Thermodynamic Properties of Sulfur Dioxide

T. L. KANG and J. J. McKETTA
University of Texas, Austin, Texas

With the widespread use of the digital computers the thermodynamic properties of a substance can be evaluated directly from its pressure-volume-temperature relationships without recourse to the specific equation of state of that substance. Based on the experimental P-V-T data (*4*, *7*) and in conjunction with other data in literature the thermodynamic properties of sulfur dioxide were evaluated from −100° to 480°F. for pressures up to 4,600 lb./sq. in. abs. Numerical methods were employed, and an IBM-650 digital computer was used to carry out the calculations. A Mollier diagram was constructed to present the enthalpy and the entropy values of superheated gaseous sulfur dioxide, the properties of saturated sulfur dioxide, and the properties in the two-phase region. In the calculations °F. + 459.688 was used as the absolute temperature.

EQUATIONS EMPLOYED

From the fundamental relationships

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad (1)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \quad (2)$$

and

$$\gamma = \frac{RT}{P} - V \quad (3)$$

Equations (4) to (9) were derived to represent the changes of enthalpy and of entropy of sulfur dioxide at any particular pressure and temperature P and T, with respect to the reference state, which was defined as the saturated liquid at the pressure P_o and the temperature T_o:

$$\Delta H_{P,T} = H^\circ_T + H_P + (\Delta H_v)_{T_o} \quad (4)$$

$$\Delta S_{P,T} = S^\circ_T + S_P + (\Delta S_v)_{T_o} \quad (5)$$

$$H^\circ_T = \int_{T_o}^{T} C^\circ_P \, dT \quad (6)$$

$$S^\circ_T = \int_{T_o}^{T} \frac{C^\circ_P}{T} dT \quad (7)$$

$$H_P = J\left[\int_o^P \left[T\left(\frac{\partial \gamma}{\partial T}\right)_P - \gamma\right]_T dP - \int_o^{P_o} \left[T\left(\frac{\partial \gamma}{\partial T}\right)_P - \gamma\right]_{T_o} dP\right] \quad (8)$$

$$S_P = J\left[\int_o^P \left[\left(\frac{\partial \gamma}{\partial T}\right)_P\right]_T dP - \int_o^{P_o} \left[\left(\frac{\partial \gamma}{\partial T}\right)_P\right]_{T_o} dP\right] \quad (9)$$

The path of integration of Equations (1) and (2) as represented by the above equations is generally as follows:

1. First at constant temperature T_o integrate from the pressure P_o to zero pressure (that is to the ideal-gas state).
2. Then at constant pressure (zero pressure in this case) integrate from the reference temperature T_o to the temperature T.
3. Again at constant temperature (this time, T) integrate from zero pressure to any desired pressure P.
4. Add the latent heat of vaporization or the entropy of vaporization at temperature T_o to obtain the total change of enthalpy or entropy relative to the saturated liquid at T_o and P_o.

Fugacity coefficients were calculated by using Equation (10):

$$\nu = \frac{f}{P} = e^{\left(-\frac{1}{RT}\int_o^P \gamma dP\right)} \quad (10)$$

SOURCES OF DATA

The literature was reviewed for the available P-V-T data and thermal data for sulfur dioxide. Following data were used in this evaluation.

Vapor Pressures

Vapor-pressure correlations of Kang and McKetta (*7*), Riedel (*11*), and Stock, Henning, and Kuss (*13*) were used to calculate the vapor pressures from −100° to 315.5°F. Smoothed values of these results were adopted in this evaluation.

Orthobaric Densities

Correlations of Kang and McKetta (*7*) were used for the specific volumes of saturated liquid and saturated vapor of sulfur dioxide for temperatures above 50°C. Riedel's data (*11*) were used for the specific volumes of the saturated vapor below 50°C. Keyes' correlation (*5*) was used to calculate the specific volumes of saturated liquid below 50°C. Smoothed values of these results were used in this evaluation. The smoothed volumes are within ± 0.2% of the true values.

Volume Residuals

Smoothed volume residuals were derived from Kang's P-V-T data (*7*) and Hirth's experimental compressibility data (*4*) for temperatures from 10° to 250°C. For lower temperatures, volume residuals were calculated from Riedel's equation of state for sulfur dioxide (*11*).

Ideal Gas Heat Capacities

For temperatures above 32°F. Kobe and Long's correlation for ideal gas heat capacities of sulfur dioxide (*8*) was adopted. Since there were no heat capacity data for sulfur dioxide available below 32°F., these low temperature heat capacities were calculated at intervals of 2 deg. from 196° to 270°K. in the same way as Cross and Brockway (*2*) did for their ideal-gas heat capacities for sulfur dioxide above 0°C. The vibrational contributions were determined from the tables of Gordon and Barnes (*3*). The vibration frequencies were taken from Badger and Bonner's reported values (*1*). The ideal gas heat capacities, thus calculated, were correlated into Equation (*11*):

$$C^\circ_p = 7.3004149 + 2.8971598\times10^{-3}T + 3.2033446\times10^{-6}T^2 - 1.7101689\times10^{-9}T^3 \quad (11)$$

In the temperature range of 352.8° to 486°R. the deviations of the values from this correlation from the results calculated from the spectroscopic data were less than ±0.01%.

Latent Heat of Vaporization

Correlations of Kang and McKetta (*7*) and Mehl (*10*) were used to calculate the latent heat data above and below 50°C., respectively. The final results, before being adopted in this evaluation, were smoothed graphically.

METHOD OF EVALUATION

The reference state, adopted in this work, is the saturated liquid sulfur dioxide at −100°F. and under its own vapor pressure which is 0.294 lb./sq. in. abs.

The temperature effects on enthalpy and entropy were evaluated analyti-

---

T. L. Kang is with The B. F. Goodrich Company, Brecksville, Ohio.

TABLE 1. THERMODYNAMIC PROPERTIES OF GASEOUS SULFUR DIOXIDE

P = absolute pressure, lb./sq. in. abs.

T = temperature, °F.

S = entropy, B.t.u./lb.

Reference state: $S = 0$ and $H = 0$ for the saturated liquid at −100°F. and 0.294 lb./sq. in. abs.

T	P	V	H	S	ν
320	1,000	0.07571	217.4	0.3577	0.7085
	1,500	0.01913	147.5	0.2608	0.5423
	2,000	0.01718	145.0	0.2558	0.4355
	2,500	0.01663	142.8	0.2510	0.3722
	3,000	0.01618	141.1	0.2468	0.3303
	3,500	0.01576	139.8	0.2432	0.3010
	4,000	0.01537	138.7	0.2400	0.2795
	4,500	0.01506	137.9	0.2372	0.2634
	4,600	0.01500	137.8	0.2367	0.2606
360	1,000	0.09486	231.5	0.3740	0.7592
	1,500	0.03698	200.0	0.3269	0.6404
	2,000	0.02225	172.8	0.2907	0.5308
	2,500	0.01925	165.6	0.2796	0.4574
	3,000	0.01787	162.5	0.2736	0.4076
	3,500	0.01713	160.8	0.2696	0.3724
	4,000	0.01652	159.7	0.2664	0.3644
	4,500	0.01614	159.0	0.2637	0.3268
	4,600	0.01605	158.8	0.2631	0.3234
400	1,000	0.1089	242.2	0.3853	0.7970
	1,500	0.05855	224.0	0.3555	0.7018
	2,000	0.03226	198.7	0.3215	0.6124
	2,500	0.02370	184.1	0.3016	0.5382
	3,000	0.02076	176.8	0.2907	0.4843
	3,500	0.01916	172.5	0.2836	0.4447
	4,000	0.01817	169.6	0.2782	0.4152
	4,500	0.01757	167.5	0.2738	0.3926
	4,600	0.01749	167.2	0.2731	0.3888
440	1,000	0.1213	251.6	0.3961	0.8296
	1,500	0.06941	237.1	0.3702	0.7508
	2,000	0.04406	222.5	0.3485	0.6768
	2,500	0.03100	205.3	0.3256	0.6116
	3,000	0.02519	194.7	0.3110	0.5587
	3,500	0.02233	188.0	0.3012	0.5179
	4,000	0.02065	183.5	0.2939	0.4865
	4,500	0.01935	180.2	0.2882	0.4622
	4,600	0.01932	179.7	0.2872	0.4581
480	1,000	0.1271	257.2	0.4020	0.8432
	1,500	0.07273	243.7	0.3769	0.7716
	2,000	0.04924	231.6	0.3585	0.7025
	2,500	0.03496	216.2	0.3377	0.6428
	3,000	0.02775	205.5	0.3229	0.5922
	3,500	0.02416	198.7	0.3129	0.5519
	4,000	0.02204	194.0	0.3055	0.5203
	4,500	0.02061	190.7	0.2998	0.4956
	4,600	0.02032	190.2	0.2988	0.4913

cally, since the ideal gas heat capacities have been correlated as a function of temperature. But the pressure effects on enthalpy and entropy had to be evaluated numerically.

The numerical operations consisted of the interpolation of volume residuals, the differentiation to obtain the $\left(\frac{\partial \gamma}{\partial T}\right)_P$ term, and the integration of the volume residuals together with their partial derivatives to the final results of enthalpies, entropies, and fugacities.

In performing the numerical interpolation of volume residuals at constant temperature Bessel's six-point interpolation formula was mainly used. For each temperature, at the very beginning and near the end of the above interpolation process, Newton's six-point forward and backward formulas were used to interpolate the volume residuals. The Lagrangian five-point interpolation formula for unequally spaced intervals was used to interpolate the volume residuals with respect to temperature at constant pressure. In performing the numerical differentiation of the volume residuals with respect to temperature at constant pressure Stirling's seven-point differentiation formula was used. Also for each pressure, at both the first and the last three temperatures, differentiation was performed by using Newton's forward and backward formulas. To integrate the volume residuals, their derivatives, and other related quantities with respect to pressure Newton-Cotes' six-paint close quadrature formula was used.

To interpolate the volume residuals first the volume residuals of sulfur dioxide at intervals of 0.5 atm. were read from the fourteen smoothed curves of γ vs. P isotherms. Then, isotherm by isotherm, they were numerically interpolated. For the isotherms of 10° to 100°C. the interpolated results were obtained at every 1 lb./sq. in. For the isotherms of 125° and 150°C. the volume residuals were interpolated at pressure intervals of 2 lb./sq. in. For the rest of the isotherms pressure intervals were 2.0 lb./sq. in. below the critical pressure and 10 lb./sq. in. between the critical pressure and 4,600 lb./sq. in. abs.

Then these interpolated volume residuals, after being sorted according to pressure, were numerically interpolated once more at the constant pressure from 50° to 480°F. at intervals of 5°F. The results, obtained after the second interpolation, were subsequently numerically differentiated.

The term $\left[T\left(\frac{\partial \gamma}{\partial T}\right)_P - \gamma\right]_T$ was also evaluated at intervals of 5°F.

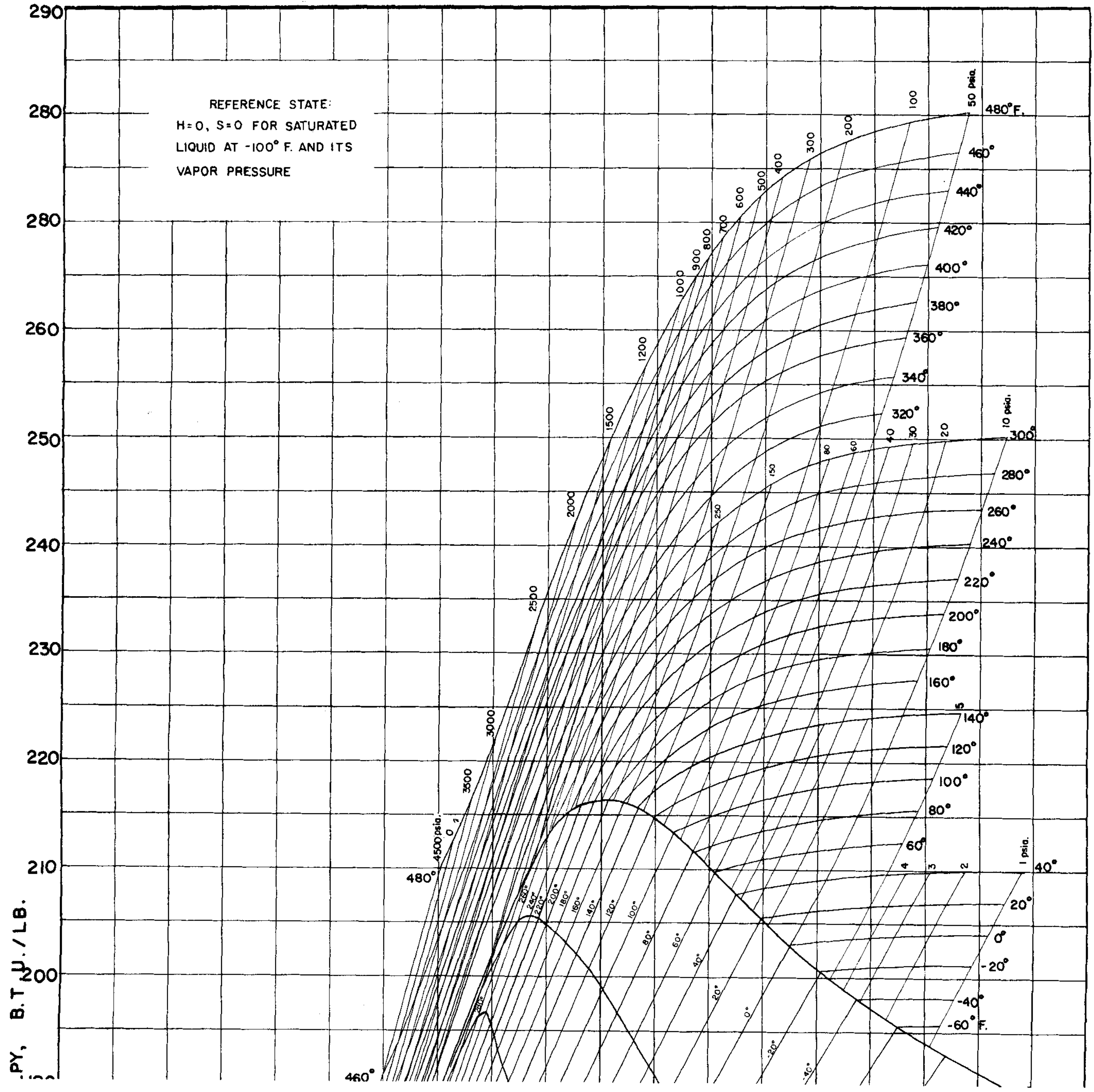
During each step results were inspected visually. They were graphically smoothed when necessary.

Since no P-V-T data of sulfur dioxide have been measured recently below 10°C., for temperatures lower than 10°C. the volume residuals and other related quantities were obtained through Riedel's equation of state (*11*). Starting from −100°F. and ending at −25°F. the volume residuals were obtained at temperature intervals of 5°F. for every 0.02 lb./sq. in. of pressure until the vapor pressure of that temperature was reached. For the temperatures between −25° and 50°F. the volume residuals and others were obtained at the same temperature intervals, but the pressure intervals were 0.2 lb./sq. in.

The effect of pressure on enthalpy and entropy in the temperature range of −100° to 480°F. was evaluated for isotherms at 5°F. intervals by means of Equations (8) and (9). The integration of $\left(\frac{\partial \gamma}{\partial T}\right)_P$ and $\left[T\left(\frac{\partial \gamma}{\partial T}\right)_P - \gamma\right]_T$ with respect to pressure was

TABLE 3. DETAILS IN CHECKING FOR INTERNAL CONSISTENCY

Pressure, lb./sq. in. abs.	50	2,000	3,500	4,500
S at 320 F.	0.4827	0.2558	0.2432	0.2372
340	0.4872	0.2740	0.2625	0.2540
360	0.4916	0.2907	0.2696	0.2637
380	0.4955	0.3065	0.2771	0.2695
400	0.4995	0.3215	0.2836	0.2738
420	0.5033	0.3355	0.2910	0.2793
440	0.5073	0.3485	0.3012	0.2882
460	0.5112	0.3585	0.3129	0.2998
480	0.5073	0.3696	0.3325	0.3207
T_1, °R.	539.688	779.688	779.688	779.688
T_2, °R.	939.688	939.688	939.688	993.688
T_1S_1	227.101	199.44	189.62	184.94
T_2S_2	483.939	347.31	312.45	301.36
$\int_{T_1}^{T_2} S\,dT$	188.841	50.97	45.72	44.13
H_1 Table 1	212.3	145.0	139.8	137.9
H_2 Equation (17)	280.297	241.94	216.91	210.19
H_2 Table 1	280.2	241.8	216.8	210.1
Deviation, %	0.036	0.058	0.051	0.043



performed numerically. The pressure intervals in both the numerical integration and the final results were set as follows:

Temperature, °F.	Pressure intervals in numerical integration, lb./sq. in	Pressure intervals in final results, lb./sq. in.
—100 to —20	0.02	0.1
—25 to 45	0.2	1.0
50 to 140	1.0	5.0
145 to 315	2.0	10.0
320 to 480	10.0	50.0

With $H°_T$, $S°_T$, H_P, and S_P thus calculated $\Delta H_{P,T}$ and $\Delta S_{P,T}$ were evaluated by means of Equations (4) and (5).

The volume of gaseous sulfur dioxide and its fugacity coefficient were calculated along with the enthalpy and entropy at that temperature and pressure. With the interpolated volume residual known at that condition the actual gaseous volume was calculated by Equation (3). The fugacity coefficient was calculated by means of Equation (10) with the integrand $\int \gamma\, dP$ numerically integrated.

THERMODYNAMIC PROPERTIES AND MOLLIER DIAGRAM

Enthalpies, entropies, volumes, and fugacity coefficients of sulfur dioxide in the gas phase are presented in Table 1. Because of the excellent agreement with Rynning and Hurd (*12*) the low pressure data below 1,000 lb./sq. in. abs. are not included in Table 1. Both the enthalpy and the entropy of the saturated vapor at each temperature were obtained by extrapolating the corresponding isotherms in Table 1 to the saturation pressure.

The enthalpy and the entropy of the saturated liquid at that temperature were calculated in accordance with the following equations:

$$H_L = H_g - \Delta H_v \qquad (12)$$

$$S_L = S_g - \Delta S_v \qquad (13)$$

The fugacity coefficients of the saturated vapor were obtained by the extrapolation of the corresponding isotherms.

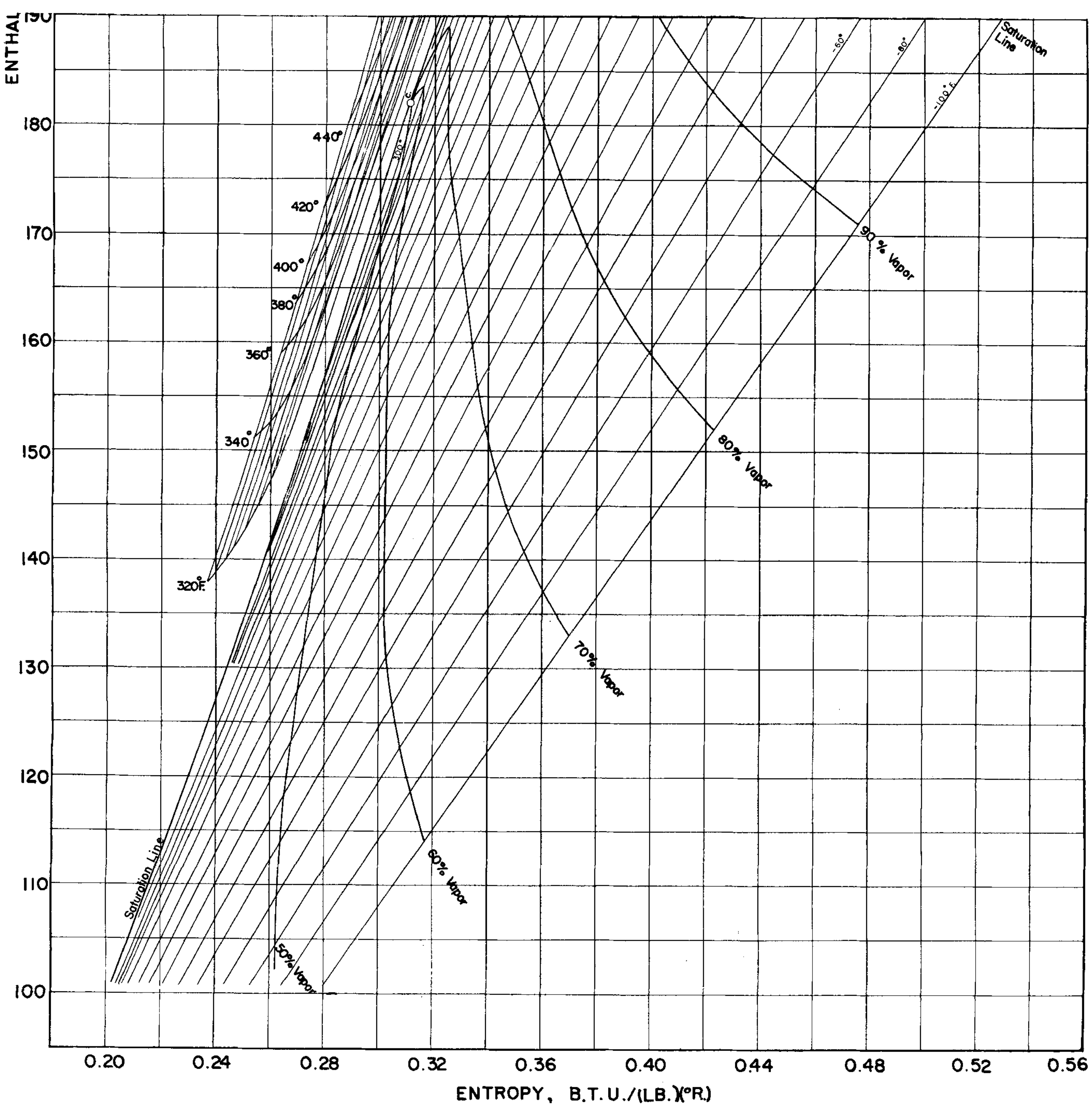


Fig. 1. Mollier diagram for sulfur dioxide.

Vapor pressures, specific volumes, and latent heats of vaporization were obtained from the literature data. The thermodynamic properties of the saturated liquid and the saturated vapor are presented in Table 2.*

The quality lines in the two-phase region were obtained by evaluating their enthalpies and entropies from the following relationships:

$$H_x = H_g - (1 - x)\,\Delta H_v \qquad (14)$$

$$S_x = S_g - (1 - x)\,\Delta S_v \qquad (15)$$

Figure 1 is the Mollier diagram of sulfur dioxide showing the enthalpy and entropy isotherms, the isobars, the saturation curve, and the quality lines.

DISCUSSION

Internal Consistency

Fundamental thermodynamic relationships are usually employed to check the internal consistency of Mollier diagrams. For any enthalpy-entropy diagram Equation (16) is the most convenient one for this purpose.

$$\left(\frac{\partial H}{\partial S}\right)_p = T \qquad (16)$$

The slope of an isobar in the diagram, thus, should equal the absolute temperature for any corresponding set of enthalpy and entropy values.

Equation (16) can be rearranged and integrated at constant pressure to give

$$\Delta H = H_2 - H_1 = \Delta(TS) - \int_{T_1}^{T_2} S\,dT \qquad (17)$$

By means of Equation (17) the internal consistency of an enthalpy-entropy diagram also can be checked. Moreover the conclusion so obtained should be more exact.

Four values of ΔH were calculated by Equation (17): the enthalpy changes between 80° and 480°F. at 50 lb./sq. in. abs. and between 320°

---

* A reprint of this article (including a large copy of Figure 1 and complete tables) is available for $1 from Director, Bureau of Engineering Research, The University of Texas, Austin 12, Texas.

and 480°F. at 2,000, 3,500, and 4,500 lb./sq. in. abs. Table 3 shows the comparison between the evaluated thermodynamic properties and those calculated from Equation (17). The integral $\int SdT$ in Equation (17) was calculated by Simpson's rule. Details in calculation are also presented in Table 3.

It is evident that the thermodynamic properties, which were obtained by means of the numerical methods, are internally consistent.

Comparison with Literature Values

Among the previous work on the thermodynamic properties of sulfur dioxide Rynning and Hurd's results (*12*) are the most reliable. A comparison is shown in Table 4* between their results and the evaluated values in this work within the temperature range of 0° to 480°F. and pressures to 1,000 lb./sq. in. abs.

Generally the agreement is very good with the maximum deviations of 1.9, 1.3, 2.2, and 1.9% for the volume, the enthalpy, the entropy, and the fugacity coefficient of the gaseous sulfur dioxide.

In the case of the saturated sulfur dioxide the vapor pressures and the specific volumes are in fair agreement with the values reported by Rynning and Hurd. Similarly the values of enthalpy and entropy are less than 1% different from theirs.

Table 5* is the comparison between the enthalpy and the entropy evaluated in this work and the values calculated from Lyderson's generalized charts (*9*). The comparison is limited to the high-pressure and high-temperature regions, in which the thermodynamic properties evaluated in this work were integrated with a large pressure interval (10 lb./sq. in.). Furthermore the high-pressure region is also a region where no thermodynamic properties of sulfur dioxide are available in literature for comparison.

From Table 5 it is seen that excellent agreement may be realized from the generalized charts. When one uses the generalized charts, the maximum deviations for both the enthalpy and the entropy are less than 5.1%. These maximum errors occur at the high pressure of 4,000 lb./sq. in. abs.; the average deviation is between 2 and 3%.

Reliability

The thermodynamic properties of sulfur dioxide, evaluated in this work and presented in Figure 1, and Tables 1 and 2 are internally consistent and accurate. Based on the experimental P-V-T measurements these properties can be expected to be reliable down to 0.1 B.t.u./lb. for enthalpy, 0.0001 B.t.u./lb. °R. for entropy, and 0.0001 for fugacity coefficient. The accuracy of the volume of the gaseous sulfur dioxide is governed by the systematic error of the compressibility factor of sulfur dioxide; it is 0.2% (*6*). The percentage deviation from the smoothed data was as follows (*6*):

vapor pressures	0.004 to 0.024%
orthobaric densities	0.02 to 0.40%
latent heats	0.06 to 0.86%

ACKNOWLEDGMENT

This work was done through an ACS-PRF Grant for which the authors are grateful.

NOTATION

C°_{P} = heat capacity at constant pressure in the ideal-gas state, B.t.u./lb. °R.
e = base of the natural logarithm
f = fugacity
H = enthalpy, B.t.u./lb.
ΔH = change in enthalpy, B.t.u./lb.
H_g = enthalpy of the saturated vapor, B.t.u./lb.
H_L = enthalpy of the saturated liquid, B.t.u./lb.
ΔH_v = latent heat of vaporization, B.t.u./lb.
$(\Delta H_v)_{T_0}$ = latent heat of vaporization at the reference temperature T_0, 190.2 B.t.u./lb.
H_P = change in enthalpy relative to zero pressure due to the change in pressure, B.t.u./lb.
H°_{T} = change in enthalpy in the ideal-gas state relative to the reference temperature due to the change in temperature, B.t.u./lb.
$\Delta H_{P,T}$ = change in enthalpy relative to the reference state due to the changes in pressure and temperature, B.t.u./lb.
H_x = enthalpy of the vapor-liquid mixture, B.t.u./lb.
J = dimensional constant = 0.0029642454 B.t.u./(lb.)(cc. g.)(lb./sq. in. abs.)
P = absolute pressure, atm.
P_0 = reference pressure, 0.294 lb./sq. in. abs.
R = gas constant, 0.031017857 B.t.u./(°R.)(lb. of sulfur dioxide) or 0.16750646 (lb./sq. in. abs.) (cu. ft./lb. of sulfur dioxide)/°R.
S = entropy, B.t.u./lb. °R.
ΔS = change in entropy, B.t.u./lb. °R.
S_g = entropy of the saturated vapor, B.t.u./lb. °R.
S_L = entropy of the saturated liquid, B.t.u./lb. °R.
ΔS_v = entropy of vaporization, B.t.u./lb. °R.
$(\Delta S_v)_{T_0}$ = entropy of vaporization at the reference temperature T_0, B.t.u./lb. °R.
S_P = change in entropy relative to zero pressure due to the change in pressure, B.t.u./lb. °R.
S°_{T} = change in entropy in the ideal-gas state relative to the reference temperature T_0 due to the change in temperature, B.t.u./lb. °R.
$\Delta S_{P,T}$ = change in entropy relative to the reference state due to the changes in pressure and temperature, B.t.u./lb. °R.
S_x = entropy of the vapor-liquid mixture, B.t.u./lb. °R.
T = absolute temperature, °R.
T_0 = reference temperature, − 100°F.
V = volume, cu ft./lb.
x = quality of the vapor-liquid mixture, lb. vapor/lb. of mixture
$\Delta(TS)$ = $T_2S_2 - T_1S_1$
γ = volume residual, cc./g. of sulfur dioxide
ν = fugacity coefficient, f/p

1 and 2 = conditions

LITERATURE CITED

1. Badger, R. M., and L. G. Bonner, *Phys. Revs.*, **43**, 305 (1933).
2. Cross, P. C., and L. O. Brockway, *J. Chem. Phys.*, **3**, 825 (1935).
3. Gordon, A. R., and C. Barnes, *ibid.*, **1**, 297 (1933).
4. Hirth, L. J., and K. A. Kobe, *Chem. Eng. Data*, **6**, 229 (1961).
5. "International Critical Tables," Vol. 3, p. 236, McGraw-Hill, New York (1928).
6. Kang, T. L., Ph.D. dissertation, Univ. Texas, Austin, Texas (1960).
7. ———, J. J. McKetta, and K. A. Kobe, *J. Chem. Eng. Data*, **6**, 220 (1961).
8. Kobe, K. A., and F. G. Long, *Petrol. Refiner*, **29**, No. 1, 126 (1950).
9. Lydersen, A. L., R. A. Greenkorn, and O. A. Hougen, *Report No. 4*, Engineering Experimental Station, Univ. Wisconsin, Madison, Wisconsin (Oct. 1955).
10. Mehl, W., *Bull. Intern. Inst. Refrig.*, **15**, 33A (1934).
11. Riedel, L., *ibid.*, **20**, No. 4; *Annex*, No. 5, B1 (1939).
12. Rynning, D. F., and C. O. Hurd, *Trans. Am. Inst. Chem. Engrs.*, **41**, 263 (1945).
13. Stock, A., F. Henning, and E. Kuss, *Ber. Deutschen Chem. Ges.*, **54**, 1119 (1921).

Manuscript received August 22, 1960; revision received February 1, 1961; paper accepted February 2, 1961.

---

* See footnote on page 421.