

# Sulfur Oxides: SO<sub>2</sub>, SO<sub>3</sub>



Physical properties of sulfur-dioxide and -trioxide, from both experimental data and theoretical correlations, are presented in a series of graphs.

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Sulfur-dioxide and -trioxide are basic industrial chemicals. Sulfur dioxide is used in producing sulfuric acid, sulfites, bisulfites, hydrosulfites, organic sulfonates and sulfonyl chlorides. Of itself, it is a fumigant, preservative and bleach.

Sulfur trioxide is used in the manufacture of sulfuric acid, oleum, organic sulfonates and sulfates.

## Critical Properties—Table 2—1

Table 2—1 shows physical properties of sulfur-dioxide and -trioxide. For sulfur trioxide, there are three forms (gamma, beta and alpha) in the solid phase. On cooling, the gamma form (icelike crystals, with a melting point of 16.8°C) is obtained. The beta variety (feathery crystals having a melting point of 32.5°C) is formed if traces of sulfuric acid are present. Additional conversion may occur to the alpha form (asbestoslike crystals, with a melting point of 62.3°C). In commercial practice, formation of the higher-melting-point forms is normally prevented by addition of inhibitors [4]. The results in Table 2—1 and subsequent data in this article apply only to the gamma form (m.p. of 16.8°C) of sulfur trioxide, which is the variety of major industrial importance.

Data for critical constants—critical temperature, pressure and volume—show close agreement for sulfur-dioxide [2,4,10,14,81,83] and -trioxide [2,4,14,83]. Deviations for critical pressure (from the average) are less than 1.2% and 1.9%, respectively, while the deviation is less than 1% for critical temperature and volume. The critical compressibility factor (a parameter in many physical property correlations) was calculated from available critical-property data with the "real gas law" relation.

At the critical point:  $Z_c = P_c V_c / RT_c$  (2—1)

## Vapor Pressure—Fig. 2—1

Vapor pressure data for sulfur-dioxide and -trioxide cover the full liquid state with deviations in most cases being less than 5.3%.

\* See Part 1 of this series, *Chem. Eng.*, June 10, 1974, p. 70, for all equations starting with a boldfaced numeral "1."

## Heat of Vaporization—Fig. 2—2

Available data for heat of vaporization were extended for the full liquid phase of both oxides with Watson's correlation (Eq. 1—1).\*

## Heat Capacity—Fig. 2—3, 2—4

The agreement among various sources is good for vapor heat-capacity at atmospheric pressure. Maximum deviations were less than 2% and 12% for sulfur-dioxide (20 data points) and -trioxide (30 data points).

The relation of liquid heat-capacity  $\times$  density = constant (Eq. 1—3 with  $n = 1$ ) was used to extend available data for coverage of the full liquid state. The calculated values compared favorably with published results. Average deviation was below 8% for sulfur dioxide (12 data points).

## Density—Fig. 2—5

Density data for sulfur trioxide cover the full liquid-phase with average deviation of 5% from the least squares fit. For sulfur dioxide, Lu's generalized correlation was used to extend the data over the full liquid state:

$$K_1/\rho_1 = K_2/\rho_2 \quad (2—2)$$

where  $K_1$  and  $K_2$ —which are a function of temperature and pressure—are read from the generalized charts in Perry [13] or Reid and Sherwood [14]. Comparison of results from Lu's correlation with experimental values showed close agreement with maximum deviation of only 1.5% for sulfur dioxide (13 data points).

## Surface Tension Fig. 2—6

Available surface tension data were expanded for full liquid-phase coverage with the Othmer linear relationship (Eq. 1—4) for log surface-tension versus log critical-temperature-difference. Each oxide yielded a straight line.

(Text continues on p. 92)



### How To Use the Graphs

Each graph is outfitted with a key that lists references and explains just what part of the curve is determined experimentally, and what part is estimated from theoretical correlations.

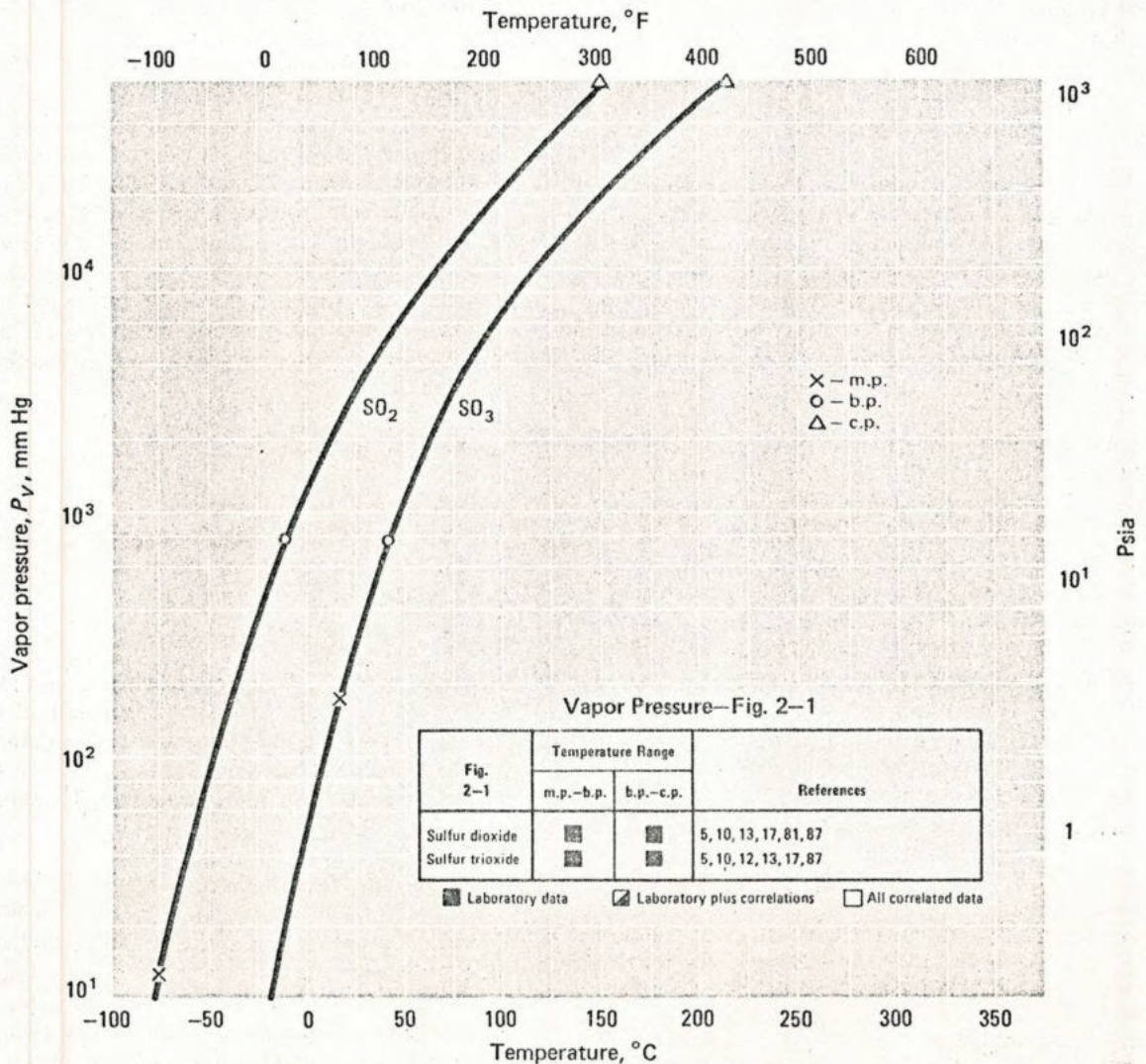
The shaded squares denote the following:

- Data in this region are experimentally known.
- ▣ Experimental and correlated data used.
- All data in this region are correlated.

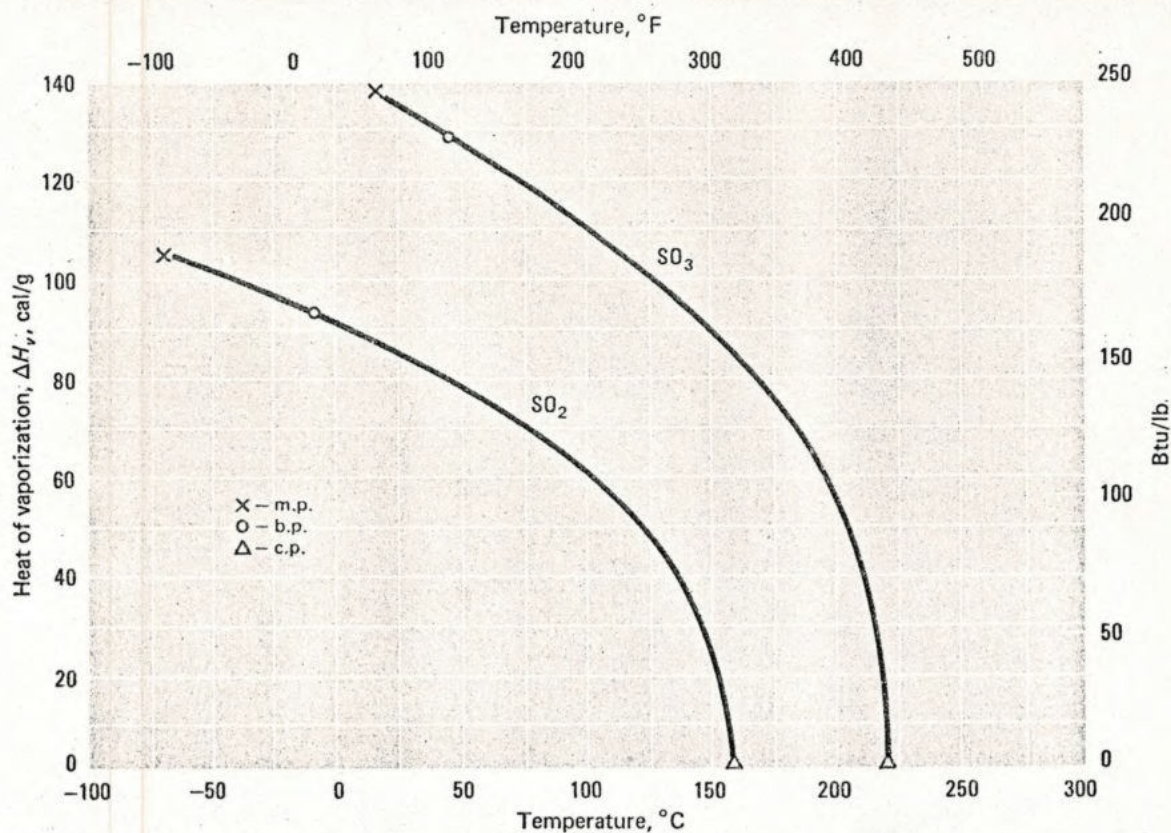
The "regions" referred to are the temperature ranges between the melting, boiling and critical points (m.p., b.p. and c.p., respectively), or in some cases, the specific temperatures noted in the key.

Physical Properties of the Sulfur Oxides  
Table 2-1

Identification	Sulfur Dioxide,	Sulfur Trioxide,
	SO <sub>2</sub>	SO <sub>3</sub>
State, (std. cond.)	Gas (colorless)	Liquid (clear)
Molecular weight, <i>M</i>	64.06	80.06
Boiling point, <i>T<sub>b</sub></i> , °C	-10.0	44.8
Melting point, <i>T<sub>m</sub></i> , °C, <i>T</i>	-72.7	16.8
Critical temp., <i>T<sub>c</sub></i> , °C	157.6	218.3
Critical pressure, <i>P<sub>c</sub></i> , atm	78.1	82.9
Critical volume, <i>V<sub>c</sub></i> , cm <sup>3</sup> /gr mol	122.0	126.1
Critical compressibility factor, <i>Z<sub>c</sub></i>	0.270	0.259







Heat of Vaporization—Fig. 2-2

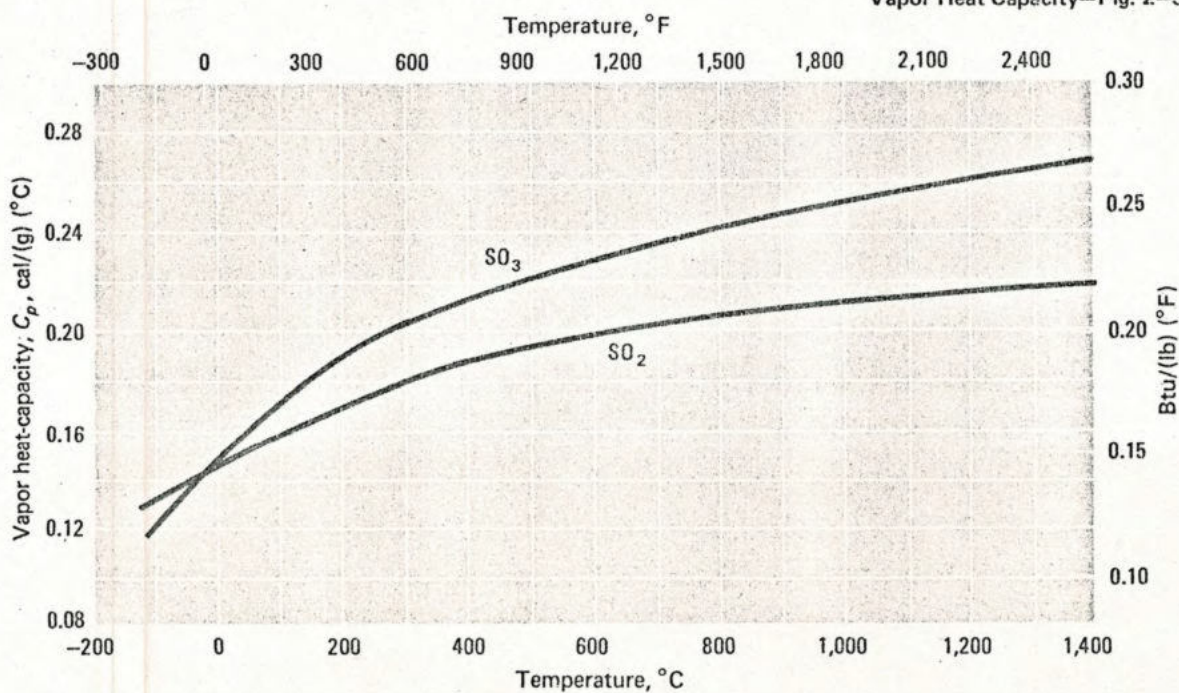
Fig. 2-2	Temperature Range		References
	m.p.-b.p.	b.p.-c.p.	
Sulfur dioxide	■	■	10, 12, 13, 73, 81, 90
Sulfur trioxide	■	■	13, 85, 91

■ Laboratory data    ■ Laboratory plus correlations    □ All correlated data

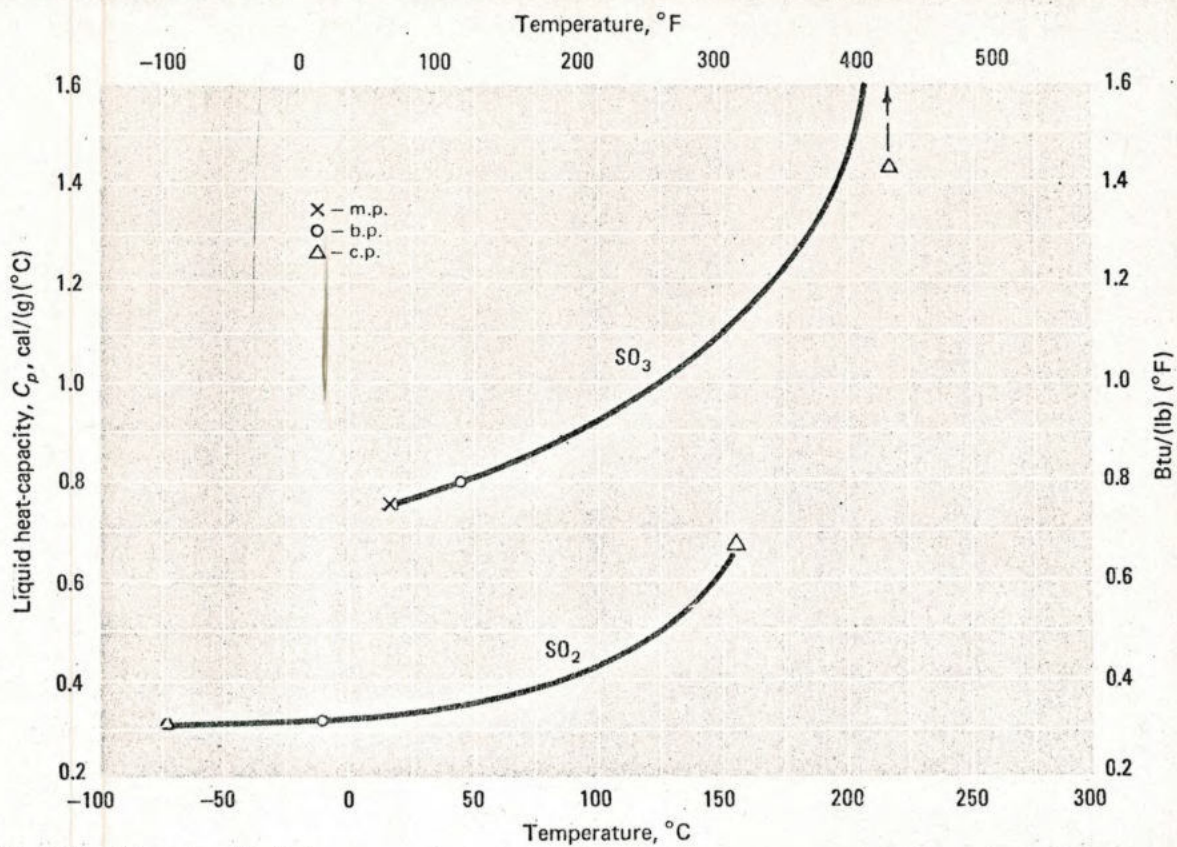
Fig. 2-3	Temperature Range, °C			References
	0-500	500-1,000	1,000-1,500	
Sulfur dioxide	■	■	■	7, 15, 19, 76, 77, 86
Sulfur trioxide	■	■	■	7, 8, 15, 76, 88

■ Laboratory data    ■ Laboratory plus correlations    □ All correlated data

Vapor Heat Capacity—Fig. 2-3







Liquid Heat Capacity—Fig. 2-4

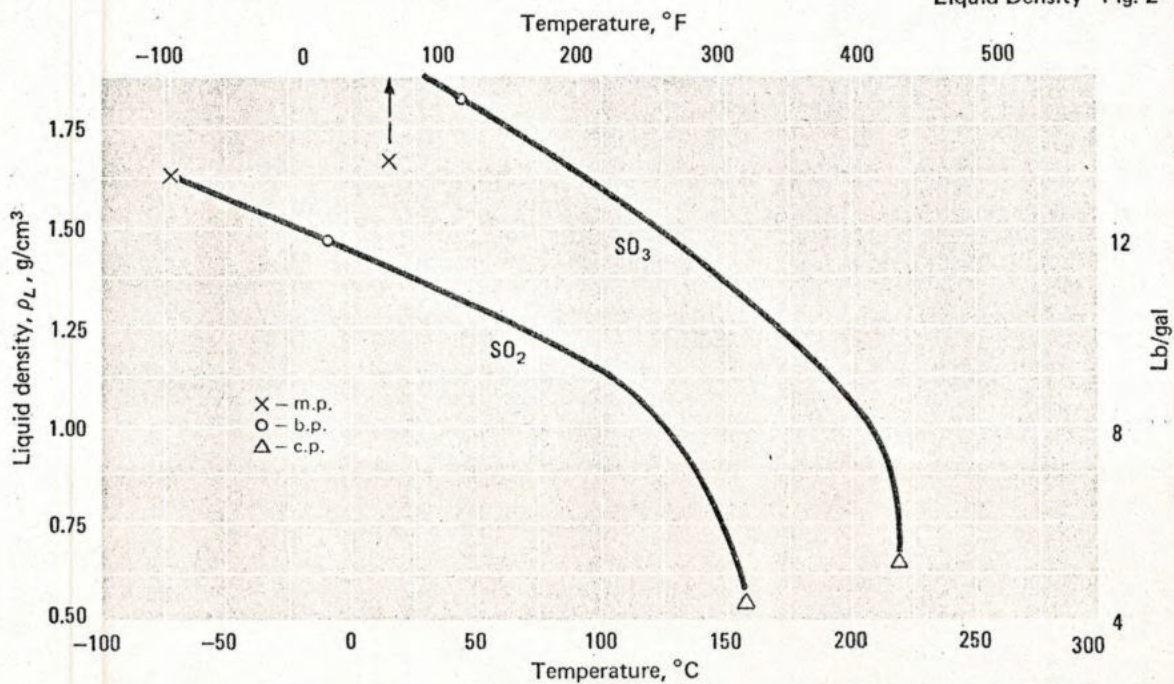
Fig. 2-4	Temperature Range		References
	m.p.—b.p.	b.p.—c.p.	
Sulfur dioxide	■	▣	4, 10, 19, 92
Sulfur trioxide	□	▣	4, 85, 91

■ Laboratory data    ▣ Laboratory plus correlations    □ All correlated data

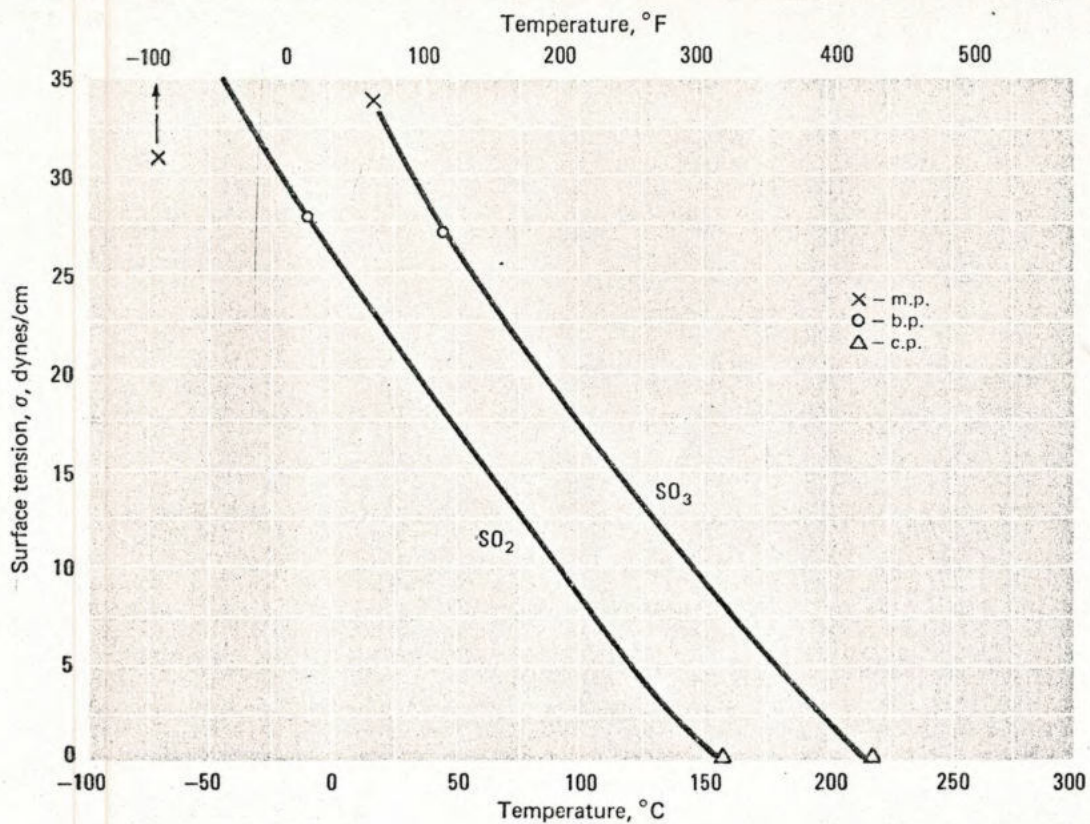
Fig. 2-5	Temperature Range		References
	m.p.—b.p.	b.p.—c.p.	
Sulfur dioxide	□	▣	4, 10, 15, 73, 81
Sulfur trioxide	■	▣	4, 6, 12, 85, 91

■ Laboratory data    ▣ Laboratory plus correlations    □ All correlated data

Liquid Density—Fig. 2-5







Surface Tension—Fig. 2-6

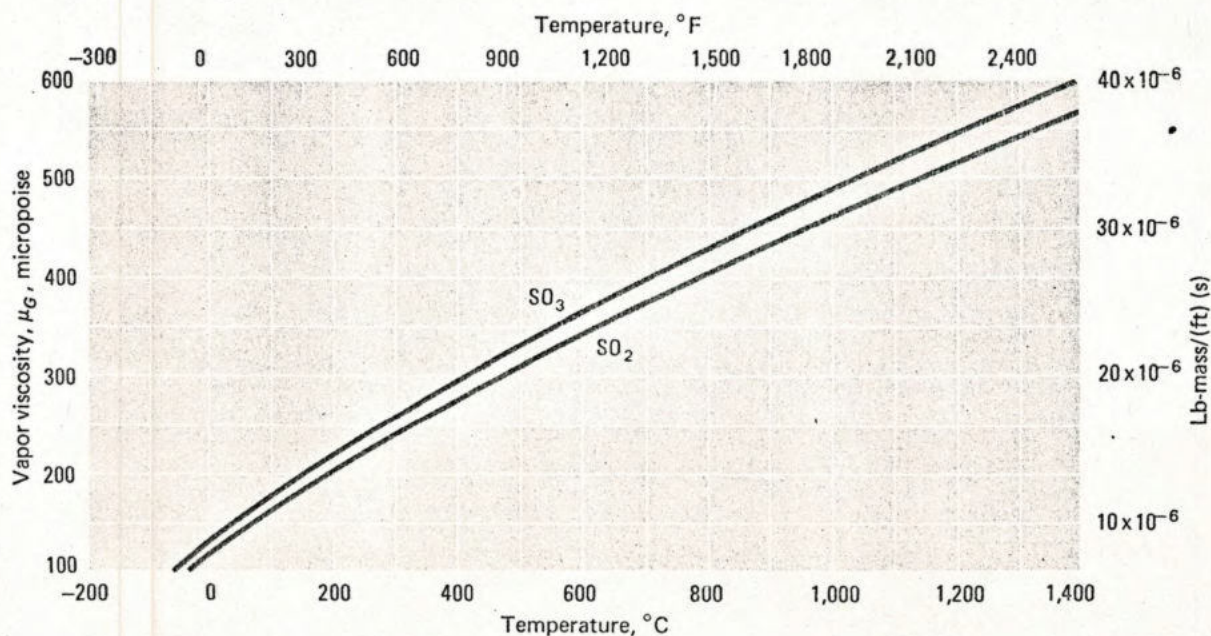
Fig. 2-6	Temperature Range		References
	m.p. - b.p.	b.p. - c.p.	
Sulfur dioxide	☒	☒	79, 92
Sulfur trioxide	☒	☒	6

☒ Laboratory data    ☒ Laboratory plus correlations    ☐ All correlated data

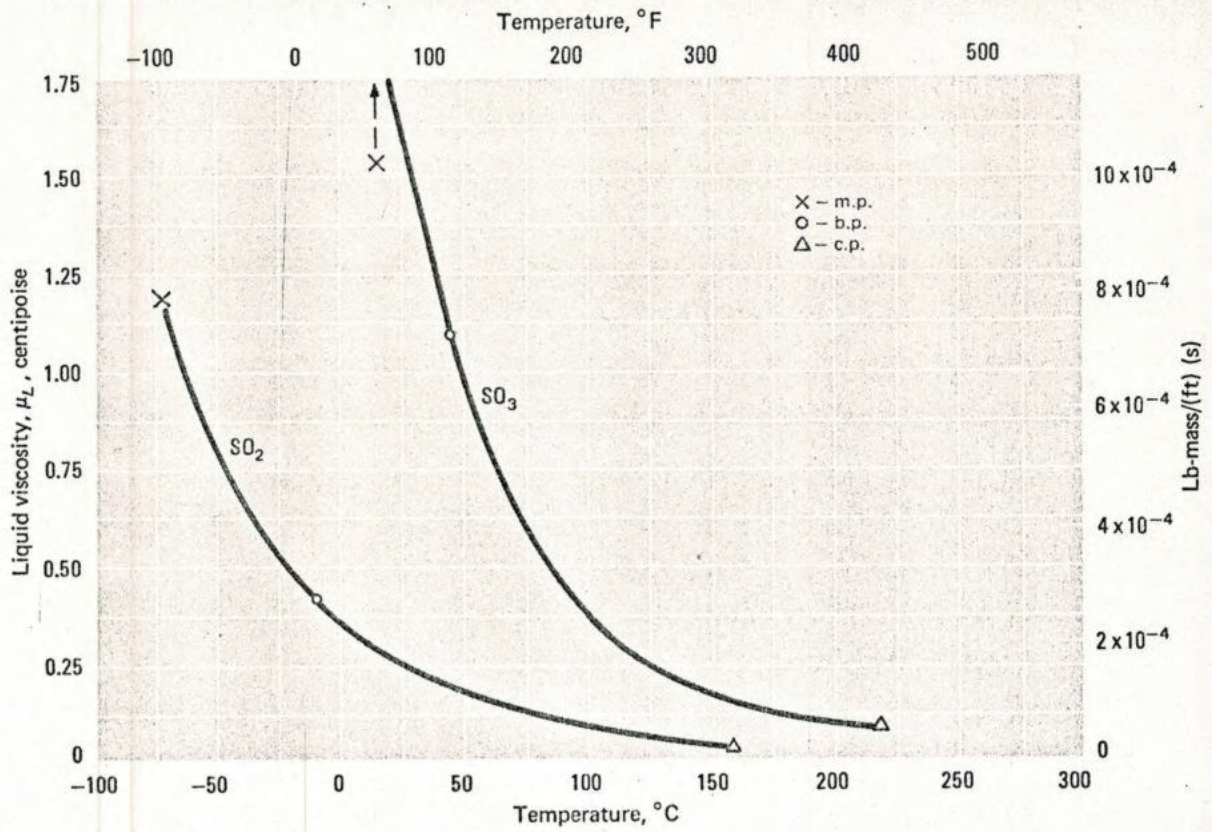
Fig. 2-7	Temperature Range, $^{\circ}\text{C}$			References
	0-500	500-1,000	1,000-1,500	
Sulfur dioxide	☒	☒	☐	10, 13, 14, 18, 19, 75, 82, 89, 92
Sulfur trioxide	☐	☐	☐	13, 14

☒ Laboratory data    ☒ Laboratory plus correlations    ☐ All correlated data

Vapor Viscosity—Fig. 2-7







Liquid Viscosity—Fig. 2-8

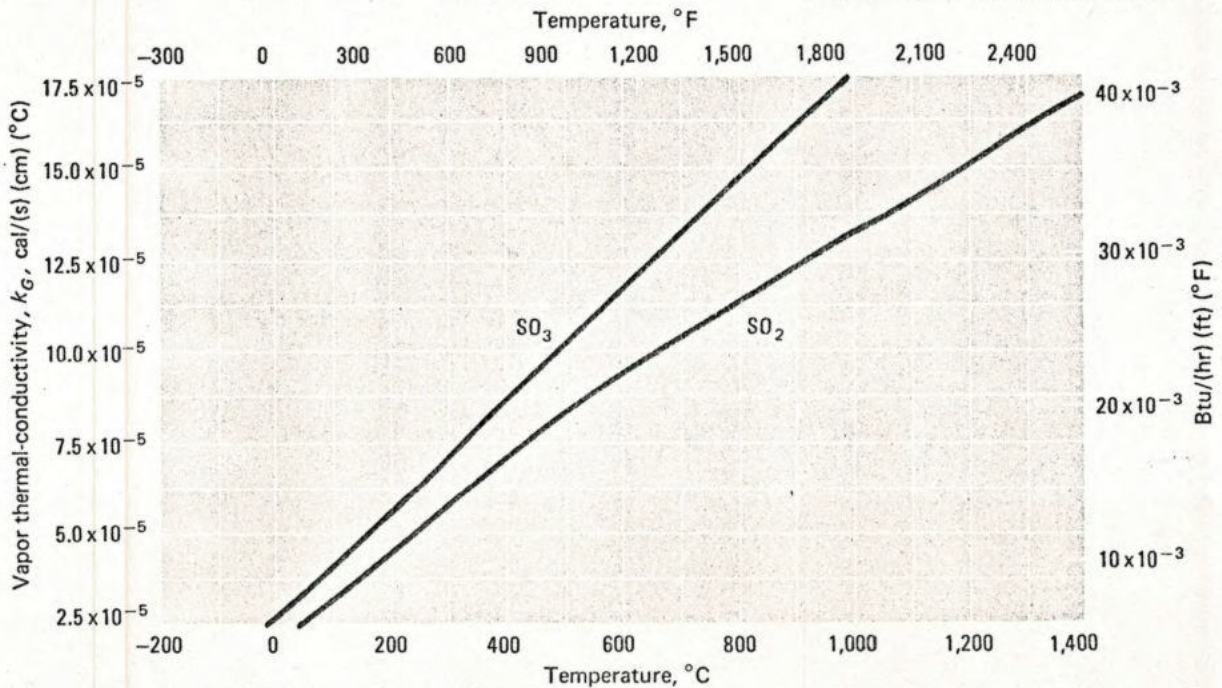
Fig. 2-8	Temperature Range		References
	m.p.—b.p.	b.p.—c.p.	
Sulfur dioxide	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	2, 4, 6, 73, 92, 93
Sulfur trioxide	<input type="checkbox"/>	<input checked="" type="checkbox"/>	4, 85

Laboratory data   
  Laboratory plus correlations   
  All correlated data

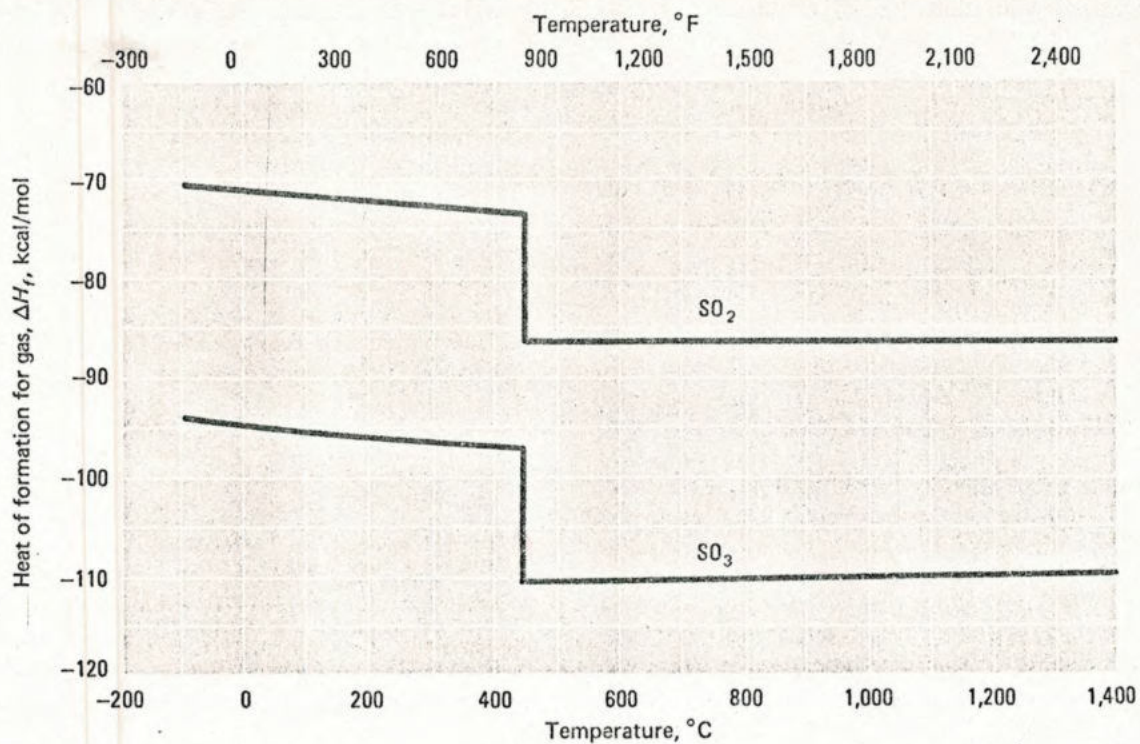
Fig. 2-9	Temperature Range, °C			References
	0-500	500-1,000	1,000-1,500	
Sulfur dioxide	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	14, 79, 92
Sulfur trioxide	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	14

Laboratory data   
  Laboratory plus correlations   
  All correlated data

Vapor Thermal Conductivity—Fig. 2-9







Heat of Formation—Fig. 2-10

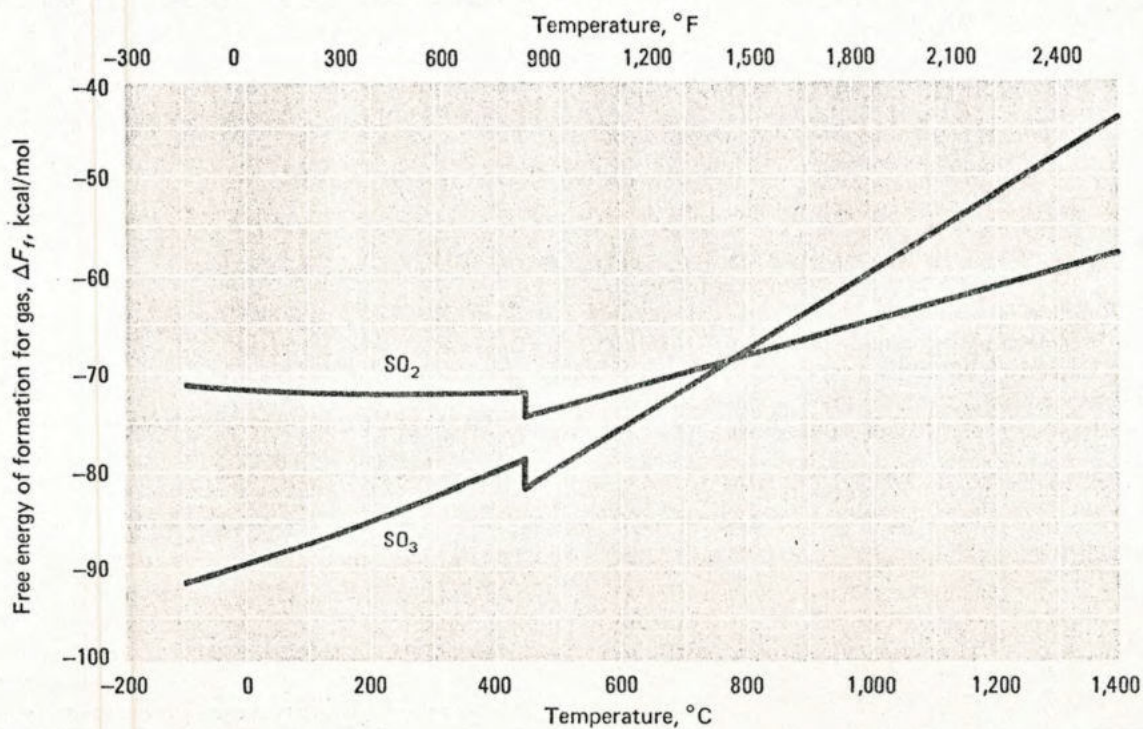
Fig. 2-10	Temperature Range, $^{\circ}\text{C}$			References
	0-500	500-1,000	1,000-1,500	
Sulfur dioxide	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	7, 8, 15, 76, 77, 86
Sulfur trioxide	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	7, 8, 15, 76, 88

Laboratory data     Laboratory plus correlations     All correlated data

Fig. 2-11	Temperature Range, $^{\circ}\text{C}$			References
	0-500	500-1,000	1,000-1,500	
Sulfur dioxide	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	7, 8, 15, 76, 77, 86
Sulfur trioxide	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	7, 8, 15, 76, 88

Laboratory data     Laboratory plus correlations     All correlated data

Free Energy of Formation—Fig. 2-11





## SULFUR OXIDES . . .

Experimental data and computed values agreed favorably, with maximum deviations of only 1.5% for sulfur dioxide (12 data points) and 2.5% for sulfur trioxide (5 data points).

### Viscosity—Fig. 2—7, 2—8

Experimental vapor-viscosity data for sulfur dioxide were extended with the Bromley and Wilke correlation:

$$\mu_g = \frac{33.3(MT_c)^{1/2}}{(V_c)^{2/3}} [f(1.33T_r)] \quad (2-3)$$

where  $\mu_g$  is expressed in micropoise,  $T_c$  in °K and  $V_c$  in  $\text{cm}^3/\text{g-mol}$ , and  $M$  is the molecular weight. The term  $f(1.33T_r)$ —which is a function of temperature and critical temperature—is available from the tables in Perry [13] or Reid and Sherwood [14]. The correlation was also used to estimate vapor viscosity for sulfur trioxide. The correlation estimates and experimental data compared favorably, with deviations being less than 3% for sulfur dioxide (25 data points).

Liquid viscosity data for both of the sulfur oxides are available for temperature below and above the boiling point. For sulfur-dioxide data extension, viscosity was determined from the reduced viscosity correlation of Thodos and Meyer:

$$\mu_L = \mu_c f(T_r, P_r) \quad (2-4)$$

where the terms  $\mu_c$  and  $f(T_r, P_r)$  are available from the graph in the original publication [93]. For sulfur trioxide, the Guzman-Andrade relationship (Eq. 1—6) was used to extend the available data for complete liquid-state coverage. Liquid viscosities from the relationship were in close agreement with the data, with an average deviation of below 5% for sulfur trioxide (10 data points). The liquid viscosities are assumed to be reasonably accurate up to 80% of critical temperature.

### Thermal Conductivity—Fig. 2—9

Vapor thermal-conductivity data for sulfur dioxide were extended using the modified Eucken correlation [14].

$$k = \mu[1.32C_p + (0.891/M)] \quad (2-5)$$

where,  $k$  = gas conductivity,  $\text{cal}/(\text{s})(\text{cm})(^\circ\text{C})$ ;  $\mu$  = gas viscosity, poise;  $C_p$  = gas heat-capacity at constant pressure,  $\text{cal}/(\text{g})(^\circ\text{C})$ ;  $M$  = molecular weight. The correlation was also used for vapor thermal conductivity of sulfur trioxide. Comparison of results from the correlation with available experimental data disclosed good agreement, with variations less than 7% for sulfur dioxide (18 data points).

Available liquid thermal-conductivity data for sulfur dioxide have been correlated by Thodos and Meyer to yield the relation:

$$k_L = k_c f(T_r, P_r) \quad (2-6)$$

where the terms  $k_c$  and  $f(T_r, P_r)$  are available from the graph in the original publication [93]. Representative results from the correlation along the saturation line are 7.5 ( $-50^\circ\text{C}$ ), 5.3 ( $0^\circ\text{C}$ ), 3.5 ( $50^\circ\text{C}$ ), 2.2 ( $100^\circ\text{C}$ ) and 1 ( $150^\circ\text{C}$ )  $\times 10^{-4}$   $\text{cal}/(\text{s})(\text{cm})(^\circ\text{C})$ . Liquid thermal-con-

ductivity data or reliable estimation methods for inorganic oxides were not identified in our literature screening for sulfur trioxide.

### Heat and Free Energy of Formation—Fig. 2—10, 2—11

Data from various sources for ideal gas state are in agreement for heat ( $\Delta H_f$ ) and free energy ( $\Delta F_f$ ) of formation for sulfur-dioxide and -trioxide. The vertical shift in each curve at  $445^\circ\text{C}$  reflects the change in the standard reference state of elemental sulfur from the liquid to the gas (diatomic). The results are sufficiently precise for practical usage in chemical thermodynamics. #

## References

- References 1-72 are listed in *Chem. Eng.*, June 10, 1974, p. 78.
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## Meet the Authors



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