Pressure-Volume-Temperature Properties of Sulfur Dioxide

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PRESSURE-VOLUME-TEMPERATURE properties of sulfur dioxide were determined using a Burnett apparatus and a Beattie-type apparatus. The temperature range was 10° to 250° C. and the pressure range was 1 to 312 atm. Critical constants of sulfur dioxide were also determined. Vapor pressures and orthobaric densities were measured and correlated. Latent heats of vaporization were evaluated from the Clapeyron equation. Based on Hirth's (*10*) and Kang's work (*13*), smoothed compressibility factors and fugacity coefficients for gaseous sulfur dioxide were calculated for pressures up to 315 atm. over the temperature range from 10° to 250° C. Second virial coefficients were evaluated by Hirth from the low-pressure *P-V-T* data.

EXPERIMENTAL

Purity. The sulfur dioxide was supplied by the Tennessee Corp., Atlanta, Ga., with the specification of 99.9975% purity. Further purification was undertaken as suggested by Couch and others (*7*) and Vohra and Kobe (*18*). Samples of the purified sulfur dioxide were analyzed in a mass spectrometer. No foreign substance was found. It was concluded that the minimum purity was 99.998%.

Method and Apparatus. The Beattie-type apparatus is essentially the same as that used by Beattie (*2*). Apparatus, experimental procedures, and data treatment have been described (*13*). The design, construction, and calibration of the Burnett apparatus used by Hirth in this investigation are described by Silberberg, Kobe, and McKetta (*16*). Couch and others (*7*) have critically evaluated these two methods of data collection.

Reproducibility of Data. During the measurements of *P-V-T* data several different sizes of samples were chosen to provide some overlap in volume ranges. The agreement of the volume measurements in the overlapping area indicated an excellent reproducibility of data. The compressibility factors thus obtained were consistent and reproducible within ±0.2%. The vapor pressure measurement reproducibility is estimated to be well within ±0.01 atm. The agreement between Hirth's data and Kang's data is generally very good. Discrepancies are discussed later.

Experimental Data. By means of the Beattie-type apparatus the pressure-volume-temperature data of sulfur dioxide in the gaseous phase were measured at 50°, 75°, 100°, 125°, 150°, 157.5°, 175°, 200°, 225°, and 250° C. from 5 atm. to either the vapor pressure at the prevailing temperature or the maximum pressure of 312 atm. Below the critical temperature, which was determined to be 157.5° C. in this work, vapor pressures as well as specific volumes of both the saturated liquid and the saturated vapor were determined at 5° intervals above 50° C.

In the liquid phase, *P-V-T* data were measured from the vapor pressures to about 312 atm. for five isotherms—50°, 75°, 100°, 125°, and 150° C. In the course of determining the critical constants of sulfur dioxide, seven additional isotherms—157°, 157.2°, 157.3°, 157.35°, 157.4°, 157.45°, and 157.5° C.—were measured.

By means of the Burnett aparatus, compressibility factor isotherms were determined at intervals of 10° C. between 10° and 50° C. and of 25° C. between 75° and 200° C. At least two runs were made to define each isotherm. Below the critical point, pressures were measured ranging from atmospheric to just below the vapor pressure. Above the critical point the maximum pressure measured was 68 atm.

Hirth's and Kang's experimental compressibility data for gaseous sulfur dioxide are shown in Figures 1 and 2, respectively. The *P-V-T* data in the high-pressure region, presented partly in Table I, are shown in Figure 3. The *P-V-T* measurements in the critical region are presented in Table II and shown in Figure 4.

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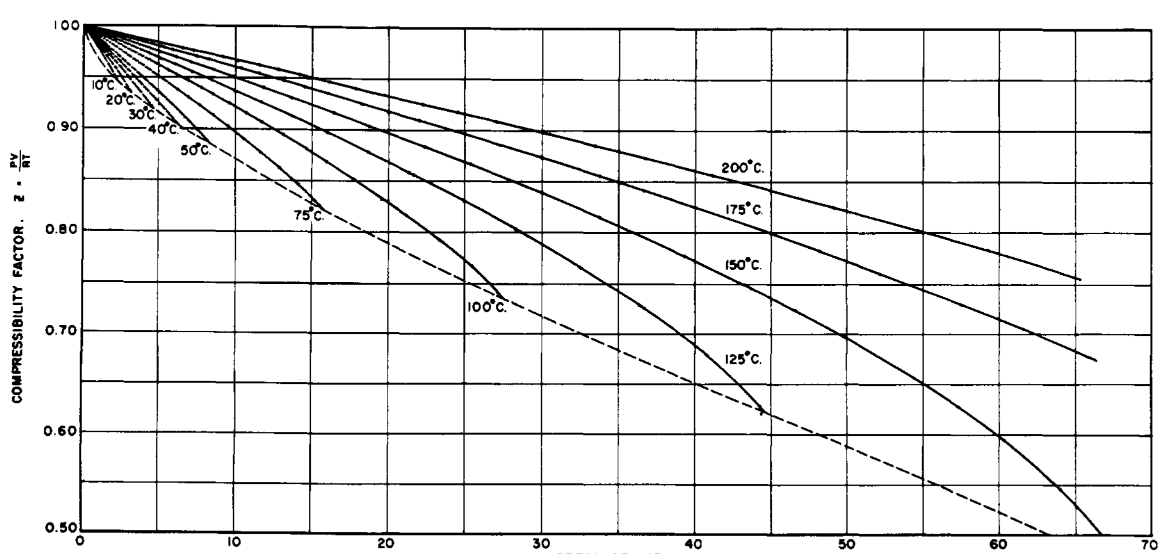

Figure 1. Compressibility factor of sulfur dioxide in the low-pressure region

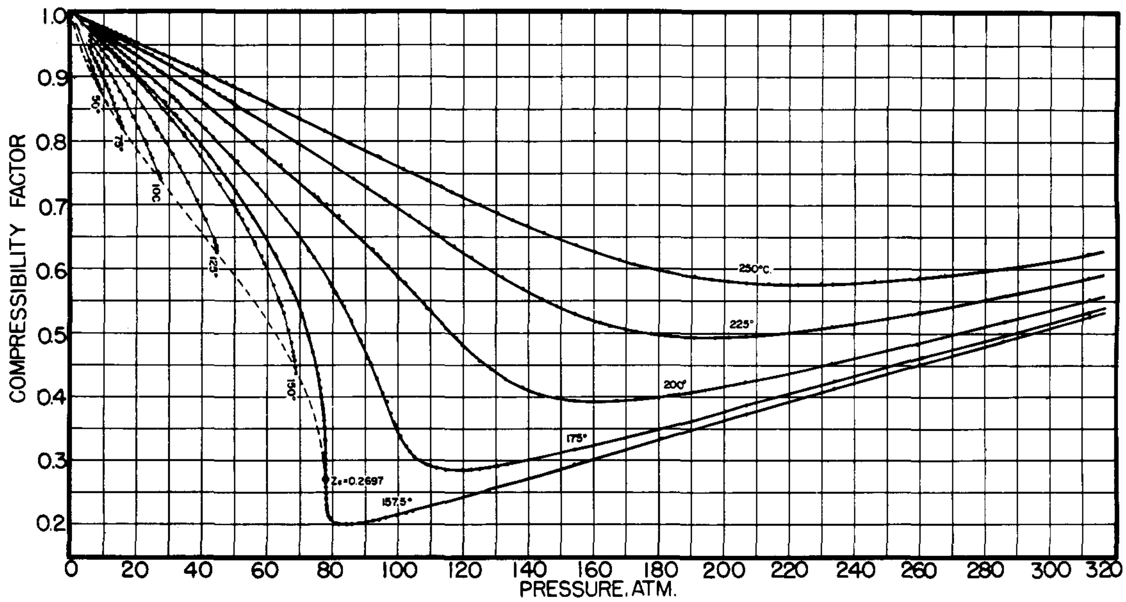

Figure 2. Compressibility factors of sulfur dioxide

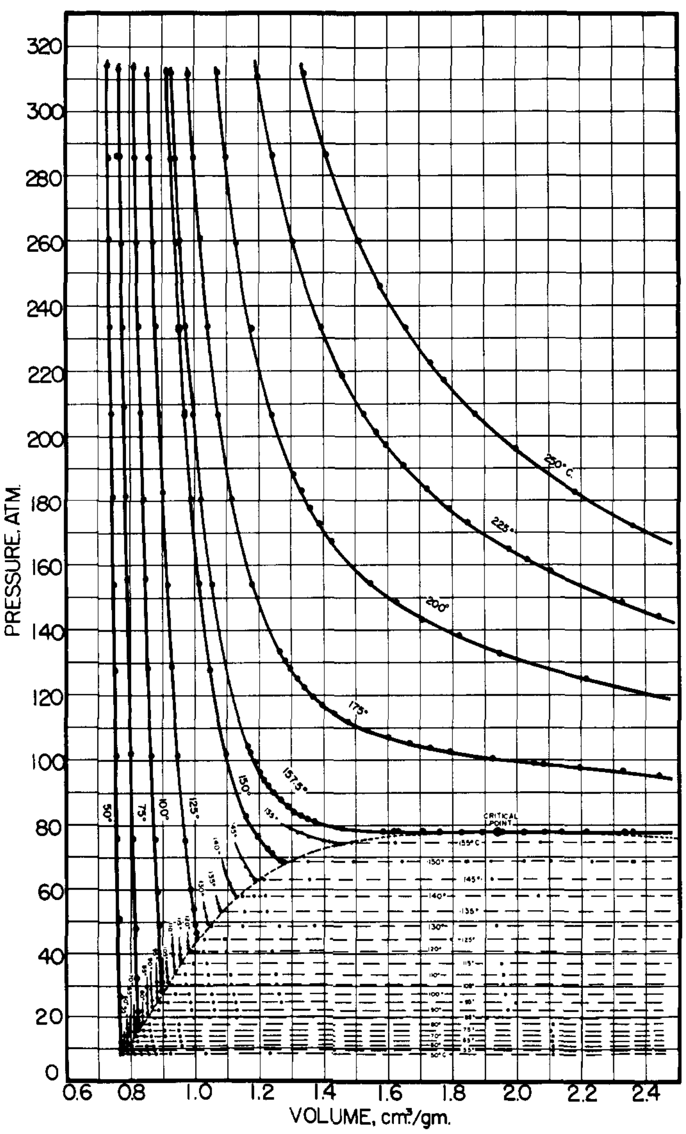

Figure 3. Pressure-volume isotherms for sulfur dioxide in the high-pressure region

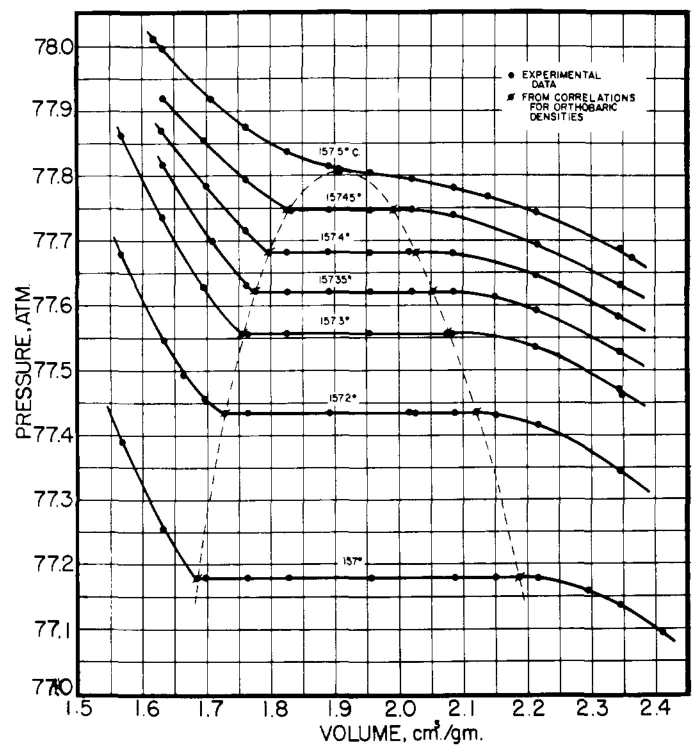

Figure 4. Pressure-volume isotherms in the critical region of sulfur dioxide

DERIVED QUANTITIES

All of the work on the correlations and calculations was done by using an IBM 650 digital computer.

Smoothed Vapor Pressures. The vapor pressures measured by Kang in this work were correlated by the method of least squares into a Nernst-type equation after appropriate weighing factors were multiplied to the observed results. Equation 1 is the final form of the correlation for temperatures between 50° and 157.5° C.

$$\log P = 14.400840 - 1437.1878/T - 4.0200950 \log T + 0.032898989\,T \qquad (1)$$

Table I. Experimental Pressure-Volume Isotherms for Liquid Sulfur Dioxide

Vol., Cc./G.	Pressure, Atm.	Vol., Cc./G.	Pressure, Atm.	Vol., Cc./G.	Pressure, Atm.
Mass of Sample = 8.1841 Grams		Mass of Sample = 5.2040 Grams			
t = 50° C.		t = 85° C.		t = 125° C.	
0.7715	8.490	0.8515	21.320	0.9145	154.07
0.7706	8.506	0.8509	24.537	0.9018	182.64
0.7704	9.981	0.8499	27.262	0.8915	206.71
0.7699	12.039	0.8489	29.772	0.8808	233.82
0.7679	26.698			0.8717	259.64
0.7641	50.998	t = 90° C.		0.8638	285.84
0.7610	75.845			0.8559	311.82
0.7573	101.58	0.8654	23.227		
0.7536	127.67	0.8645	25.361	t = 130° C.	
0.7499	154.29	0.8631	28.959		
0.7465	181.31			1.0384	49.496
0.7430	207.15	t = 95° C.		1.0338	51.822
0.7399	233.75			1.0290	54.369
0.7369	260.58	0.8819	26.349		
0.7339	285.85	0.8809	28.144	t = 135° C.	
0.7309	314.31	0.8799	31.399		
				1.0775	53.756
t = 55° C.		t = 100° C.		1.0735	54.661
				1.0707	55.842
0.7795	10.320	0.8986	28.396		
0.7794	12.043	0.8967	31.265	t = 140° C.	
0.7789	14.074	0.8949	34.302		
		0.8881	49.118	1.1340	58.152
t = 60° C.		0.8831	59.430	1.1173	59.412
		0.8763	75.694	1.1065	62.088
0.7891	12.050	0.8656	101.52	1.0973	64.696
0.7889	13.840	0.8547	128.26		
0.7885	14.813	0.8480	155.91	t = 145° C.	
0.7882	16.636	0.8407	180.47		
		0.8341	207.41	1.1750	64.611
t = 65° C.		0.8282	233.73	1.1573	67.375
		0.8217	259.74	1.1431	69.989
0.7993	13.858	0.8169	285.89		
0.7989	15.402	0.8118	313.78	t = 150° C.	
0.7986	16.539				
0.7984	18.009	t = 105° C.		1.2745	68.892
				1.2683	69.052
t = 70° C.		0.9157	31.139	1.2539	70.039
		0.9138	33.007	1.2396	71.164
0.8114	14.578	0.9121	35.328	1.1950	76.561
0.8109	15.551			1.0992	101.51
0.8105	17.485	t = 110° C.		1.0500	127.82
				1.0170	154.15
t = 75° C.		0.9364	34.143	0.9915	180.42
		0.9350	35.996	0.9708	207.31
0.8229	16.576	0.9316	39.494	0.9546	233.02
0.8225	17.678	0.9296	42.586	0.9437	259.53
0.8223	18.934				
0.8220	21.920				
0.8194	32.576			Mass of Sample =	
0.8151	41.979	t = 115° C.		8.6522 Grams	
0.8085	75.882			t = 150° C.	
		0.9540	37.011	1.2248	72.627
		0.9528	38.232	1.1583	83.154
0.8024	102.12	0.9513	39.748	1.0980	101.96
0.7968	129.88	0.9503	41.444	1.0476	128.07
0.7917	155.87			1.0159	154.51
0.7868	181.60	t = 120° C.		0.9909	180.41
0.7821	209.23			0.9709	206.82
0.7779	233.59	0.9798	41.719	0.9535	233.57
0.7735	259.26	0.9788	42.550	0.9433	259.55
0.7698	286.36	0.9771	43.820	0.9268	285.67
0.7665	313.50			0.9149	312.50
t = 80° C.		t = 125° C.		Mass of Sample = 8.1841 Grams	
		1.0078	45.274	t = 155° C.	
0.8357	18.325	1.0054	46.381	1.4406	74.859
0.8350	20.162	1.0021	49.166	1.4301	74.911
0.8345	22.098	0.9949	54.132	1.4176	74.974
		0.9870	60.313	1.3956	75.311
		0.9706	75.376	1.3525	76.393
		0.9477	101.68	1.3192	77.708
		0.9294	128.99	1.2944	79.047

The observed vapor pressures and the smoothed results calculated from Equation 1 indicate that the maximum residual is about 0.02 atm., while the maximum deviation is within ±0.05%. Hirth smoothed his vapor pressure data by means of pressure residuals. The maximum uncertainty of Hirth's smoothed vapor pressures is estimated to be 0.30% from 0° to 40° C. and 0.25% from 50° to 150° C. Both sets of smoothed data are tabulated in Table III.

Table IV compares the smoothed vapor pressures with the literature values for sulfur dioxide. Hellwig's results (*8*) agree within 0.5% with the smoothed vapor pressures in this work. The deviations between the reported values of Cardoso and Fiorentino (*4*) and the smoothed values in this work are generally less than 1%. Toriumi and Hara's data (*18*) are consistently lower. The International Critical Tables (*11*) give the least reliable vapor pressure data for sulfur dioxide. Riedel's vapor pressure at 50° C. (*15*) was extrapolated from his vapor pressure correlation.

Orthobaric Densities. Kang's observed orthobaric densities were smoothed by fitting them to Equations 2 and 3 by means of the method of the steepest descent.

Table II. Experimental Pressure-Volume Isotherms in the Critical Regions of Sulfur Dioxide

Volume, Cc./G.	Pressure, Atm.	Volume, Cc./G.	Pressure, Atm.
Mass of Sample = 2.8466 Grams			
t = 157° C.		t = 157.3° C.	
2.4109	77.094	2.3476	77.465
2.3461	77.136	2.3460	77.470
2.2296	77.160	2.2141	77.536
2.2168	77.179	2.0844	77.556
2.1519	77.183	1.9550	77.557
2.0871	77.182	1.8258	77.557
1.9575	77.185	1.7621	77.557
1.8277	77.185	1.6956	77.639
1.6730	77.186	1.6319	77.736
1.6984	77.182	1.5672	77.862
1.6336	77.256		
1.5682	77.391		
t = 157.2° C.		t = 157.35° C.	
2.3478	77.344	2.3455	77.524
2.2179	77.416	2.2158	77.592
2.1523	77.432	2.1507	77.614
2.0881	77.434	2.0860	77.619
2.0228	77.435	2.0212	77.620
2.0208	77.435	1.9566	77.620
1.8921	77.435	1.8917	77.620
1.7632	77.435	1.8269	77.621
1.6972	77.456	1.7621	77.633
1.6648	77.494	1.7080	77.699
1.6332	77.546	1.6327	77.813
1.5676	77.678		
t = 157.4° C.		t = 157.5° C.	
2.3440	77.585	2.3453	77.686
2.2143	77.646	2.2156	77.744
2.0847	77.681	2.0860	77.782
2.0194	77.682	2.0212	77.799
1.9545	77.682	1.9563	77.804
1.8897	77.683	1.8915	77.815
1.8250	77.683	1.8268	77.837
1.7602	77.716	1.7620	77.876
1.7007	77.784	1.7080	77.919
1.6308	77.870	1.6319	77.997
t = 157.45° C.		Mass of Sample = 8.6522 Grams	
2.3463	77.631	2.3633	77.673
2.2159	77.693	2.1393	77.767
2.0858	77.740	1.6186	78.122
2.0211	77.747		
1.9560	77.748		
1.8907	77.748		
1.8263	77.749		
1.7611	77.794		
1.6968	77.854		
1.6327	77.921		

Table III. Smoothed Vapor Pressure Orthobaric Density and Latent Heat of Vaporization Data for Sulfur Dioxide

t, °C.	Vapor Pressure, Atm.		Density, G./Cc.			ΔH_v, Cal. per G.
			Vapor			
	Kang	Hirth	Kang	Hirth	Liquid, Kang	Kang
10		2.268		0.00661		
20		3.260		0.00930		
30		4.556		0.01274		
40		6.218		0.01715		
50	8.484	8.302	0.02336	0.02264	1.2970	74.81
55	9.683		0.02667		1.2804	74.08
60	11.010		0.03029		1.2635	73.23
65	12.474		0.03424		1.2464	72.26
70	14.085		0.03858		1.2289	71.16
75	15.853	15.760	0.04338	0.04302	1.2111	69.93
80	17.787		0.04868		1.1928	68.57
85	19.898		0.05458		1.1740	67.06
90	22.198		0.06117		1.1546	65.40
95	24.696		0.06854		1.1344	63.57
100	27.406	27.425	0.07684	0.07798	1.1134	61.57
105	30.337		0.08623		1.0914	59.38
110	33.503		0.09689		1.0682	56.98
115	36.916		0.1091		1.0435	54.34
120	40.589		0.1232		1.0170	51.45
125	44.534	44.572	0.1396	0.1404	0.9882	48.25
130	48.767		0.1589		0.9566	44.69
135	53.299		0.1821		0.9212	40.68
140	58.147		0.2107		0.8805	36.09
145	63.324		0.2474		0.8317	30.66
150	68.845	68.824	0.2980	0.2903	0.7691	23.86
155	74.727		0.3831		0.6721	13.84
157			0.4571		0.5933	
157.5	77.807					

$$d = \left(\frac{d_L + d_g}{2}\right) = 0.52462015 + 1.1863691 \times 10^{-3}(t_c - t) + 6.9451764 \times 10^{-7}(t_c - t)^2 \quad (2)$$

$$\Delta = \left(\frac{d_L - d_g}{2}\right) = 9.8206457 \times 10^{-2}(t_c - t)^{0.48913} - 3.7254523 \times 10^{-3}(t_c - t) + 6.0192965 \times 10^{-6}(t_c - t)^2 \quad (3)$$

During the equation fitting, suitable weighing factors were multiplied to the observed values, to obtain the correlations with the best fit to the experimental data. Table III lists the smoothed orthobaric densities. The deviations between the observed and the smoothed values are less than ±0.37%. Hirth's molal volumes for the saturated vapor were obtained by extending his compressibility isotherms to the smoothed vapor pressures given in Table III. The maximum error in his smoothed values is estimated to be slightly greater than 0.55% at 150° C. but falls off to 0.1 to 0.3% at temperatures further from the initial temperature. Tables V and VI compare the smoothed saturated volumes of both liquid and vapor of sulfur dioxide with values reported in the literature. The saturated liquid specific volumes reported in International Critical Tables (*11*) are in close agreement with this work. There is a maximum deviation of 2.1% between Hellwig's saturated vapor specific volumes (*8*) and the smoothed results of this work. Riedel's (*15*) high specific volume of the saturated vapor at 50° C. again was an extrapolated value from his correlation. The saturated vapor specific volumes reported in International Critical Tables (*11*) are in complete disagreement with the smoothed results in this work.

Critical Constants. Figure 4 plots the pressure-volume isotherms in the critical region. The critical constants were determined graphically. Table VII presents the comparison with other experimental results in the literature. The agreement is good.

The critical volume, then, is 1.905 cc. per gram, and the critical compressibility factor is 0.2697.

Latent Heat of Vaporization. The latent heats of vaporization were evaluated by means of the Clapeyron equation,

$$\Delta H_v = T(V_g - V_L)\frac{dP}{dT} \quad (4)$$

using V_L taken from Table V, V_g from Table VI, and dP/dT from Equation 1. The calculated latent heats of vaporization of sulfur dioxide are presented in Table III. These were also correlated using Equation 5 for temperatures between 50° and 157.5° C.

$$\Delta H_v = 8.7759469(t_c - t)^{0.49945} - 1.0021178 \times 10^{-2}(t_c - t) - 1.2866153 \times 10^{-3}(t_c - t)^2 \quad (5)$$

The deviations between the values from Equation 5 and the values from the Clapeyron equation are less than 0.9%.

Smoothed Compressibility Factors. The volume residuals of gaseous sulfur dioxide were calculated from Hirth's compressibility data and the P-V-T data in Kang's work. Fourteen isotherms of volume residuals—10°, 20°, 30°, 40°, 50°, 75°, 100°, 125°, 150°, 157.5°, 175°, 200°, 225°, and 250° C.—were plotted *vs.* pressure on a large graph readable to ±0.001 cc. per gram. Smooth curves were drawn through these points. The volume residuals read from the smoothed curves were regarded as the smoothed values. The smoothed compressibility factors of sulfur dioxide in this work were calculated with a high degree of accuracy from these smoothed volume residuals by using Equation 6.

$$Z = 1 - \gamma P/RT \quad (6)$$

The smoothed compressibility factors, thus obtained, are tabulated in Table VIII. The smoothed compressibility factors in Kang's work are in close agreement with Hirth's smoothed values. However, higher deviations (up to 0.37%) were found in the vicinity of the two-phase region and at high pressures. The maximum errors in Hirth's smoothed values are estimated to be less than 0.55% at 150° C., decreasing to 0.1 to 0.3% at temperatures further removed from the critical. Hellwig's experimental compressibility factors (*8*) are generally higher than Kang's smoothed results in this work. The maximum deviation is 1.87%.

Fugacity Coefficient. The fugacity coefficient, ν, is defined by Equation 7.

Table IV. Comparison of Smoothed Vapor Pressures with Literature Values for Sulfur Dioxide

Temp., t, °C.	Kang's (*13*) P., Atm.	Hirth (*10*)		Cardoso (*4*)		I.C.T. (*11*)		Toriumi (*17*)		Hellwig (*8*)		Riedel (*15*)	
		P	Dev.	P^a	Dev.[b]	P	Dev.	P	Dev.	P	Dev.	P	Dev.
50	8.484	8.302	2.15	8.34	1.70	8.176	3.63	8.35	1.58	8.45	0.40	8.583	−1.17
75	15.853	15.760	0.57	15.87	−0.11	15.684	1.07			15.94	−0.49		
100	27.406	27.425	−0.09	27.25	0.57	27.714	−1.12	27.25	0.57	27.45	−0.16		
125	44.534	44.572	−0.09	44.34	0.44	45.457	−2.07			44.50	0.08		
150	68.845	68.824	0.03	68.40	0.65	68.405	0.64	68.20	0.94	68.75	0.14		

[a] P = atmosphere.
[b] Deviation, % = (smoothed vapor pressure − literature value) × 100/smoothed vapor pressure.

Table V. Comparison of Smoothed Saturated Liquid Specific Volumes with Literature Values for Sulfur Dioxide

Temp., t, ° C.	Smoothed V_L, Cc./G.	I.C.T. (11)		Cailletet (3)		Hellwig (8)		Cardoso (5)	
		V_L	Dev.[a]	V_L	Dev.	V_L	Dev.	V_L	Dev.
50	0.7710	0.7722	−0.16	0.7740	−0.39	0.7750	−0.52		
75	0.8257	0.8254	0.04	0.8264	−0.08	0.8266	−0.11		
100	0.8981	0.8977	0.04	0.8981	0.00	0.9002	−0.23		
125	1.0119	1.0111	0.08	1.0103	0.16	1.0136	0.17		
150	1.3003	1.3038	−0.27	1.3179	−1.35	1.2783	1.59	1.1980	7.87
155	1.4880			1.5699	−5.99			1.3026	12.46

[a] Deviation, % = (smoothed value − literature value) × 100/smoothed value.

Table VI. Comparison of Smoothed Saturated Vapor Specific Volumes with Literature Values for Sulfur Dioxide

Temp., t, ° C.	Kang's (13) V_g, Cc./G.	Hirth (8)		I.C.T. (11)		Hellwig (8)		Cardoso (5)		Riedel (15)	
		V_g	Dev.[a]	V_g	Dev.	V_g	Dev.	V_g	Dev.	V_g	Dev.
50	42.812	44.215	−3.27	40.65	5.05	42.10	1.66			44.6	−4.18
75	23.054	23.242	−0.82	23.29	−1.02	22.83	0.97				
100	13.013	12.823	1.46	12.94	0.56	12.92	0.71				
125	7.1655	7.124	0.58	7.069	1.35	7.191	−1.35				
150	3.3553	3.445	−2.69	3.256	2.96	3.285	2.10	3.4352	2.38		

[a] Deviation = (smoothed value − literature value) × 100/smoothed value.

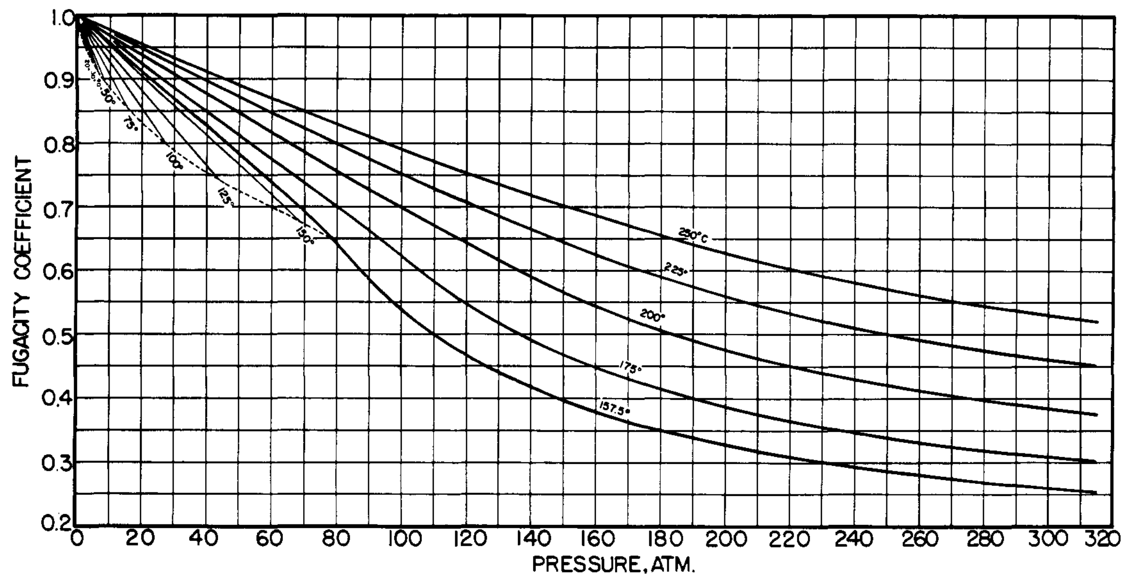

Figure 5. Fugacity coefficients for sulfur dioxide

$$\nu = \frac{f}{P} = e^{[-(1/RT)\int_0^P \gamma dP]} \quad (7)$$

In calculating the fugacity coefficients of sulfur dioxide, the smoothed volume residuals were first read from the smoothed curves. Then the integrand, $\int_0^P \gamma dP$, was evaluated numerically by using Weddle's rule. The fugacity coefficients, which were calculated from Equation 7, are presented in Figure 5.

Second Virial Coefficients. Hirth's experimental residual volume isotherms of sulfur dioxide appear in Figure 6. The experimental second virial coefficients, obtained by extrapolation of the curves in Figure 6 to zero pressure, are presented in Table IX and plotted in Figure 7. Smoothed values of the second virial coefficient read from the curve in Figure 7 are also shown in Table IX. The smoothed second virial coefficients are estimated to have a maximum error of 0.020 liter per gram mole at 10° C., which decreases to 0.007 liter per gram mole at 200° C.

Second virial coefficients calculated from the low pressure measurements of Baume (1), Cawood and Patterson (6), Jacquerod and Scheurer (12), and Leduc (14) are shown in Figure 7 along with the values from the present work. The maximum deviation does not exceed 0.008 liter per gram

Table VII. Critical Constants for Sulfur Dioxide

Investigators	t_c, ° C.	P_c, Atm.	d_c, G./Cc.
Cailletet and Mathias (3)	156.0	...	0.52
Cardoso and Fiorentino (4)	157.5 ± 0.05	77.79 ± 0.05	...
Cardoso and Sorrentino (5)	...	...	0.524
Helllwig (8)	157.5 ± 0.05	77.803 ± 0.005	0.522
This work	157.5 ± 0.02	77.808 ± 0.02	0.525 ± 0.001

Table VIII. Smoothed Compressibility Factors of Sulfur Dioxide

P, Atm.	Z 10° C.	20° C.	30° C.	40° C.
0.5	0.9889	0.9903	0.9917	0.9928
1	0.9775	0.9806	0.9835	0.9855
1.5	0.9657	0.9707	0.9751	0.9782
2	0.9531	0.9607	0.9667	0.9709
2.268[a]	0.9459			
2.5		0.9502	0.9582	0.9635
3		0.9392	0.9495	0.9560
3.260[a]		0.9330		
3.5			0.9405	0.9484
4			0.9313	0.9406
4.5				0.9328
4.556[a]			0.9204	
5				0.9248
5.5				0.9166
6				0.9080
6.218[a]				0.9038

P, Atm.	Z 50° C.	75° C.	100° C.	125° C.	150° C.
1	0.9871	0.9902	0.9925	0.9938	0.9951
2	0.9742	0.9804	0.9849	0.9877	0.9901
3	0.9611	0.9706	0.9773	0.9815	0.9852
4	0.9478	0.9606	0.9696	0.9752	0.9802
5	0.9344	0.9505	0.9619	0.9690	0.9752
6	0.9207	0.9403	0.9540	0.9627	0.9702
7	0.9065	0.9298	0.9460	0.9564	0.9652
8	0.8906	0.9191	0.9379	0.9500	0.9601
8.484[b]	0.8775				
10		0.8968	0.9213	0.9371	0.9500
12		0.8731	0.9042	0.9240	0.9398
14		0.8470	0.8865	0.9106	0.9294
15.853[b]		0.8196			
16			0.8682	0.8970	0.9188
18			0.8492	0.8830	0.9081
20			0.8292	0.8687	0.8973
22			0.8077	0.8539	0.8862
24			0.7849	0.8388	0.8749
26			0.7608	0.8232	0.8634
27.406[b]			0.7462		
28				0.8070	0.8515
30				0.7902	0.8394
32				0.7723	0.8269
34				0.7536	0.8141
36				0.7339	0.8009
38				0.7130	0.7875
40				0.6905	0.7737
42				0.6659	0.7597
44				0.6391	0.7451
44.534[b]				0.6258	
46					0.7300
48					0.7144
50					0.6981
52					0.6809
54					0.6628
56					0.6434
58					0.6226
60					0.6002
62					0.5758
64					0.5488
66					0.5150
68					0.4712
68.845[b]					0.4262

[a] Vapor pressures determined by Hirth (*10*).
[b] Vapor pressures determined by Kang.

P, Atm.	Z 157.5° C.	175° C.	200° C.	225° C.	250° C.
1	0.9953	0.9961	0.9967	0.9973	0.9977
2	0.9906	0.9922	0.9934	0.9946	0.9954
5	0.9765	0.9804	0.9836	0.9864	0.9884
10	0.9528	0.9605	0.9671	0.9728	0.9769
15	0.9286	0.9399	0.9504	0.9592	0.9653
20	0.9037	0.9185	0.9334	0.9454	0.9538
25	0.8655	0.8963	0.9157	0.9315	0.9422
30	0.8507	0.8732	0.8976	0.9173	0.9306
35	0.8222	0.8492	0.8791	0.9030	0.9191
40	0.7916	0.8243	0.8602	0.8883	0.9075
45	0.7588	0.7983	0.8407	0.8734	0.8958
50	0.7241	0.7713	0.8208	0.8583	0.8840
55	0.6858	0.7429	0.8004	0.8429	0.8719
60	0.6435	0.7133	0.7795	0.8273	0.8597
65	0.5960	0.6820	0.7580	0.8115	0.8476
70	0.5359	0.6492	0.7360	0.7956	0.8353
75	0.4473	0.6127	0.7134	0.7794	0.8231
80	0.2062	0.5721	0.6900	0.7628	0.8107
85	0.1992	0.5255	0.6660	0.7464	0.7984
90	0.2050	0.4718	0.6412	0.7294	0.7860
95	0.2093	0.4093	0.6156	0.7123	0.7737
100	0.2145	0.3470	0.5891	0.6952	0.7612
105	0.2218	0.3074	0.5614	0.6780	0.7487
110	0.2310	0.2922	0.5339	0.6607	0.7365
115	0.2419	0.2856	0.5066	0.6435	0.7242
120	0.2477	0.2849	0.4810	0.6264	0.7121
125	0.2518	0.2872	0.4577	0.6099	0.7003
130	0.2564	0.2910	0.4371	0.5939	0.6887
135	0.2612	0.2949	0.4226	0.5785	0.6776
140	0.2684	0.2984	0.4120	0.5643	0.6670
145	0.2768	0.3036	0.4037	0.5512	0.6564
150	0.2869	0.3102	0.3985	0.5395	0.6461
155	0.2983	0.3187	0.3946	0.5287	0.6364
160	0.3104	0.3276	0.3927	0.5198	0.6274
165	0.3178	0.3344	0.3931	0.5121	0.6191
170	0.3224	0.3403	0.3952	0.5060	0.6116
175	0.3278	0.3457	0.3980	0.5014	0.6052
180	0.3340	0.3510	0.4011	0.4976	0.5993
185	0.3405	0.3572	0.4055	0.4953	0.5941
190	0.3478	0.3633	0.4090	0.4944	0.5894
195	0.3551	0.3694	0.4134	0.4942	0.5850
200	0.3631	0.3766	0.4182	0.4947	0.5818
205	0.3711	0.3843	0.4223	0.4959	0.5790
210	0.3789	0.3925	0.4272	0.4973	0.5772
215	0.3872	0.3998	0.4320	0.4992	0.5761
220	0.3946	0.4069	0.4370	0.5014	0.5755
225	0.4020	0.4140	0.4428	0.5049	0.5760
230	0.4089	0.4206	0.4485	0.5076	0.5764
235	0.4154	0.4272	0.4544	0.5114	0.5777
240	0.4224	0.4345	0.4598	0.5154	0.5785
245	0.4292	0.4417	0.4654	0.5193	0.5804
250	0.4362	0.4477	0.4711	0.5235	0.5822
255	0.4434	0.4546	0.4775	0.5278	0.5844
260	0.4519	0.4612	0.4837	0.5324	0.5871
265	0.4587	0.4678	0.4900	0.5373	0.5898
270	0.4659	0.4746	0.4954	0.5421	0.5930
275	0.4730	0.4811	0.5017	0.5472	0.5961
280	0.4799	0.4839	0.5077	0.5524	0.5597
285	0.4869	0.4959	0.5142	0.5576	0.6036
290	0.4941	0.5032	0.5209	0.5627	0.6074
295	0.5013	0.5101	0.5276	0.5685	0.6110
300	0.5086	0.5170	0.5342	0.5740	0.6148
305	0.5157	0.5236	0.5415	0.5792	0.6185
310	0.5230	0.5298	0.5488	0.5844	0.6224
315	0.5307	0.5362	0.5565	0.5891	0.6260

mole, which is considered excellent for second virial coefficients.

Second virial coefficients computed from the Berthelot relation using Kang's critical constants are presented in Table IX, as well as second virial coefficients calculated by the Stockmayer potential function (*9*) for polar gases. The parameters used were $t^* = 0.6$, $\epsilon/k = 455°$ K., and $b_o = 0.03029$ liter per gram mole. The maximum difference between the values calculated by the Stockmayer potential and those of this work is 0.007 liter per gram mole.

Table IX. Second Virial Coefficients of Sulfur Dioxide

Temp., °C.	$-B$, Liters/G. Mole Exptl.	Smoothed	Berthelot[a]	Stockmayer[b]
10	0.5000	0.503	0.412	0.5000
20	0.4520	0.448	0.382	0.4447
30	0.4040	0.404	0.355	0.4026
40	0.3675	0.366	0.330	0.3654
50	0.3328	0.334	0.309	0.3331
75	0.2790	0.276	0.262	0.2718
100	0.2325	0.234	0.255	0.2272
125	0.2010	0.199	0.192	0.1934
150	0.1711	0.170	0.167	0.1672
175	0.1441	0.145	0.145	0.1463
200	0.1258	0.124	0.126	0.1293

[a] From equation. $B = \frac{9RT_c}{128P_c}\left[1 - \frac{6}{T_r^2}\right]$.

[b] Parameters. $t^* = 0.6$, $e/k = 455°$ K., $b_o = 0.03029$ liter/g. mole.

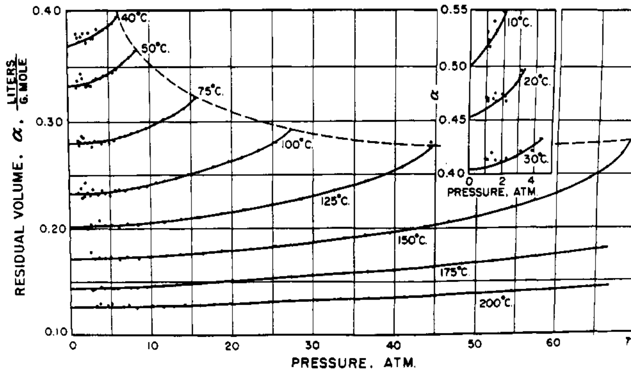

Figure 6. Experimental residual volume isotherms for sulfur dioxide

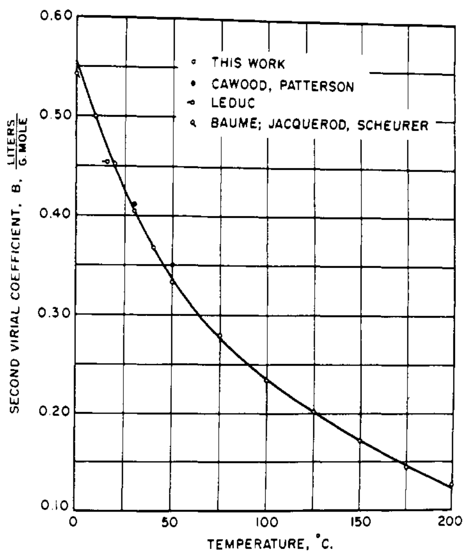

Figure 7. Second virial coefficients for sulfur dioxide

NOMENCLATURE

- B = second virial coefficients
- b_o = parameter in Stockmayer potential function
- d_c = critical density, g./cc.
- d_g = density of saturated vapor, g./cc.
- d_L = density of saturated liquid, g./cc.
- e/k = parameter in Stockmayer potential function
- f = fugacity
- ΔH_v = latent heat of vaporization
- P = absolute pressure
- P_c = critical pressure, atm.
- R = gas constant
- T = absolute temperature
- t = temperature, ° C.
- t^* = parameter in Stockmayer potential function
- T_c = critical temperature, ° K.
- t_c = critical temperature, ° C.
- T_r = reduced temperature
- V = volume
- V_g = specific volume of saturated vapor, cc./g.
- V_L = specific volume of saturated liquid, cc./g.
- Z = compressibility factor, PV/RT
- γ = volume residual, $RT/P - V$
- ν = fugacity coefficient, f/P

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