PHYSICAL & THERMODYNAMIC PROPERTIES 4

Carbon Oxides: CO and CO_2

Concise graphical formats permit rapid evaluation of the major physical and thermodynamic properties of carbon monoxide and carbon dioxide.

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Carbon monoxide and carbon dioxide occur in the products of combustion of all carbonaceous fuels.

Carbon monoxide, a highly toxic chemical, is made from synthesis gas and other types of manufactured gas for the production of a great variety of chemicals such as acids, esters and hydroxyacids. In addition, it is used in the Mond process for recovery of nickel from ores, in the manufacture of steel as a deoxidant, and in the preparation of some catalysts.

Carbon dioxide is widely produced as a byproduct of many chemical and fermentation processes, by separation from flue gases, and from natural-gas wells. It is used in solid (dry ice), liquid and gaseous forms in such widely diversified applications as beverage carbonation, chemical manufacture, fire fighting, food preservation, foundry-mold preparation, greenhouses, mining operations, oil-well secondary recovery, rubber tumbling, therapeutical work, and welding [*4*].

Physical-property and thermodynamics-property data for carbon monoxide and dioxide are required both in producing and using these basic chemicals.

Critical Properties—Table 4—I

Selected properties of carbon monoxide and dioxide are shown in Table 4—I. The critical constants have been reported in many references [*2,4,6,9,13,83*] with good agreement. The reported values for critical temperature and critical volume from various sources agree, with variations being below 1.1%. The maximum deviation among the experimental critical pressures is 3.5% for both oxides. The boiling point of carbon dioxide is the same as its sublimation point (−78.5°C at atmospheric pressure). The melting point for carbon dioxide is −56.6°C at 5.2 atm.

Vapor Pressure—Fig. 4—1

Vapor-pressure data, which cover a wide temperature range, are in close agreement, with maximum deviation of 5%.

Heat of Vaporization—Fig. 4—2

Heat of vaporization outside the data range was determined with the Watson correlation (Eq. **1**—1).†

Heat Capacity—Fig. 4—3, 4—4

Vapor heat capacities for the ideal gas are primarily computed from spectroscopic measurements and have an

(*Text continues on p. 122*)

* To meet your authors, see *Chem. Eng.*, July 8, 1974, p. 92.

† See Part 1 of this series, *Chem. Eng.*, June 10, 1974, for all equations starting with a boldfaced numeral "**1**." Part 2 appeared in the July 8, 1974 issue, and Part 3 in the Aug. 19, 1974 issue.

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:

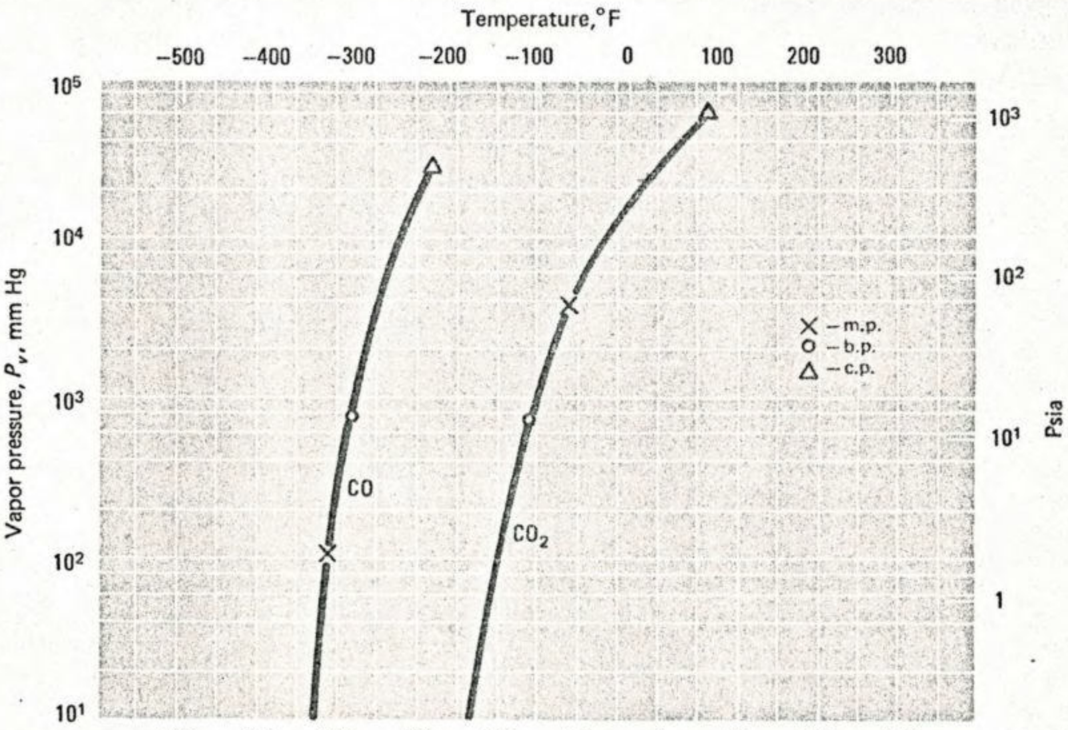
- ■ Data in this region are experimentally known.
- ◩ Experimental and correlated data used.
- □ All data in this region are correlated.

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 Carbon Oxides
Table 4–I

Identification	Carbon Monoxide CO	Carbon Dioxide CO_2
State, (std. cond.)	Gas*	Gas*
Molecular weight, M	28.01	44.01
Boiling point, T_b, °C	−191.5	−78.5†
Melting point, T_m, °C,	−205.0	−56.5**
Critical temp., T_c, °C	−140.1	31.1
Critical pressure, P_c, atm	34.6	72.9
Critical volume, V_c, cm³/gr mol	93.1	94.0
Critical compressibility factor, Z_c	0.295	0.275

*Colorless. †Sublimes. **At 5.2 atm.



Vapor Pressure—Fig. 4–1

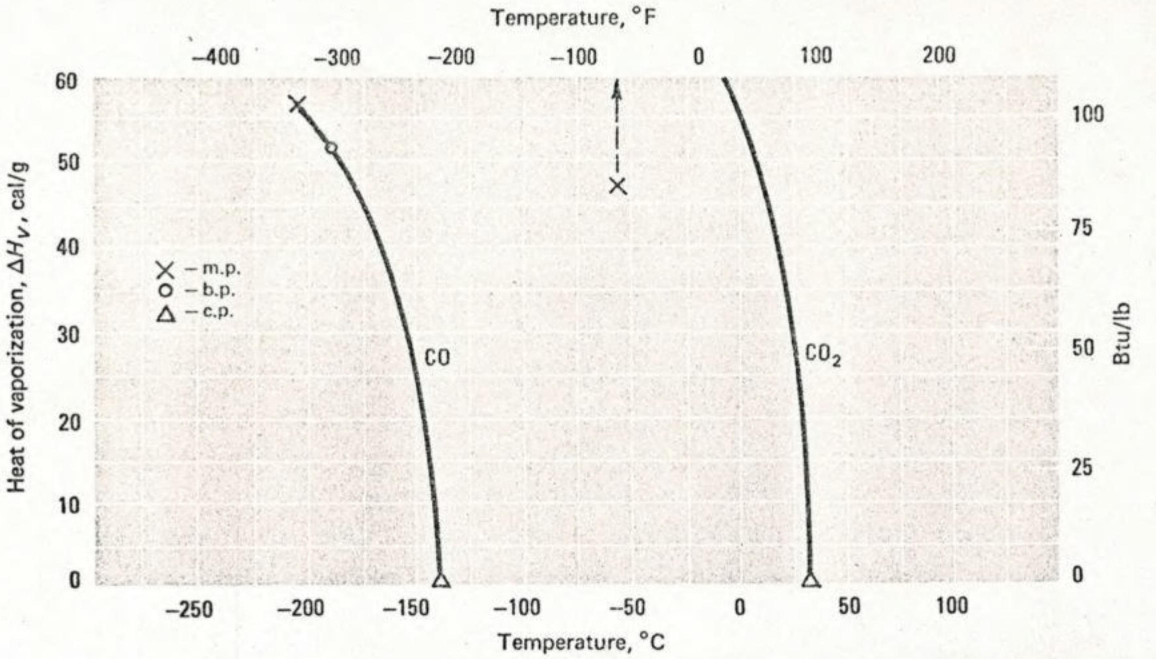
Fig. 4–1	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Carbon monoxide	■	■	5,12,13,17,146
	b.p.–m.p.	m.p.–c.p.	
Carbon dioxide	Solid	■	4,5,12,13,17

■ Laboratory data ◩ Laboratory plus correlations □ All correlated data

Fig. 4–4	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Carbon monoxide	□	◩	12,14,19
	b.p.–m.p.	m.p.–c.p.	
Carbon dioxide	Solid	◩	19,147,157

■ Laboratory data ◩ Laboratory plus correlations □ All correlated data

Liquid Heat Capacity—Fig. 4–4 →



Heat of Vaporization—Fig. 4–2

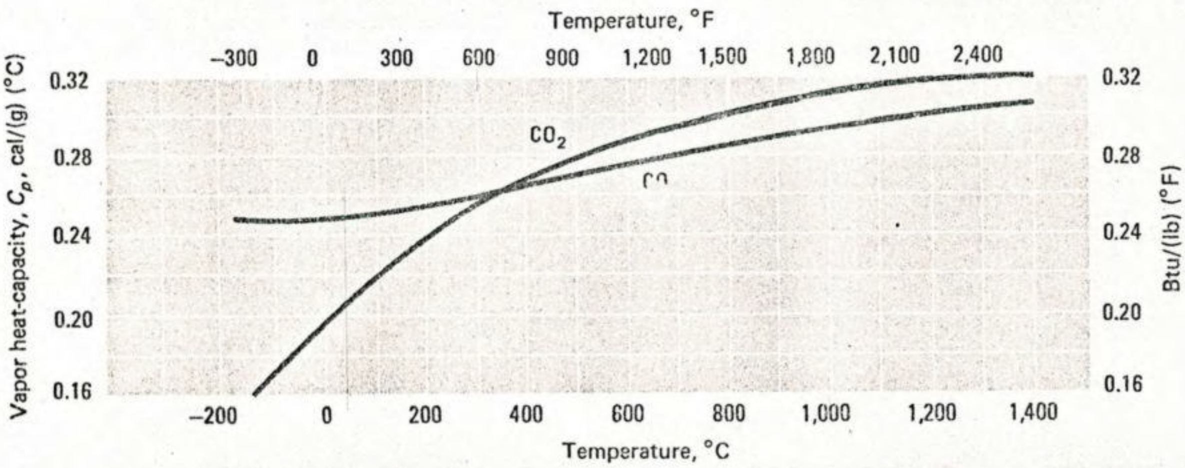
Fig. 4–2	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Carbon monoxide	◪	◪	9, 10, 13, 14, 115
	b.p.–m.p.	m.p.–c.p.	
Carbon dioxide	Solid	◪	9, 10, 13, 14, 115, 157

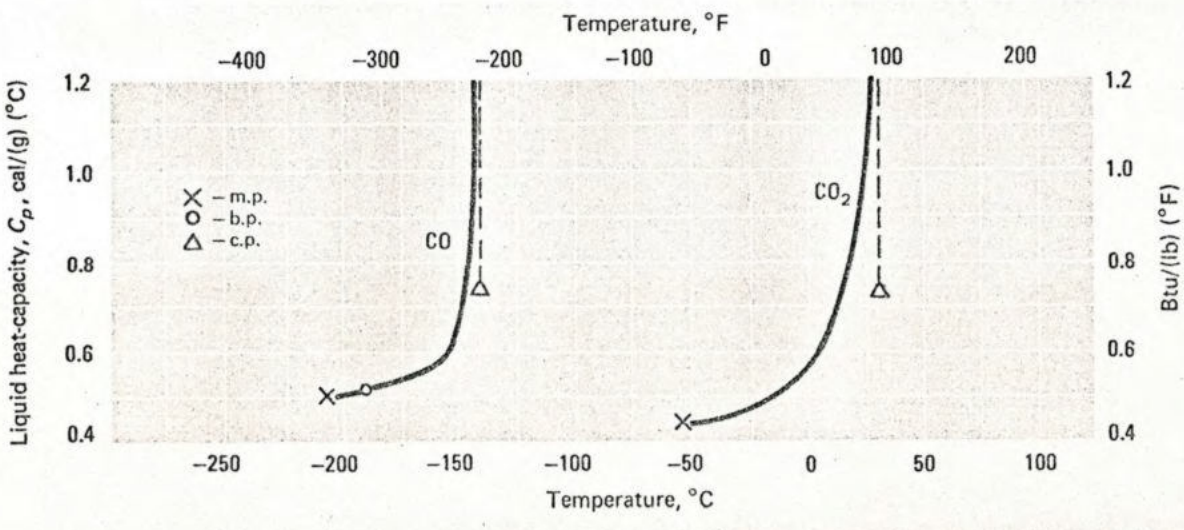
■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

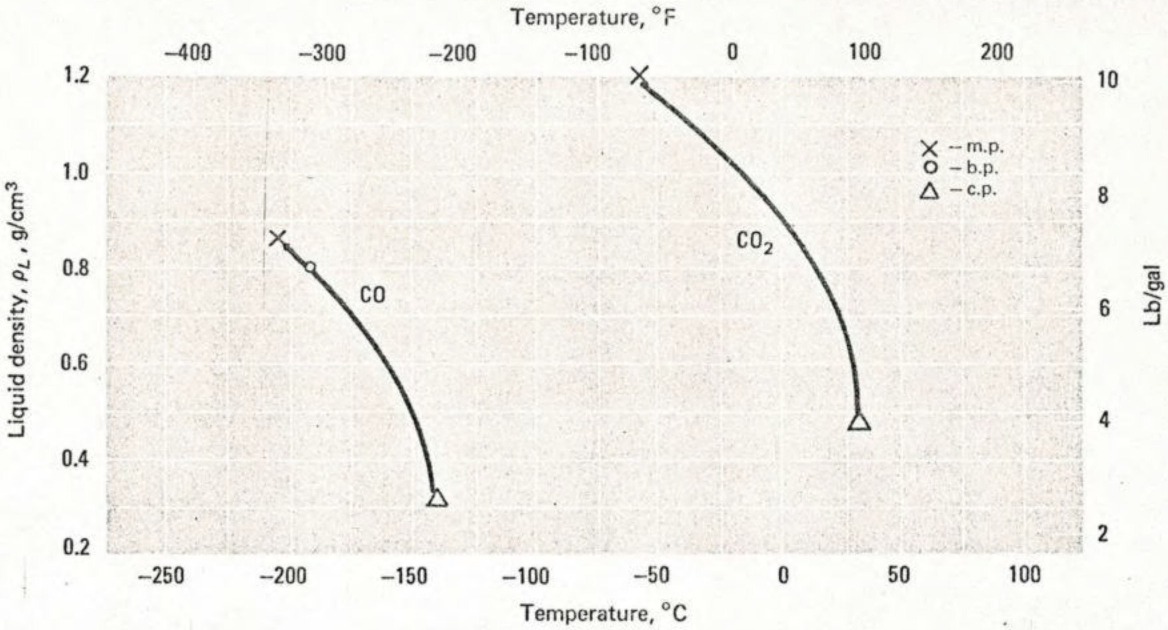
Fig. 4–3	Temperature Range, °C			References
	0–500	500–1,000	1,000–1,500	
Carbon monoxide	◪	◪	◪	4, 8, 18, 19, 76, 86, 155
Carbon dioxide	◪	◪	◪	8, 18, 19, 76, 77, 135

■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Vapor Heat Capacity—Fig. 4–3







Liquid Density—Fig. 4–5

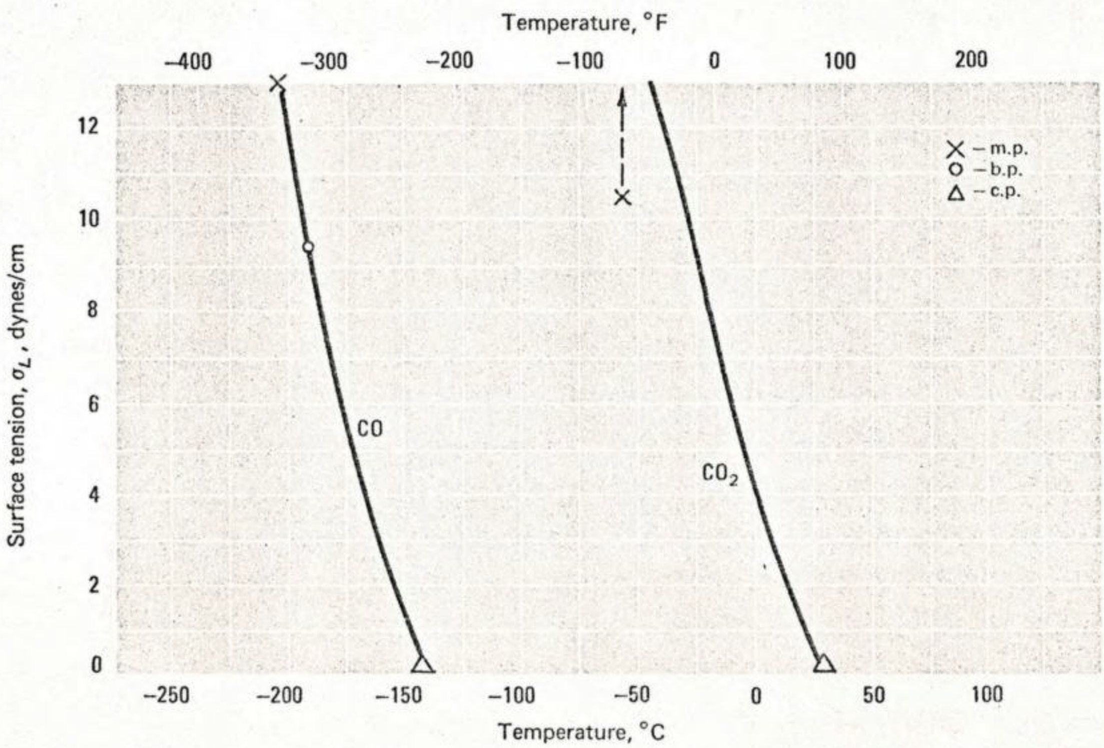
Fig. 4–5	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Carbon monoxide	■	◪	12, 149, 150
	b.p.–m.p.	m.p.–c.p.	
Carbon dioxide	Solid	■	140, 141, 145, 146, 148, 153, 154

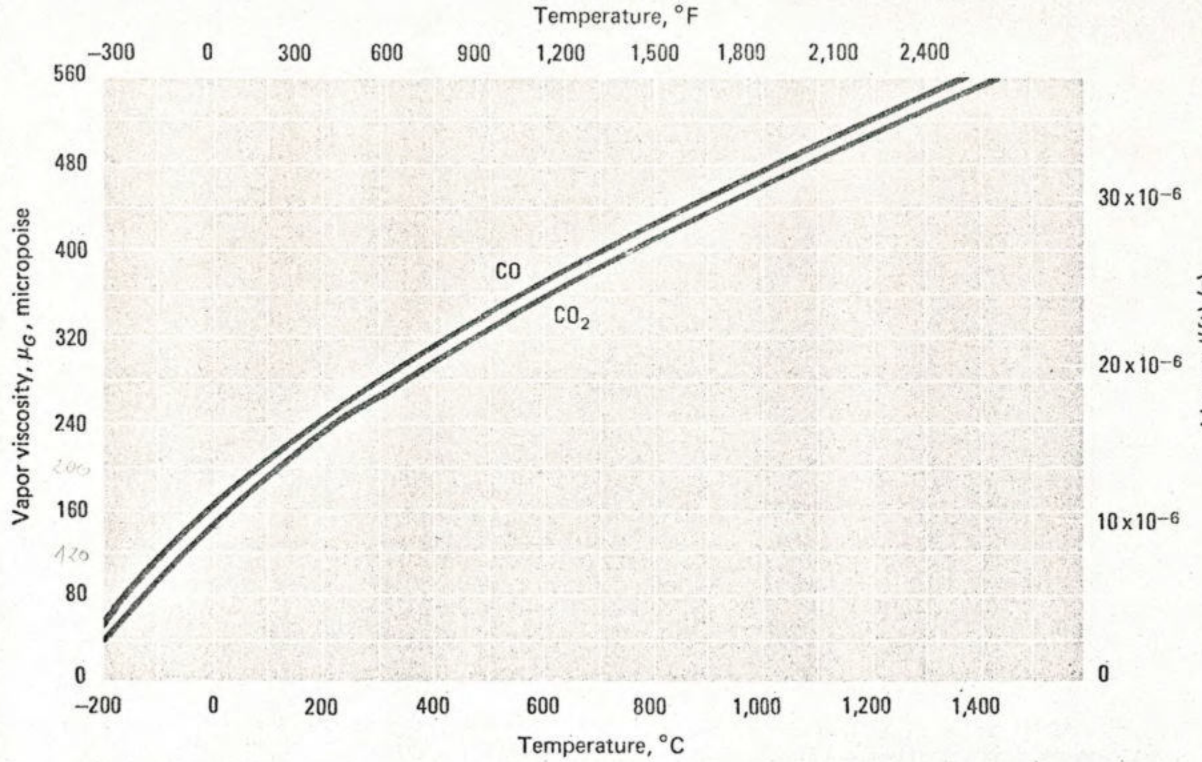
■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Fig. 4–6	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Carbon monoxide	◪	◪	2, 6, 79
	b.p.–m.p.	m.p.–c.p.	
Carbon dioxide	Solid	◪	2, 6, 9, 79

■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Surface Tension—Fig. 4–6





Vapor Viscosity—Fig. 4–7

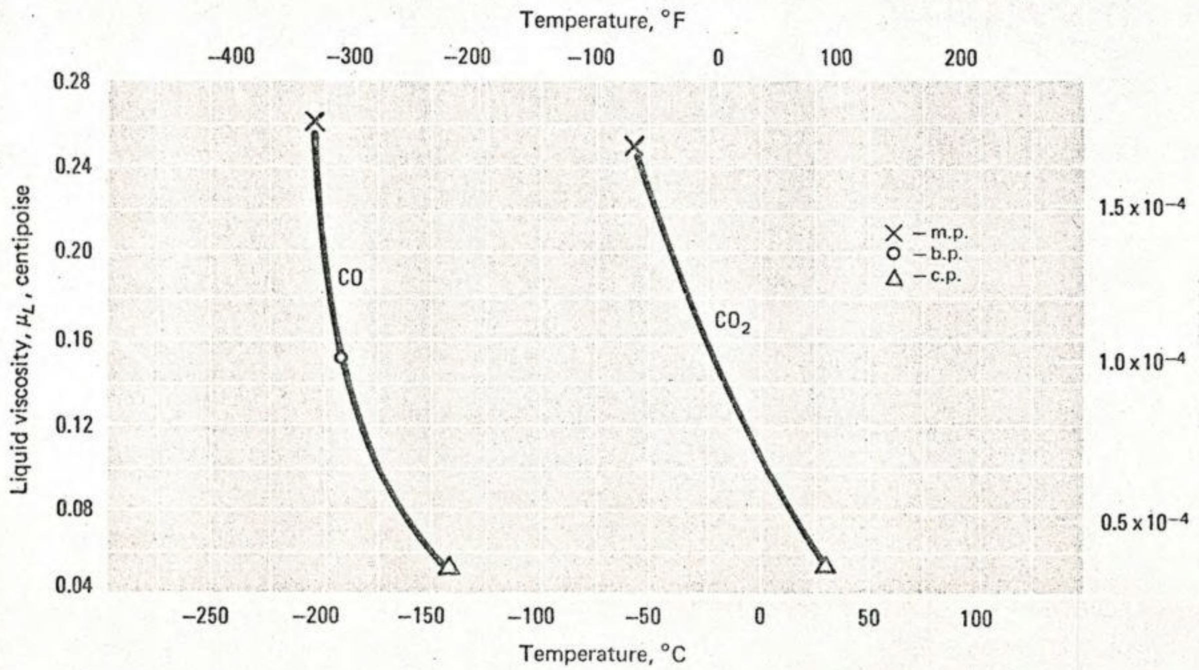
Fig. 4–7	Temperature Range, °C			References
	0–500	500–1,000	1,000–1,500	
Carbon monoxide	◪	□	□	9, 12, 13, 18, 137, 139
Carbon dioxide	◪	□	□	9, 12, 18, 82, 136, 156

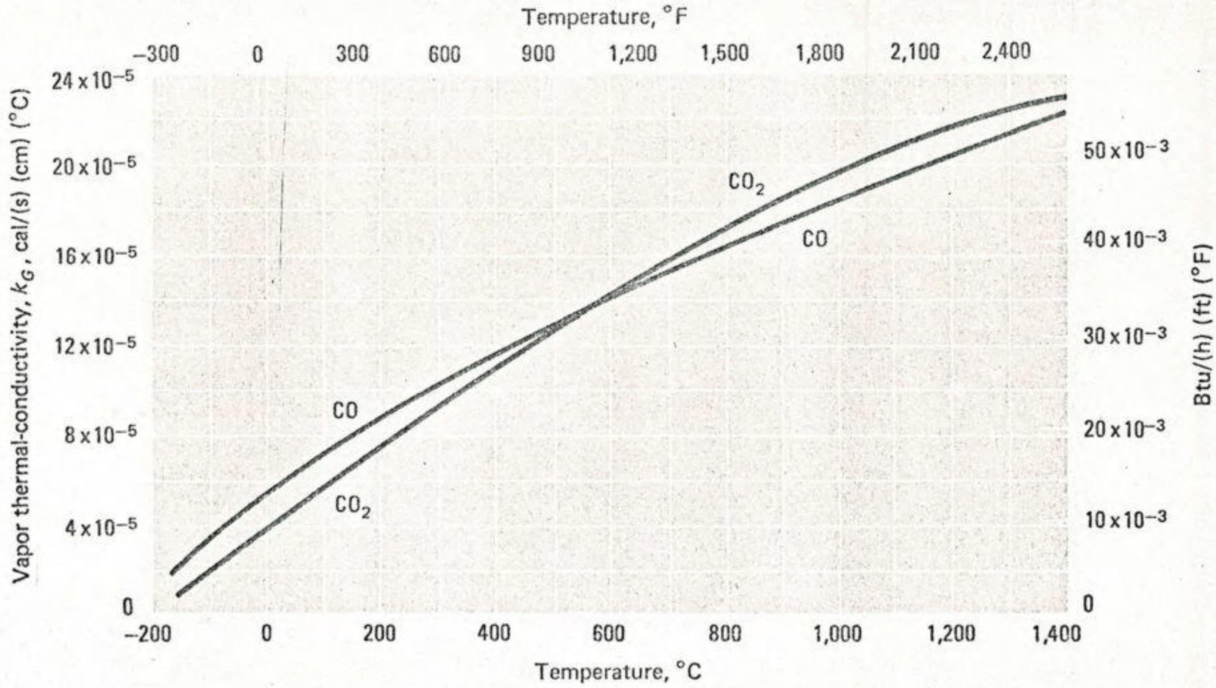
■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Fig. 4–8	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Carbon monoxide	◪	□	138
	b.p.–m.p.	m.p.–c.p.	
Carbon dioxide	Solid	■	6, 9, 13, 144

■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Liquid Viscosity—Fig. 4–8





Vapor Thermal Conductivity—Fig. 4–9

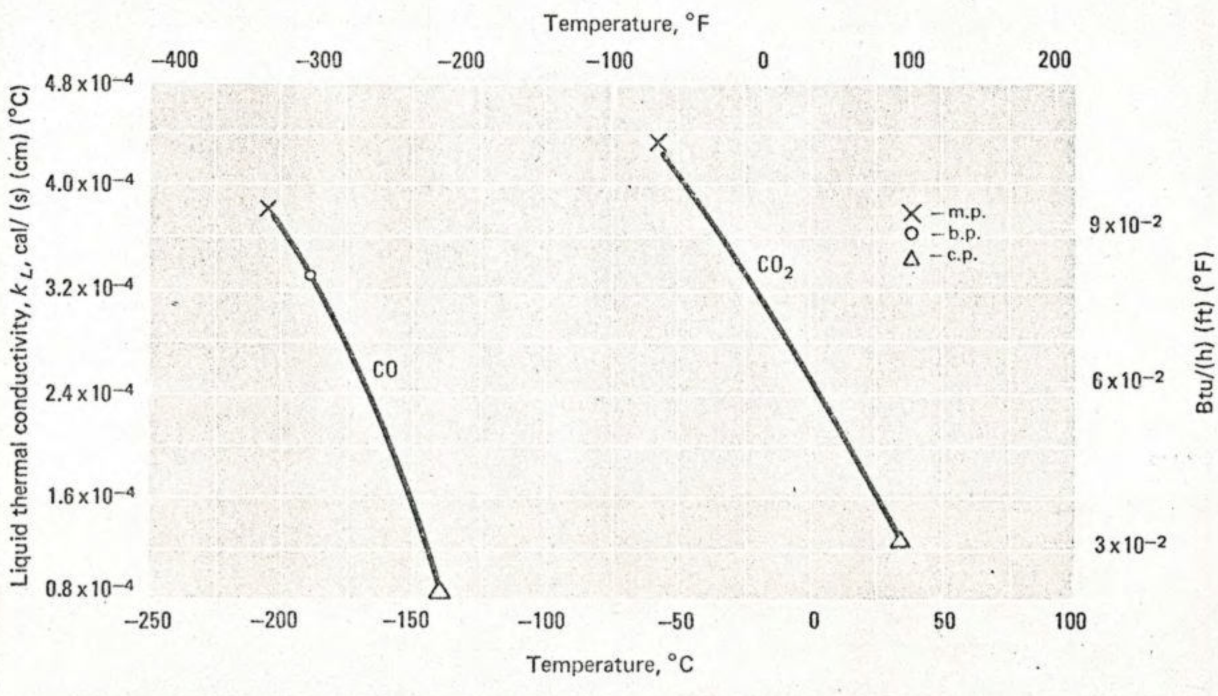
Fig. 4–9	Temperature Range, °C			References
	0–500	500–1,000	1,000–1,500	
Carbon monoxide	■	◪	□	18,19,65,97
Carbon dioxide	■	■	□	18,19,96,143

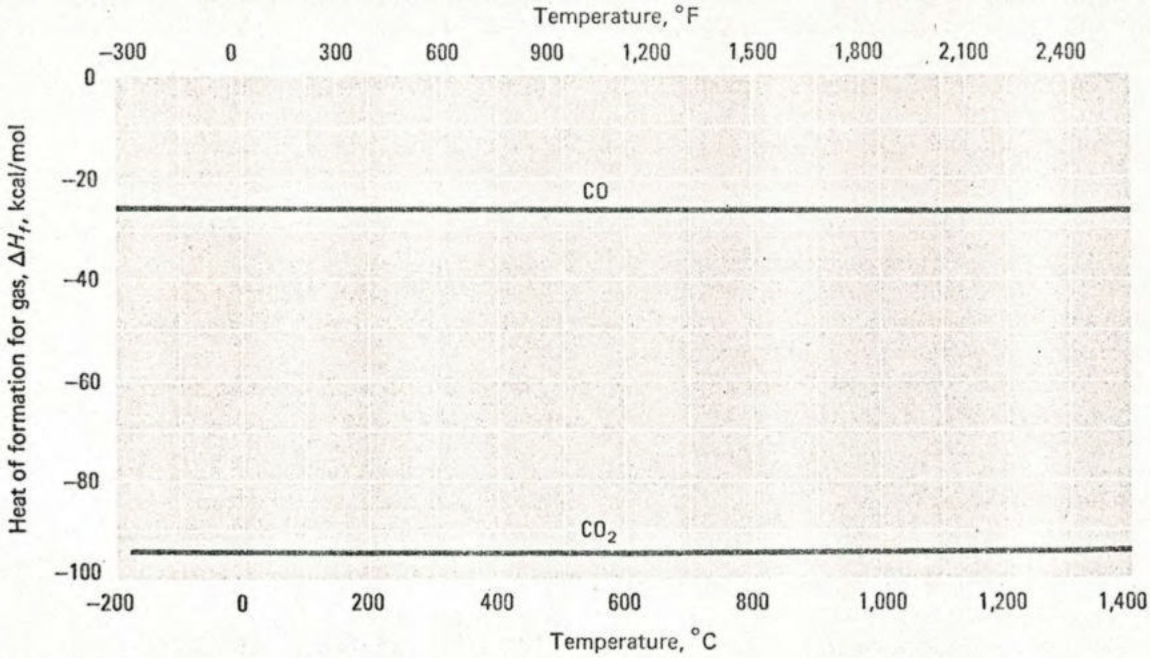
■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Fig. 4–10	Temperature Range		References
	m.p.–b.p.	b.p.–c.p.	
Carbon monoxide	◪	◪	14,19,65
	b.p.–m.p.	m.p.–c.p.	
Carbon dioxide	Solid	◪	14,19,142,151,152

■ Laboratory data ◪ Laboratory plus correlations □ All correlated data

Liquid Thermal Conductivity—Fig. 4–10





Heat of Formation—Fig. 4—11

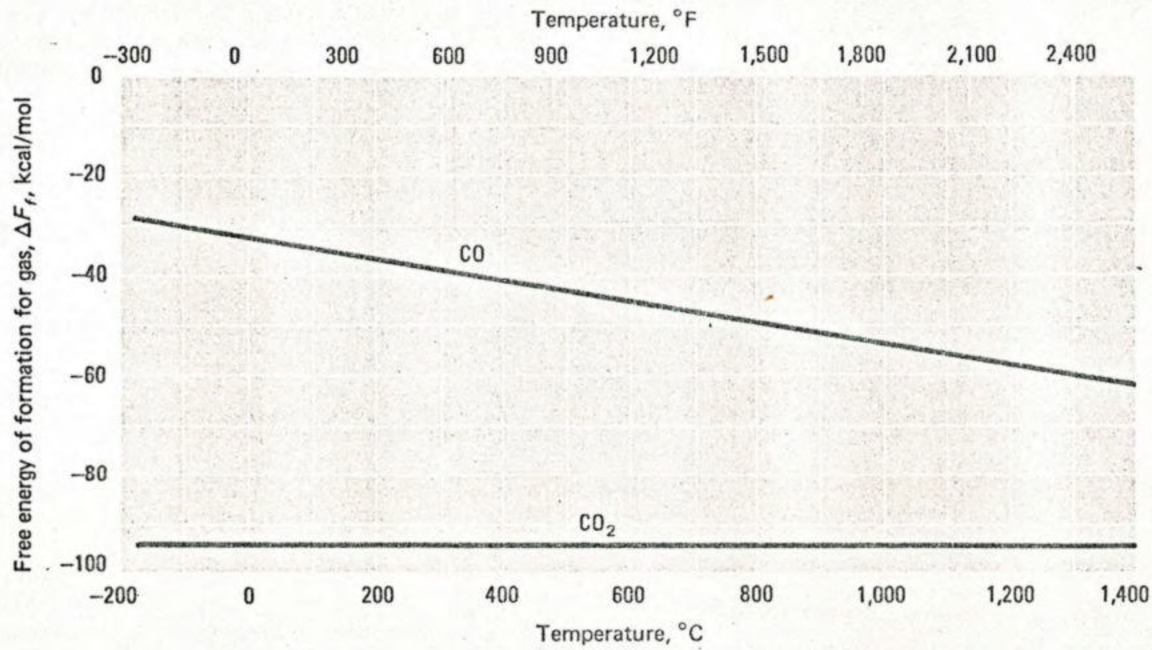
Fig. 4—11	Temperature Range, °C			References
	0–500	500–1,000	1,000–1,500	
Carbon monoxide	◩	◩	◩	1,2,7,15,21
Carbon dioxide	◩	◩	◩	1,2,7,13,15,21

■ Laboratory data ◩ Laboratory plus correlations □ All correlated data

Fig. 4—12	Temperature Range, °C			References
	0–500	500–1,000	1,000–1,500	
Carbon monoxide	◩	◩	◩	1,2,7,15,21
Carbon dioxide	◩	◩	◩	1,2,7,15,21

■ Laboratory data ◩ Laboratory plus correlations □ All correlated data

Free Energy of Formation—Fig. 4—12



average standard deviation of less than 1% among the various data sources.

Reported liquid heat capacities of carbon dioxide are in agreement, with a maximum deviation of 4% (10 data points). Experimental heat capacities for carbon monoxide were extended to near the critical point with the Watson method as modified by Sobel [*14*].

Density—Fig. 4—5

Liquid-density data for carbon monoxide were extended to its critical temperature by the reduced-state method by using Lu's correlation (Eq. 2—2), which gives a standard deviation of less than 2%. Experimental density values for carbon dioxide cover a wide temperature range and are in good agreement. The maximum deviation is found to be 1%.

Surface Tension—Fig. 4—6

Experimental surface-tension measurements for both oxides were extended for full liquid-phase coverage with the Othmer relationship (Eq. **1**— 4). Results from the relationship were in close agreement with the experimental data. Deviations were less than 2% for carbon monoxide (10 data points), and 3% for carbon dioxide (14 data points).

Viscosity—Fig. 4—7, Fig. 4—8

Vapor-viscosity data at atmospheric pressure are available for carbon monoxide and dioxide. The results of Svehla [*18*] were used to extend the data to higher temperatures. Svehla has estimated vapor viscosity at high temperatures by using the Chapman-Enskog treatment, which provides intermolecular potential energy and interactions between colliding molecules in determining transport properties:

$$\mu_\sigma = 26.69\sqrt{MT}/\sigma^2\Omega_v \qquad (4—1)$$

where μ_σ is gas viscosity, micropoise; M is molecular weight; T is absolute temperature, °K; σ is collision diameter, Å; and Ω_v is the collision integral.

The term σ^2 is available in Svehla [*18*] or Reid and Sherwood [*14*]. Values of Ω_v, which is a function of temperature, for the Lennard-Jones and Stockmayer potentials are available in Reid and Sherwood [*14*] for various substances. Most of the experimental data from various references are in good agreement, with a deviation of less than 3%.

Liquid-viscosity data for carbon monoxide were extended to cover the entire liquid phase with the relationship of Guzman-Andrade (Eq. **1**—6). Liquid viscosities of carbon dioxide have been measured by several investigators at temperatures ranging from the melting point to the critical point. In general, the results from the different sources are in close agreement. The deviation of the curve from the available experimental data is less than 2% for carbon monoxide (8 data points) and 4.2% for carbon dioxide (12 data points).

Thermal Conductivity—Fig. 4—9, Fig. 4—10

Vapor thermal-conductivity data for carbon monoxide and carbon dioxide are available in a wide temperature range, with results from the various investigators being in very close agreement. In general, deviations from the best fit of the data are less than 7% for carbon monoxide (more than 80 data points) and 8% for carbon dioxide (more than 90 data points).

Liquid thermal-conductivity data for both oxides were expanded for full liquid-phase coverage. The correlation of Schaefer and Thodos (Eq. **3**—2) was used for carbon monoxide, and Stiel and Thodos (Eq. **3**—3 and **3**—4) for carbon dioxide. The results of the correlation were in general agreement with the available tabulated experimental data. Deviations were less than 15% for carbon monoxide (13 data points) and 12% for carbon dioxide (11 data points).

Heat of Formation and Free Energy of Formation—Fig. 4—11, Fig. 4—12

The results of Stull [*7,15*], which include the JANAF tables, and Wicks [*2*] were adopted for heat of formation and free energy of formation for the ideal gas. For heat of formation, the agreement of results from the sources is very close, with differences being less than 0.5% for both oxides. For free energy of formation, the differences are less than 0.5% for carbon monoxide and 0.3% for carbon dioxide.

The next article in this series will appear in the Oct. 28, 1974 issue and will cover the properties of anhydrous hydrogen halides. #

References

References 1-72 are listed in *Chem. Eng.*, June 10, 1974, p. 78; 73-93, July 8, 1974, p. 92; 94-134, Aug. 19, 1974.

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