Vapor Liquid Equilibrium Data for the Binary System, Sulfur Dioxide and Water

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Equilibrium concentrations of liquid and vapor were measured over the liquid concentration range 0.59 to 4.48 grams per 100 grams and the temperature range 30° to 80° C. A unique static cell that employs mercury to sample the gas phase is described. The data are correlated by taking into account the dissociation of the molecular species in solution and the variation of the activity coefficient of the ionic species. The resulting equations are used to construct a table presenting data over the range 0.01 to 20.0 grams per 100 grams and 0° to 130° C. These values are compared with data reported in the literature.

DESPITE THE industrial importance of physico-chemical data for the sulfur dioxide–water system, large differences still exist between the tabulated values of partial vapor pressures taken from the generally available sources (*3*, *9*). Three critical reviews of the vapor pressure data (*9*, *12*, *16*) have been made, the most recent of which (*12*) correlated the available data so that extrapolation could be made into the regions of high temperature and low concentrations, areas where little experimental data have been obtained. Unfortunately, the equations used to represent the system were thermodynamically unsound and the resulting correlation is only reliable in the well-explored region from which the correlating data were drawn.

The present article reports some additional measurements of the partial vapor pressures of sulfur dioxide solutions. A novel static experimental technique was used, and the method of analysis for sulfur dioxide was not the usual iodometric method that apparently has introduced appreciable errors into much of the earlier work.

The data gathered have been correlated, using a thermodynamically consistent model. The parametric values obtained from the correlation have been used to calculate the partial vapor pressure of sulfur dioxide over wide ranges of temperature and concentration (Table III), and these values have been compared with direct experimental measurements where possible.

EXPERIMENTAL

Apparatus. The cell used to equilibrate the phases is illustrated in Figure 1. It consists of a large bulb containing approximately 100 ml. of the liquid under test, and a vapor sampling bulb, 10 to 12 ml. capacity, the volume of which is accurately known. The liquid under test is confined to the space between levels *A* and *B*. The right-hand side of the apparatus is filled with mercury, which occupies the space from level *B* to the very tip of the projection which extends into the vapor space above level *A*.

The experimental procedure used is as follows:

With all valves (*A*, *B*, and *C*) open, the clean, dry bulb is evacuated to a pressure below 0.1 mm. of Hg.; the required volume of mercury (clean, dry, and degassed) is charged and maneuvered to occupy the entire right-hand side of the apparatus (including the tip extending into the vapor space). Valve *C* is then closed; this fixes the mercury in position. A small globule of mercury should protrude from the capillary tip and be ready to drop into the vapor space. With the bulb still under vacuum, about 100 ml. of the test solution are drawn in through valve *A*. The first liquid entering the evacuated bulb vaporizes, but this has no effect on the final state of the system because no vapor escapes, and the volume of the vapor space is relatively small.

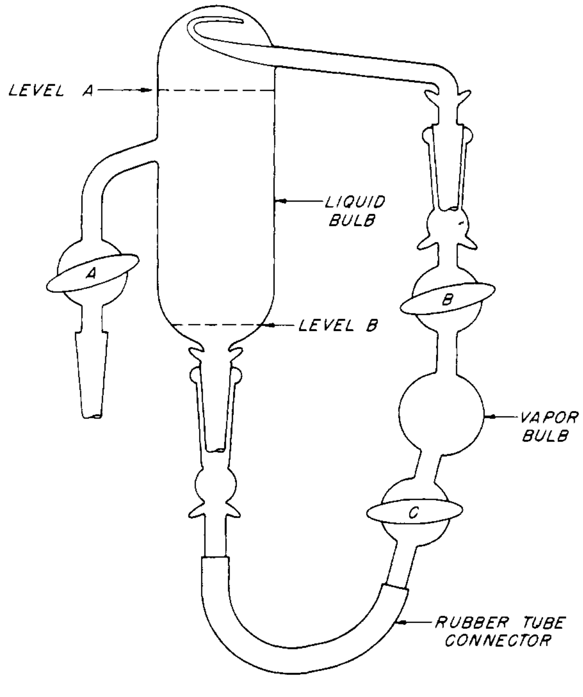

Figure 1. Static apparatus for vapor-liquid equilibrium experiments

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The liquid-filled bulb is next mounted on a support and placed in a thermostatic bath to equilibrate. Once equilibrium is reached, a vapor sample is obtained by first tapping the apparatus to detach the small droplet of mercury clinging to the glass tip in the vapor space, and then, after tilting the apparatus, valve *C* is opened slightly and the mercury allowed to pass slowly from the vapor bulb into the liquid bulb. Once the vapor bulb is filled with gas, valves *B* and C are closed, the apparatus is removed from the bath, and the vapor bulb detached.

The use of this mercury displacement method for sampling overcomes inherent difficulties encountered in the use of static equilibrium apparatus of previous design; there is no possibility of condensation of the saturated vapor phase in the sample chamber before sampling and no change in volume of the vapor volume during sampling. The advantages of the static method are retained. In particular, the certainty of establishing equilibrium is assured by the length of time the sample can be kept in the apparatus, the absence of pressure or thermal gradients, and the intimate contact of the gas and liquid phases. It was experimentally determined that the gas composition had reached the equilibrium value within approximately 15 minutes, although much longer periods were used.

The thermostatic bath that was used (*13*) maintained the controlled temperature to within at least ±0.02° C. at 80° C. and to within ±0.002° C. in the interval of 30° to 40° C.

Analytical Procedure. The gas sample containing 1.5 to 30.0 mg. of sulfur dioxide, is dissolved in a dilute aqueous acetaldehyde solution, being careful to exclude all traces of air. The acetaldehyde, present in considerable excess over that required to combine with the sulfur dioxide, reduces vaporization and oxidation losses appreciably. The α-hydroxy sulfonic acid formed by the combination of sulfur dioxide and acetaldehyde is a strong acid and can be determined by potentiometric titration with sodium hydroxide. It is necessary, however, to protect the solutions from oxidation and also from absorption of carbon dioxide. The particular apparatus used in this work is described in detail in the original theses work (*13*). Correction was made for the presence of a small amount of acetic acid in the acetaldehyde by using a blank.

This method was superior to the iodiometric method, which uses a starch indicator. Over the range of concentrations employed, it had a standard deviation of ±0.44% with a relative error of ±1.11% (*1*).

DATA AND DATA ANALYSIS

The experimental measurements for the SO_2-H_2O system are presented in Table I. Analysis and correlation of these data were performed in accordance with the following:

The SO_2 above the solution is in equilibrium with the uncombined gas in solution,

$$SO_2(g) = SO_2(l) \tag{1}$$

and Henry's Law constant, *H*, is defined by the relationship,

$$H = a_{SO_2}(l)/a_{SO_2}(g) \tag{2}$$

where *a* is the activity of the species indicated by the subscript.

Recent studies, including Raman (*14, 17, 18*), infrared (*6, 11*), and ultraviolet (*4*) absorption techniques, indicated that in aqueous solutions of SO_2 the unionized sulfur species consists almost exclusively of uncombined SO_2 molecules. No evidence has been found yet for H_2SO_3 molecules. The predominant ionic sulfur species is the bisulfite ion; the presence of SO_3^{-2} and $S_2O_5^{-2}$ may be disregarded for the present purpose.

Following the suggestion of Falk and Giguère (*6*), the equilibrium may be written,

$$SO_2(l) + 2H_2O = HSO_3^- + H_3O^- \tag{3}$$

and the equilibrium constant may be defined by the relationship,

$$K = (a_{HSO_3^-} \times a_{H_3O^-})/(a^2{}_{H_2O} \times a_{SO_2(l)}) \tag{4}$$

If the variation in the activity of the water at these high dilutions is ignored, the molality of the bisulfite ion may be obtained from the following relationship, derived from Equation 4,

$$[HSO_3^-] = -(K/2\gamma_\pm^2) + \tfrac{1}{2}\ [(K/\gamma_\pm^2)^2 + (4K \times m/\gamma_\pm^2)]^{1/2} \tag{5}$$

where *m* is the stiochiometric molality of sulfur dioxide in solution, $[HSO_3^-]$ is the molality of the bisulfite ion, and $\gamma_\pm$ is the mean molar activity coefficient for the hydrogen and bisulfite ions.

From Equation 2, assuming that the vapor is a perfect gas,

$$P_{SO_2} = \{m - [HSO_3^-]\}/H \tag{6}$$

Equations 5 and 6 relate the partial pressure of sulfur dioxide to the total concentration of sulfur dioxide in solution, *m*; the equilibrium constant, *K*; the mean activity coefficient, $\gamma_\pm$; and Henry's Law coefficient, *H*. Values for *K*, $\gamma_\pm$, and *H* were obtained as follows:

The Equilibrium Constant, *K*. When the standard state for the solvent, at each temperature, is chosen as the pure liquid at atmospheric pressure, and the solutions are dilute, the equilibrium constant defined by Equation 4 is the same as the "first dissociation constant for sulfurous acid." This constant has been accurately determined as 0.0172 at 25° C. by Tartar and Garretson (*19*), but only data at this single temperature are reported. However, the equilibrium constant has also been calculated from conductivity measurements (*5, 10*) taken at several temperatures, and the heat of reaction may be obtained from these data. The result of combining gives

$$K = \exp\left(\frac{1972.5}{T} - 10.9670\right) \tag{7}$$

where *T* is the absolute temperature,

Table I. Experimental Values of the Partial Vapor Pressure of Sulfur Dioxide Over Aqueous Solutions

Temp., ° C.	Total SO_2 Concen., G. SO_2 100 G. H_2O	SO_2 Partial Pressure, Mm. Hg	Temp., ° C.	Total SO_2 Concen., G. SO_2 100 G. H_2O	SO_2 Partial Pressure, Mm. Hg
30.0	4.46	443.5	50.0	3.20	583.3
	4.46	443.9		3.20	592.9
	4.46	442.4		3.20	608.4
	4.48	444.5		3.21	583.3
	4.48	451.6		3.21	585.7
	3.21	308.6		1.92	324.6
	3.21	304.9		1.92	328.5
	3.21	308.4		1.92	330.9
	3.21	309.0		1.92	335.1
	3.21	312.0		0.59	85.8
	1.92	172.2		0.59	86.7
	1.92	181.0			
	1.92	177.0			
	0.59	39.2	60.0	3.21	742.0
	0.59	42.7		3.21	756.0
				1.92	447.5
40.0	4.48	624.4		1.92	437.1
	4.48	638.8		0.59	114.0
	3.21	418.0		0.59	116.0
	3.21	420.0			
	1.92	242.0	70.0	0.59	151.0
	1.92	249.0		0.59	153.0
	0.59	57.8			
	0.59	60.6	80.0	0.59	189.0

Mean Activity Coefficient. Very few experimental measurements of $\gamma_{\pm}$ for sulfurous acid were available. The mean activity coefficient was assumed to be equal to that of hydrochloric acid, in aqueous solution, at the same ionic strength. Values for hydrochloric acid reported by Harned and Owen (*8*) were used. For temperatures above the reported range (0° to 60° C.), values of $\gamma_{\pm}$ were obtained by extrapolation assuming $(\delta \ln \gamma_{\pm}/\delta T)_m$ to be constant. The activity coefficients used are listed in Table II. Very recently, some measurements of $\gamma_{\pm}$ for the sulfurous acid system were made (*15*). However, the experiments covered a very limited concentration range and involved only one temperature. There is a maximum discrepancy of about 6% between these values and those listed in Table II. This difference does not seem significant.

Calculation of Henry's Law Constant. A value of H was calculated for each experimental data point listed in Table I using Equations 5, 6, and 7, and the values of $\gamma_{\pm}$ given in Table II. These values were then correlated, by least mean squares, to give the equation,

$$H = \exp\left(\frac{2851.1}{T} - 9.3795\right) \tag{8}$$

DISCUSSION

Equations 5, 6, 7, and 8 together with the mean activity coefficients of Table II may be used to calculate the vapor pressure of sulfur dioxide solutions at any set of conditions within the range of Table II. Table III presents values obtained by calculation. These agreed with the experimental values of Table I, with a relative error (*1*) of ±2.6%.

Table II. Estimated Mean Activity Coefficient of Sulfur Dioxide in Water

HSO_3^-	Temperature, ° C.													
Molality	0	10	20	30	40	50	60	70	80	90	100	110	120	130
0.0001	0.9890	0.9890	0.9892	0.9890	0.9885	0.9879	0.9879	0.9876	0.9874	0.9872	0.9870	0.9868	0.9867	0.9866
0.0002	0.9848	0.9846	0.9844	0.9835	0.9833	0.9831	0.9831	0.9825	0.9823	0.9822	0.9820	0.9816	0.9815	0.9813
0.0005	0.9756	0.9756	0.9759	0.9747	0.9741	0.9738	0.9734	0.9729	0.9724	0.9720	0.9715	0.9712	0.9708	0.9705
0.001	0.9668	0.9666	0.9661	0.9650	0.9643	0.9639	0.9632	0.9625	0.9620	0.9614	0.9609	0.9605	0.9599	0.9596
0.002	0.9541	0.9544	0.9527	0.9515	0.9505	0.9500	0.9491	0.9485	0.9479	0.9472	0.9467	0.9460	0.9456	0.9450
0.005	0.9303	0.9300	0.9294	0.9275	0.9265	0.9250	0.9235	0.9224	0.9213	0.9202	0.9192	0.9183	0.9174	0.9165
0.01	0.9065	0.9055	0.9052	0.9034	0.9016	0.9000	0.8987	0.8964	0.8948	0.8933	0.8919	0.8906	0.8894	0.8882
0.02	0.8774	0.8773	0.8768	0.8741	0.8715	0.8690	0.8666	0.8638	0.8620	0.8598	0.8577	0.8557	0.8539	0.8519
0.05	0.8346	0.8338	0.8317	0.8285	0.8246	0.8211	0.8168	0.8136	0.8104	0.8072	0.8045	0.8024	0.7989	0.7965
0.1	0.8027	0.8016	0.7985	0.7940	0.7891	0.7850	0.7813	0.7773	0.7736	0.7704	0.7670	0.7640	0.7612	0.7584
0.2	0.7756	0.7740	0.7694	0.7630	0.7569	0.7508	0.7437	...	...	...	...	...	...	...
0.5	0.7761	0.7694	0.7616	0.7526	0.7432	0.7344	0.7237	...	...	...	...	...	...	...

Table III. Partial Vapor Pressure of Sulfur Dioxide over Aqueous Solutions, Mm. of Hg

Grams SO_2/100 Grams Water	Temperature, ° C.													
	0	10	20	30	40	50	60	70	80	90	100	110	120	130
0.01	0.02	0.04	0.07	0.12	0.19	0.29	0.43	0.62	0.87	1.21	1.63	2.16	2.82	3.61
0.02	0.08	0.14	0.24	0.39	0.60	0.91	1.33	1.89	2.62	3.55	4.71	6.13	7.86	9.92
0.03	0.16	0.28	0.47	0.76	1.16	1.73	2.49	3.49	4.78	6.41	8.41	10.9	13.8	17.3
0.04	0.26	0.46	0.75	1.19	1.81	2.67	3.81	5.29	7.19	9.56	12.5	16.0	20.2	25.2
0.05	0.38	0.66	1.07	1.68	2.53	3.69	5.24	7.24	9.78	12.9	16.8	21.5	27.0	33.6
0.10	1.15	1.91	3.03	4.62	6.80	9.71	13.5	18.3	24.3	31.7	40.7	51.4	63.9	78.6
0.15	2.10	3.44	5.37	8.07	11.7	16.5	22.7	30.6	40.3	52.2	66.6	83.6	104	127
0.20	3.17	5.13	7.93	11.8	17.0	23.8	32.6	43.6	57.1	73.7	93.5	117	145	177
0.25	4.34	6.93	10.6	15.7	22.5	31.4	42.8	57.0	74.5	95.8	121	151	186	227
0.30	5.57	8.84	13.5	19.8	28.2	39.2	53.3	70.7	92.3	118	149	186	229	279
0.35	6.85	10.8	16.4	24.0	34.1	47.2	63.9	84.7	110	141	178	222	272	331
0.40	8.17	12.8	19.4	28.3	40.1	55.3	74.7	98.9	129	164	207	257	316	384
0.45	9.53	14.9	22.5	32.7	46.2	63.6	85.7	113	147	188	236	293	360	437
0.50	10.9	17.0	25.6	37.1	52.3	72.0	96.8	128	166	211	266	329	404	490
1.00	25.8	39.5	58.4	83.7	117	159	212	278	358	454	567	701	856	
1.50	42.0	63.6	93.2	132	184	249	331	433	555	703	877			
2.00	58.6	88.5	129	183	253	342	453	590	756	955				
2.50	75.7	114	165	234	323	435	576	749	958					
3.00	93.2	139	202	285	393	530	700	908						
3.50	111	166	240	337	464	625	825							
4.00	129	192	277	389	535	720								
4.50	147	218	315	442	607	816								
5.00	165	245	353	496	679									
6.00	202	299	430	602	824									
7.00	238	353	507	710										
8.00	275	407	585	818										
9.00	313	462	663											
10.00	351	517	741											
11.00	389	573	819											
12.00	427	628												
13.00	465	684												
14.00	504	740												
15.00	542	796												
16.00	581	852												
17.00	619													
18.00	658													
19.00	697													
20.00	735													

Calculated values were also compared with the reviews of van Arsdell (*9*), Sherwood (*3, 16*), and Plummer (*12*). Comparison was made over the experimental range employed to obtain the present correlation and also over the entire range of conditions given by each of the listed reviews.

The comparison with the values given by van Arsdell in the International Critical Tables was superior to all other comparisons. The comparison over the experimental range had a relative error of ±3.5 %, and over the entire set of data a relative error of ±5.4 %. Similar comparisons with the data of Sherwood resulted in ±6.4 % and ±11.7 %. Plummer's correlation could be compared only in the region of experimental overlap, in which case the relative error was ±4.7 %.

In the region of very high dilution the correlation checks well (±5.0 % mean error) with the data of Johnstone and Leppla (*10*), which appears to be the only available data in the very low concentration range. Literature data available for high temperatures (*2, 7, 9*) are extremely erratic; values calculated from this correlation fall near the recommended values of van Arsdell (*9*).

NOMENCLATURE

a = activity
g = gaseous state
H = Henry's law constant
K = equilibrium constant
l = liquid state
m = molality of dissolved SO_2
P = pressure
$\gamma_{\pm}$ = mean molar activity coefficient

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RECEIVED for review October 3, 1962. Accepted March 11, 1963.

Equations of State and Compressibilities for Gaseous Carbon Dioxide in the Range 0° to 600°C. and 0 to 150 Atm.

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Three volume-explicit equations of state are reported that fit the compressibility data of gaseous CO_2 with an average deviation of 0.09% and a maximum of 0.5% over the range 0° to 600° C. and 0 to 150 atm. The three equations were generated from the experimental data of Michels and Michels, MacCormack and Schneider, and Kennedy by a least squares program using an IBM650 digital computer. A table of compressibilities for CO_2 is presented.

COMPRESSIBILITY DATA for gaseous CO_2 were first obtained by the classic experiments of Andrews (*2*) in 1876, followed by the higher pressure work of Amagat (*1*) in 1892 and Keesom (*8*) in 1903. For an account of subsequent work on the *P-V-T* behavior of CO_2 up to 1959 the summary of Liley (*10*) should be consulted. The most extensive and accurate *P-V-T* measurements for CO_2 are those of Michels and coworkers (*13, 14, 16*) covering the range 0 to 150° C. and 16 to 3000 atm. and the data of MacCormack and Schneider (*11*) for the lower pressure region below 50 atm. and the temperature range 0° to 600° C. both sets of data having a precision of 0.01%. The more recent data of Kennedy (*9*) with a precision of 0.2% cover the range 0° to 1000° C. and 25 to 1470 atm. However, the data finally tabulated by Kennedy can differ from the experimental values by as much as 0.4% or 0.002 gram/cc., whichever is the greater.

With respect to equations of state for CO_2, Beattie and Bridgeman (*4*) have obtained a pressure-explicit equation up to the third power in $1/V$, based on the data of Andrews (*2*). Beattie (*3*) subsequently inverted this equation to obtain a volume-explicit form of lower accuracy. A pressure-explicit equation up to the eighth power in $1/V$, but omitting the fifth and sixth powers, has been presented by Michels and Michels (*15*) that represents their data along specific isotherms within 0.3% for pressures up to 3000 atm. MacCormack and Schneider (*11*) represent their data by a fourth power volume-explicit equation of state in which the second virial coefficient could be predicted within 3% and the experimental data within 0.02% along specific isotherms in the range 0° to 600° C. Houghton, McLean, and Ritchie (*7*) report a third power volume-explicit equation for the range 0° to 100° C. and 0 to 36 atm. that fits the data of Michels and Michels (*14*) with an average