[Contribution from the Chemistry Department, University of Washington]

Solubility of Sulfur Dioxide in Water

By W. L. Beuschlein and Louis O. Simenson

A knowledge of the equilibrium solubilities of sulfur dioxide in water is essential in connection with calculations and research work on absorption. In 1925, Sherwood[1] presented some values calculated from the data of previous workers and in 1928 the "International Critical Tables"[2] published some values. W. Boyd Campbell and O. Maass[3] have determined the solubility of sulfur dioxide in water for the temperature range 25–120° and the concentration range 1.00–7.40%. O. M. Morgan and O. Maass[4] have reported the solubility of sulfur dioxide in water at temperatures between 0 and 25°. This investigation was undertaken to check and extend existing data.

Experimental

The investigation was carried out with the apparatus shown in Fig. 1, consisting of a vertical glass solution tube containing a buoyant stirrer C and a mercury relay G attached to the upper part of the tube. The stirrer contained an iron core B and was activated by means of a solenoid A circumscribing the solution tube, the solenoid being intermittently energized. The whole apparatus was immersed below the oil level E of the temperature controlling bath. The solutions to be run were prepared by passing sulfur dioxide through freshly boiled, distilled water until saturated and then diluting to the desired concentration.

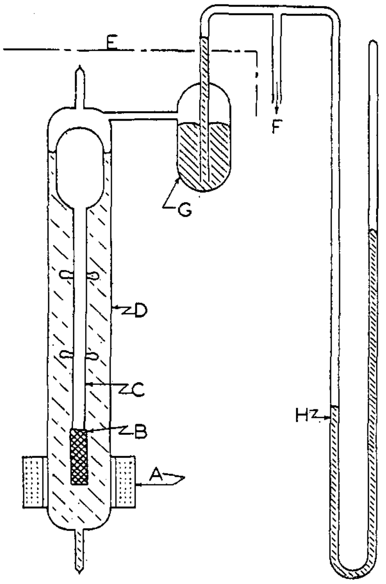

Fig. 1.

The solution was run into the apparatus through the small bottom tube shown in Fig. 1. The inflowing solution was allowed to fill completely all the free space in the solution tube and mercury pressure relay, displacing all the air through the small tube at the top. The end of the upper small tube, previously having been drawn to a hair-like capillary, was sealed with a small flame. The absence of air in the apparatus was indicated by the liquid completely filling the sealed capillary after the latter had cooled. Next, some of the solution was drawn out of the apparatus through the bottom tube by which it entered, great care being taken to maintain equal pressures on each side of the mercury pressure relay. This was done by branching the suction line, running one branch to the external side of the relay and drawing the solution out of the other. Just enough solution was removed to form a vapor space such that the stirrer could function. At this time, a sample of the solution was taken for analysis as to concentration and density. The bottom filling tube was flamed quickly and drawn to a seal at a point where it had previously been drawn to a very fine capillary.

The whole apparatus was then immersed into a thermostated oil-bath maintained to within ±0.2° and held constant for ten minutes before a pressure reading was recorded. The pressures were read to within ±0.5 mm. of mercury on a mercury, sealed in manometer H.

The external pressure on the relay was balanced in such a manner that the mercury head in the relay was constant throughout the whole run. This head, as shown in Fig. 1, was measured with a cathetometer. No particular temperature was selected for a reading, but approximately equal intervals were taken to ensure equilibrium conditions; the temperature of the bath was raised very slowly, one run consuming five hours in going from 20 to 110°.

The pressures were checked by taking measurements as the bath cooled. At the end of the run, a sample of the solution was withdrawn, analyzed and found to check with that at the beginning.

The sulfur dioxide used in this work was "refrigeration dry" and warranted by the manufacturer to be 99.99% pure. No trace of trioxide was found and freshly boiled, distilled water was used in making up the solutions.

The method of analysis consisted of running the sulfur dioxide solution into an excess of iodine with constant agitation and back titrating with sodium thiosulfate.[5] A check was made on the method of pressure measurement by determining the vapor pressure of water. The results

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(1) T. K. Sherwood, *Ind. Eng. Chem.*, **17**, 745–747 (1925).

(2) "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., p. 302 (1928).

(3) W. Boyd Campbell and O. Maass, *Can. J. Res.*, **2**, 42–64 (1930).

(4) O. M. Morgan and O. Maass, *Can. J. Res.*, **5**, 162–179 (1931).

(5) F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1935, pp. 88–89.

agreed with accepted values[6] within the limits of accuracy of the thermometer and manometer.

Experimental Results

In Table I are given the densities at 23° of the sulfur dioxide solutions used for the vapor pressure determinations. In Table II are given the partial vapor pressure data for the four concentrations, which are expressed as grams of sulfur dioxide in 100 g. of water. The partial vapor pressure of sulfur dioxide above the solution was calculated as the total pressure minus the vapor pressure of pure water at the temperature of the experiment.

TABLE I

DENSITIES OF SULFUR DIOXIDE SOLUTIONS

Temp., °C.	Concn., g. SO_2 per 100 g. H_2O	Density, g./cc.
23.0	0.51	1.0019
23.0	1.09	1.0043
23.0	4.36	1.0199
23.0	7.45	1.0338

TABLE II

PARTIAL VAPOR PRESSURE OF THE SYSTEM SULFUR DIOXIDE–WATER

Temp., °C.	SO_2 press., mm.	Temp., °C.	SO_2 press., mm.
0.51 g. SO_2/100 g. H_2O		1.09 SO_2/100 g. H_2O	
35.6	49.0	26.8	70.5
41.0	57.0	33.6	96.0
47.0	70.0	39.4	124.5
52.0	80.0	44.2	147.0
62.6	118.0	50.6	178.0
71.0	150.0	61.6	245.0
78.6	185.0	67.4	280.5
85.0	215.5	73.4	327.5
92.2	250.0	79.2	372.0
99.0	285.5	86.4	445.5
105.2	320.5	98.4	510.0
111.8	358.0	100.6	600.0
113.0	367.5	106.6	668.0
4.36 g. SO_2/100 g. H_2O		7.45 g. SO_2/100 g. H_2O	
23.2	332.0	25.2	647.0
27.2	373.0	31.4	780.5
30.0	420.0	34.2	838.0
33.0	465.5	37.4	915.5
36.0	513.0	41.0	989.0
38.2	551.5	44.0	1069.0
42.2	619.0	47.2	1152.5
45.2	680.5	50.4	1255.5
48.2	741.0	54.4	1391.0
52.0	818.0	55.6	1443.5
55.3	896.0		
58.4	970.5		
61.2	1036.5		
63.0	1085.5		
67.2	1200.5		
70.8	1292.0		
72.4	1323.5		

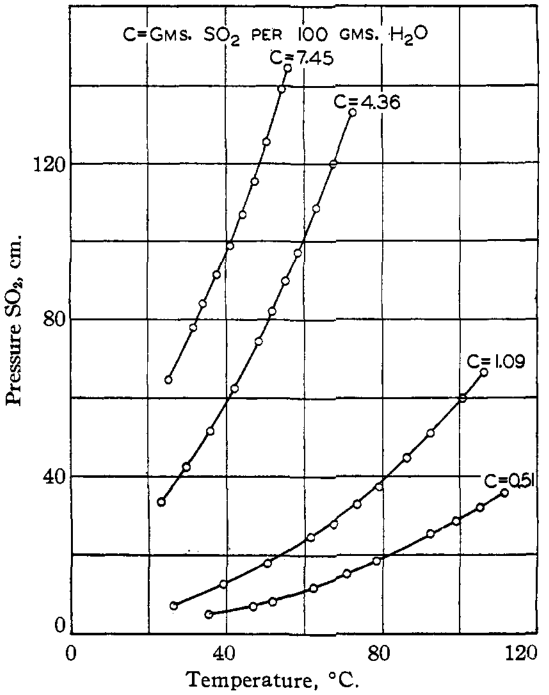

Fig. 2.

In the "International Critical Tables" the partial pressure of the water was calculated using Fulda's values for the ionization constant of sulfurous acid; however, this was neglected in this work because the effect is within the experimental error of the apparatus.

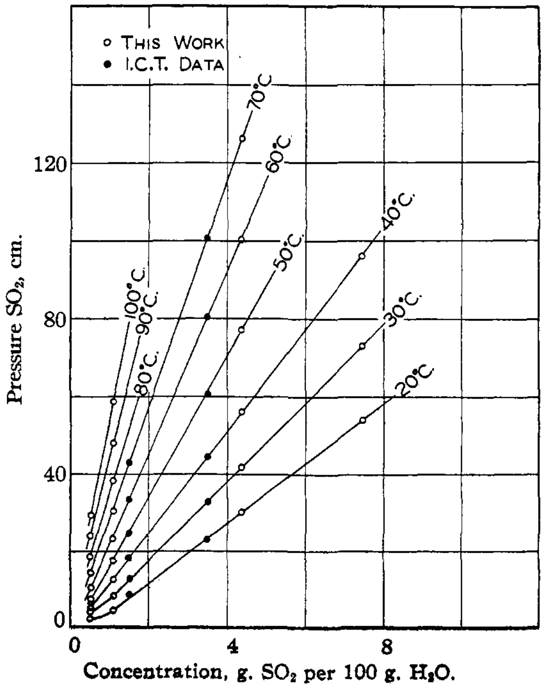

Fig. 3.

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[6] "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., p. 212.

The vapor pressure data are shown graphically in Fig. 2 and Fig. 3 shows the isotherms plotted by taking values from Fig. 2. According to the results of Fig. 3, the concentration is a linear function of the sulfur dioxide content except at the lower temperatures of the low concentrations.

Summary

1. Partial vapor pressures for sulfur dioxide in the system sulfur dioxide in water have been determined over the temperature range 20–110° and total pressure range of 10 to 150 cm. of mercury for concentrations of 0.51, 1.09, 4.36 and 7.45 grams of sulfur dioxide in 100 grams of water.

2. These data extend the values of the International Critical Tables and show excellent agreement over the coincident ranges.

SEATTLE, WASHINGTON RECEIVED JANUARY 15, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

The Energy and Entropy of Activation of the Hydrolysis of Ethyl Orthoformate in Deuterium Oxide

BY FRANK BRESCIA* AND VICTOR K. LAMER

Introduction

Current theory of chemical kinetics recognizes the energy of activation and the entropy of activation as the important factors governing the specific rate of a reaction in the presence or absence of a catalyst. LaMer[1] derived the equation

$$k = e^{-\Delta H^*/RT}\, e^{\Delta S_{\text{act}}/R}\, Z^\circ \qquad (1)$$

or

$$\log k = -(\Delta H^*/2{\cdot}3RT) + B \qquad (2)$$

where

$$\Delta H^* = RT^2\frac{\mathrm{d}\ln k}{\mathrm{d}T} \qquad (3)$$

from Tolman's statistical treatment[2] and a collisional mechanism for formation of the intermediate complex. In Eyring's treatment[3]

$$k = \kappa e^{-\Delta H^*/RT}\, e^{\Delta S^*/R}\, RT/Nh \qquad (4)$$

Hence

$$B = \frac{\Delta S^*}{2{\cdot}3R} + \log \kappa\, \frac{T}{Nh} \qquad (5)$$

Classical theory ascribed the entropy contribution $\Delta S^*/2{\cdot}3R$, to a so-called "steric or probability factor" expressed by P in the equation

$$k = e^{-\Delta H^*/RT}\, PZ^\circ \qquad (6)$$

The symbols have been defined in the literature cited.

Many previous investigators[4] have shown that the deuterium ion is a more effective catalyst than the hydrogen ion in many reactions. A noteworthy exception is the mutarotation of glucose.[5]

This increase in reactivity has been ascribed[6] to an increase in the equilibrium constant for the process Substrate + H^+ = SH^+ on passing from H^+ to D^+. The ratio of the equilibrium constants would be equal to the measured ratio for the specific rates. This is apparent when the theoretical equations for the rate constant are expressed in the form

$$k = \nu K^* \qquad (7)$$

where ν is a frequency term. Several investigators[7] have expressed the view that the increase in the concentration of the deutero complex can be accounted for by the lower zero point energy of the d-complex or, hence, by an observable difference in the activation energies, $\delta\Delta H^*$, of the two systems. ($\delta\Delta H^* = \Delta H^*_{\text{H}} - \Delta H^*_{\text{D}}$.) This is equivalent to the assumption that the ΔH^* factor

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(1) LaMer, *J. Chem. Phys.*, **1**, 289 (1933); LaMer and Kamner, THIS JOURNAL, **57**, 2662, 2669 (1935); Liotta and LaMer, *ibid.*, **60**, 1972 (1938).

(2) Tolman, "Statistical Mechanics," Chemical Catalog Co., New York, 1927, Chaper 21.

(3) Eyring, *J. Chem. Phys.*, **3**, 107 (1935); Wynne-Jones and Eyring, *ibid.*, **3**, 492 (1935).

(4) Moelwyn-Hughes and Bonhoeffer, *Naturwissenschaften*, **22**, 174 (1934); Gross, Suess and Steiner, *ibid.*, **22**, 662 (1934); Schwartz, *Akad. Anzeiger*, 26 April, 1934, Wien; Gross, Steiner and Suess, *Trans. Faraday Soc.*, **32**, 883 (1936); Hornel and Butler, *J. Chem. Soc.* (London), 1361 (1936); Gross, Steiner and Krauss, *Trans. Faraday Soc.*, **32**, 877 (1936); Reitz, *Naturwissenschaften*, **24** 814 (1936); *Z. physik. Chem.*, **179A**, 119 (1937); Brescia and LaMer, THIS JOURNAL, **60**, 1962 (1938); Nelson and Butler, *J. Chem. Soc.*, 957 (1938); Reitz, *Z. physik. Chem.*, **A183**, 371 (1939).

(5) Hammill and LaMer, *J. Chem. Phys.*, **2**, 891 (1934); **4**, 395 (1936).

(6) Moelwyn-Hughes, *Z. physik. Chem.*, **B26**, 272 (1934). LaMer, *Chem. Revs.*, **19**, 363 (1936); Bonhoeffer and Reitz, *Z. physik. Chem.*, **A179**, 135 (1937); Bonhoeffer, *Trans. Faraday Soc.*, **34**, 252 (1938); Wynne-Jones, *ibid.*, **34**, 245 (1938); *J. Chem. Phys.*, **2**, 381 (1934); Brescia and LaMer, THIS JOURNAL, **60**, 1962 (1938).

(7) Wynne-Jones, *J. Chem. Phys.*, **2**, 381 (1394); *Chem. Revs.*, **17**, 115 (1935); Halpern, *J. Chem. Phys.*, **2**, 456 (1935).