfrac{1}{2}\Delta\Gamma_2 T^2 - \tfrac{1}{6}\Delta\Gamma_3 T^3 + IT \quad (4)$$
$$\Delta F = -RT \, ln \, K$$

in which ΔH_0, $\Delta\Gamma_1$, $\Delta\Gamma_2$, $\Delta\Gamma_3$, and I are constants for any given reaction. Hence,

$$-RT \, ln \, K = \Delta H_0 - \Delta\Gamma_1 T \, ln \, T - \tfrac{1}{2}\Delta\Gamma_2 T^2 - \tfrac{1}{6}\Delta\Gamma_3 T^3 + IT \quad (5)$$

By substitution of the actual values of these constants the calculation is made as follows:

$CO + \tfrac{1}{2}O_2 \rightleftarrows CO_2$:[2] $-RT \, ln \, K_2 = -67510 +$

$$2.75T \, ln \, T - 0.0028T^2 + 0.00000031T^3 + 4.30T \quad (6)$$

$CO + \tfrac{1}{2} SO_2 \rightleftarrows CO_2 + \tfrac{1}{4}S_2$: $-RT \, ln \, K_1 = -25915 +$

$$1.375T \, ln \, T - 0.0014T^2 + 0.000000155T^3 + 3.99T \quad (7)$$

Subtract (7) from (6) and substitute K for $(K_2/K_1)^2$:

$O_2 + \tfrac{1}{2}S_2 \rightleftarrows SO_2$: $-RT \, ln \, K = -83190 +$

$$2.75T \, ln \, T - 0.0028T^2 + 0.00000031T^3 + 0.62T \quad (8)$$

[1] G. N. Lewis, THIS JOURNAL, **35**, 1 (1913).

[2] G. N. Lewis and Merle Randall, *Ibid.*, **37**, 458 (1915).

or:

$$\log K = 1818°/T - 1.38 \log T +$$
$$0.00061T - 0.000000067T^2 - 0.135 \quad (9)$$

By means of Equation 9 the equilibrium constants for temperatures from 1000° to 1500° have been calculated. These are given in Table I. If ΔF be substituted for $-RT \ln K$ in Equation 8, this equation then becomes the equation for the free energy of the formation of sulfur dioxide from sulfur vapor and oxygen at these temperatures. The same equation may be derived by combining the free energy equations of the reactions

$$S_R + O_2 \rightleftarrows SO_2[1] \text{ and } 2S_R = S_2.[2]$$
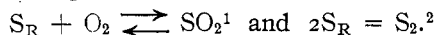
The degree of dissociation may readily be calculated from the equilibrium constants. The pressure of the sulfur dioxide, since the dissociation is slight, may be assumed to equal the total pressure p and the pressure of the sulfur vapor according to the reaction equation is one-half that of the oxygen. Therefore the equation for K may be written

$$K = \frac{p}{\sqrt{P^3_{O_2}/2}} \text{ and hence } P_{O_2} = \sqrt[3]{\frac{2p^2}{K^2}}.$$

But the amount of the oxygen formed is equivalent to the amount of sulfur dioxide dissociated, and the fraction x of the original sulfur dioxide which is dissociated is represented by the equation

$$x = \frac{P_{O_2}}{p} = \frac{1}{p}\sqrt[3]{\frac{2p^2}{K^2}} = \frac{1.26}{\sqrt[3]{K^2p}}.$$

The values of x for the temperature range 1000–1500° for several pressures are also given in Table I.

TABLE I.

The Equilibrium Constant K for the Dissociation of Sulfur Dioxide and the Corresponding Degree of Dissociation x, Calculated for Various Temperatures and Pressures.

Temperature degrees		Log K.	$10^{-3} K$.	$10^5 \times$ degree of dissociation, x. Pressure in atmospheres.			
Centigrade.	Absolute.			1.0.	0.1.	0.01.	0.001.
1000	1273	10.545	350	0.012	0.026	0.056	0.12
1100	1373	9.476	30	0.061	0.13	0.28	0.61
1200	1473	8.586	3.8	0.24	0.52	1.1	2.4
1300	1573	7.796	0.63	0.80	1.7	3.8	8.0
1400	1673	7.109	0.13	2.3	5.0	11	23
1500	1773	6.493	0.031	5.9	13	27	59

The degree of dissociation of sulfur dioxide is thus found to be somewhat less than the degree of dissociation of either carbon dioxide or water vapor.

Summary.

The degree of dissociation and the equilibrium constants for the dissociation of sulfur dioxide have been calculated from the equilibrium

[1] J. B. Ferguson. THIS JOURNAL, 40, 1626 (1918).
[2] G. N. Lewis and Merle Randall, *Ibid.*, 36, 2474 (1914).

measurements of the reduction of sulfur dioxide by carbon monoxide. The details of the calculation and the tabulated results are presented.

WASHINGTON, D. C.

STUDIES IN CONDUCTIVITY. IV. THE CONDUCTIVITY OF ALKALINE EARTH FORMATES IN ANHYDROUS FORMIC ACID.

BY H. I. SCHLESINGER AND R. D. MULLINIX.[1]

In previous work[2] on the behavior of the alkali metal formates dissolved in (anhydrous) formic acid, it was shown that when the degree of ionization is calculated from the conductivity uncorrected for viscosity, these very highly dissociated salts obey the law of chemical equilibrium up to relatively high concentrations. It was therefore considered important to investigate also some of the formates of bivalent metals, especially as there lay in this direction a possibility that light might be shed on the problem of the existence of intermediate ions in highly ionized salts. For this purpose we chose the formates of the alkaline earth metals.

The method and apparatus for preparing the formic acid and for making the conductivity measurements are described in a paper of this series by Schlesinger and Reed.[3] Calcium formate was prepared from a Kahlbaum sample by recrystallization until no further change in the conductivity resulted. The stronium salt was prepared by dissolving the carbonate in an aqueous solution of formic acid and evaporating the resulting solution, recrystallizing the resulting salt and drying it at a sufficiently high temperature to drive out the water. While all of the salts were analyzed and found pure within the limits of the ordinary analytical error, we used as criterion of their purity the fact that further recrystallizations produced no change in the conductivity of the salts when made up to a definite concentration in formic acid solutions.

In Tables I and II are given the experimental results found for calcium and strontium formate solutions, respectively. In the first column of each table is given the concentration c expressed in gram equivalents per liter, in the second column the specific conductivity χ in reciprocal ohms, in the third column the specific conductivity in reciprocal ohms

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[2] THIS JOURNAL, 36, 1599 (1914); 38, 271 (1916).
[3] To be published in THIS JOURNAL in the near future.