

Major Diatomic Gases— H_2 , N_2 , O_2



Here are the major physical, thermodynamic and transport properties of the most important diatomic gases—hydrogen, nitrogen and oxygen.

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The major diatomic gases—hydrogen, nitrogen and oxygen—make a significant industrial impact. Hydrogen finds extensive use in the production of ammonia, in the hydrogenation of vegetable and animal oils and fats (for soaps, lubricants, paints, varnishes, textiles, etc.), and in the production of such substances as glycols from aldols, and alcohols from esters and glycerides. Hydrogenation of coal to prepare gasoline and fuels is also increasing in importance.

Nitrogen's largest use occurs in the synthesis of ammonia, but it is also widely used in the chemical, polymer, petroleum, glass and food industries.

A Note About Hydrogen

The hydrogen molecule exists in two isomeric forms: (1) the *ortho*-hydrogen (parallel spin), in which the two atomic nuclei are spinning in the same direction; and (2) the *para*-hydrogen (anti-parallel spin), in which the nuclear spins occur in opposite directions. At ambient or higher temperatures, the equilibrium concentration of hydrogen is 75% *ortho* (three parts *ortho*, one part *para*). In this 3:1 ratio, the element is called "normal" hydrogen.

When hydrogen gas is quickly liquefied by cooling from ambient or higher temperatures, the liquid hydrogen thus obtained is also 75% *ortho*-hydrogen. However, this liquid will slowly change to the *para* form. The conversion is essentially complete at the boiling point (-252.7°C), with an equilibrium concentration of 99.8% *para*-hydrogen [4,14,43,306,317,336].

In this article, the liquid-phase properties of hydrogen apply to the *para*-hydrogen state, which is the form of major industrial importance at cryogenic temperatures. The gas-phase properties presented here apply to "normal" hydrogen, which is of major importance at ambient or higher temperatures.

Oxygen is used in the production of synthesis gas, aldehydes, acids, alcohols and other oxygenated chemicals. Prominent examples include methanol, ethylene and propylene oxides.

Critical Properties—Table 8—1

All critical properties have been determined experimentally [4,43,283,301,302,303,306,317,324,332,334,335]. Recent tabulated results by Roder and others at the National Bureau of Standards (NBS) were selected for hydrogen, nitrogen and oxygen. Agreement of these results with reported values from various sources is good; deviations are less than 0.3%, 0.8% and 1.4% for the respective critical temperatures, pressures and volumes.

Vapor Pressure—Fig. 8—1

Comprehensive vapor-pressure data cover the full liquid state for hydrogen, nitrogen and oxygen. The agreement of results—both from data and correlations from various sources—is very close. Deviations in most cases are much less than 1% [268,275,301].

Heat of Vaporization—Fig. 8—2

Heat of vaporization data based on calorimetric and pressure-volume-temperature (PVT) measurements cover the full liquid phase for the three elements. The reported results are in close agreement, with variations being less than 1.4%.

Heat Capacity—Fig. 8—3, 8—4

Experimental results for gas heat-capacity at atmospheric pressure are numerous, and in agreement with

(Text continues on p. 105)

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.

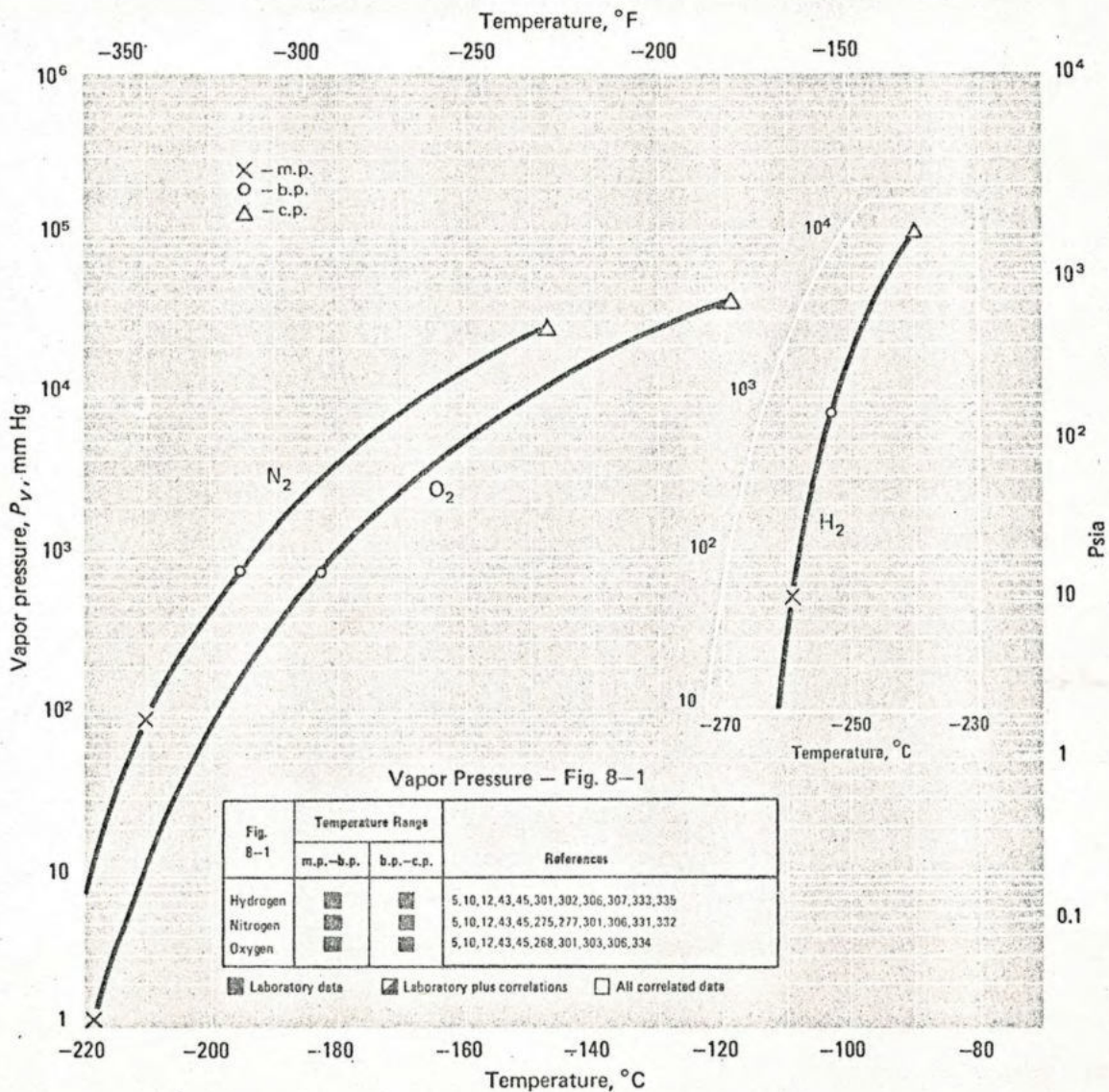
The shaded squares denote the following:

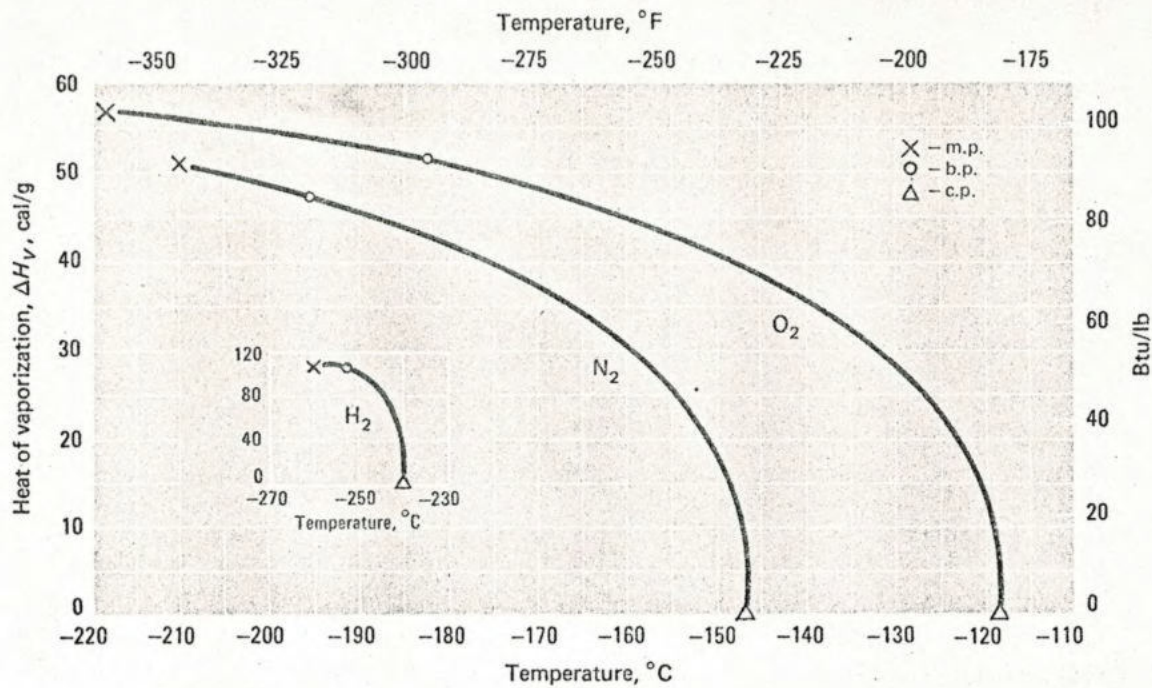
- Data in this region are experimentally known.
- ▣ Experimental and correlated data used.
- All data in this region are correlated.

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 Diatomic Gases — Table 8-1

Identification	Hydrogen, H ₂	Nitrogen, N ₂	Oxygen, O ₂
State (std. conditions)	Gas	Gas	Gas
Molecular weight, <i>M</i>	2.016	28.01	32.0
Boiling point, <i>T_b</i> , °C	-252.8	-195.8	-183.0
Melting point, <i>T_m</i> , °C	-259.4	-209.9	-218.4
Critical temp., <i>T_c</i> , °C	-240.2	-146.8	-118.5
Critical pressure, <i>P_c</i> , atm	12.8	33.56	49.8
Critical volume, <i>V_c</i> , cm ³ /g-mol	64.14	89.05	73.37
Critical compressibility factor, <i>Z_c</i>	0.303	0.291	0.292





Heat of Vaporization — Fig. 8-2

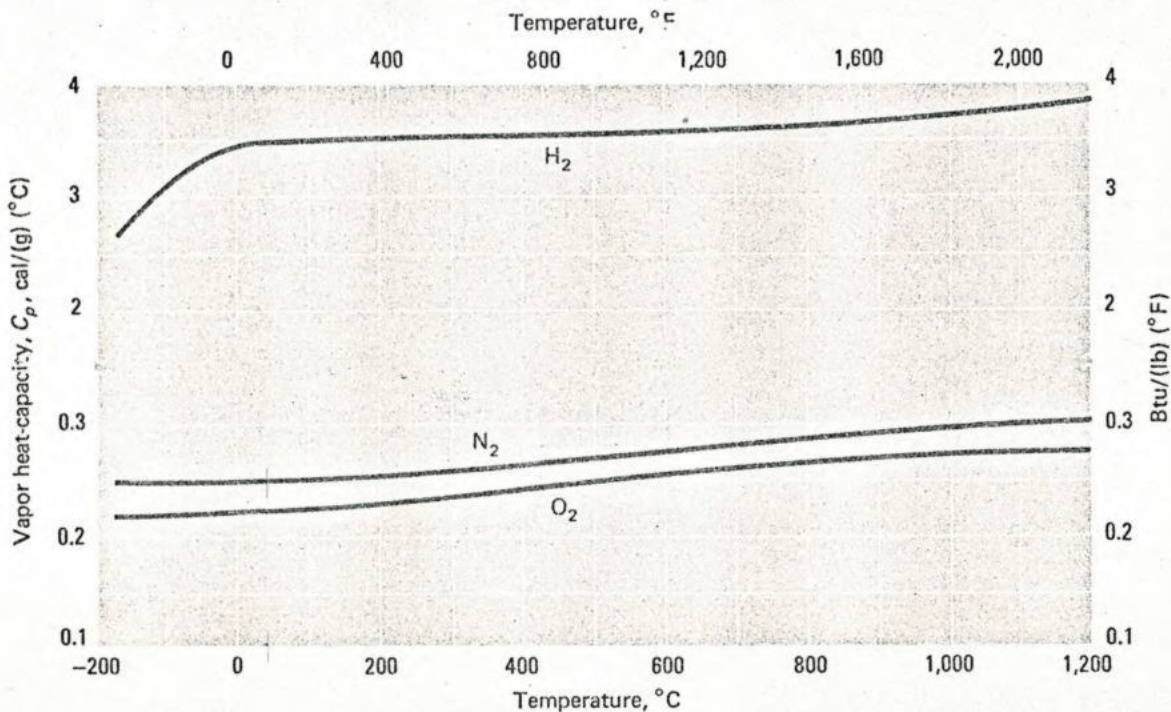
Fig. 8-2	Temperature Range		References
	m.p.-b.p.	b.p.-c.p.	
Hydrogen	☒	☒	10, 284, 293, 302, 306, 307, 309, 335
Nitrogen	☒	☒	10, 43, 45, 47, 277, 300, 306, 317
Oxygen	☒	☒	10, 43, 45, 47, 296, 300, 306, 309, 317

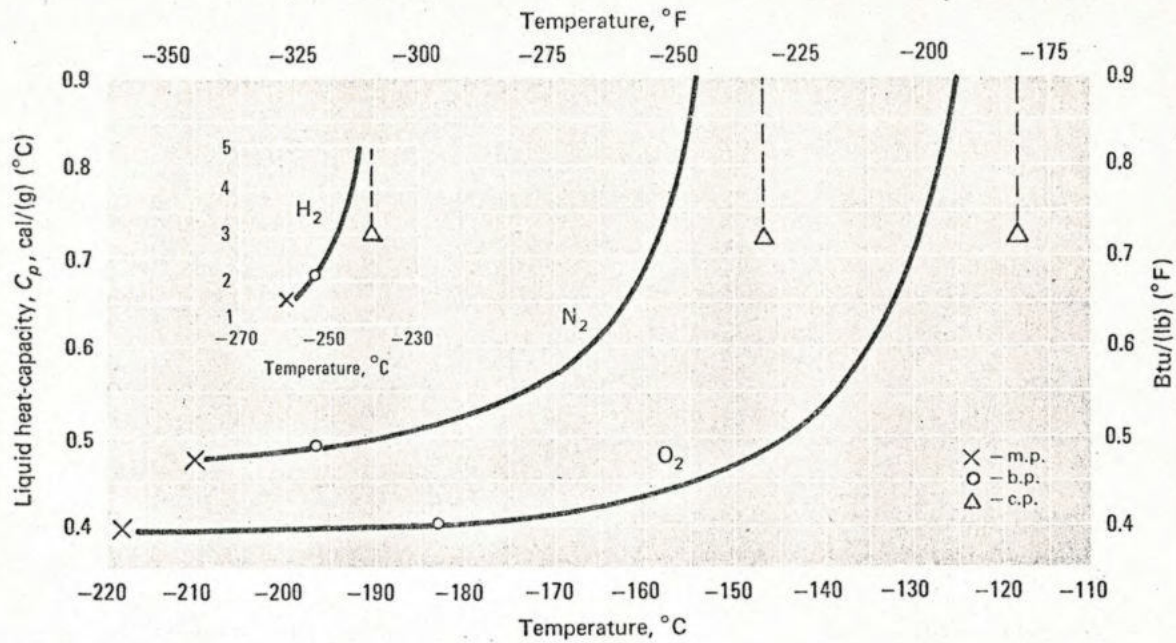
☒ Laboratory data ☒ Laboratory plus correlations ☐ All correlated data

Fig. 8-3	Temperature Range, °C			References
	0-500	500-1,000	1,000-1,500	
Hydrogen	☒	☒	☒	7, 10, 15, 16, 19, 43, 47, 289, 317
Nitrogen	☒	☒	☒	7, 10, 15, 16, 19, 47, 289, 317
Oxygen	☒	☒	☒	7, 10, 15, 16, 19, 43, 47, 289, 303, 317, 322

☒ Laboratory data ☒ Laboratory plus correlations ☐ All correlated data

Vapor Heat Capacity — Fig. 8-3





Liquid Heat Capacity — Fig. 8-4

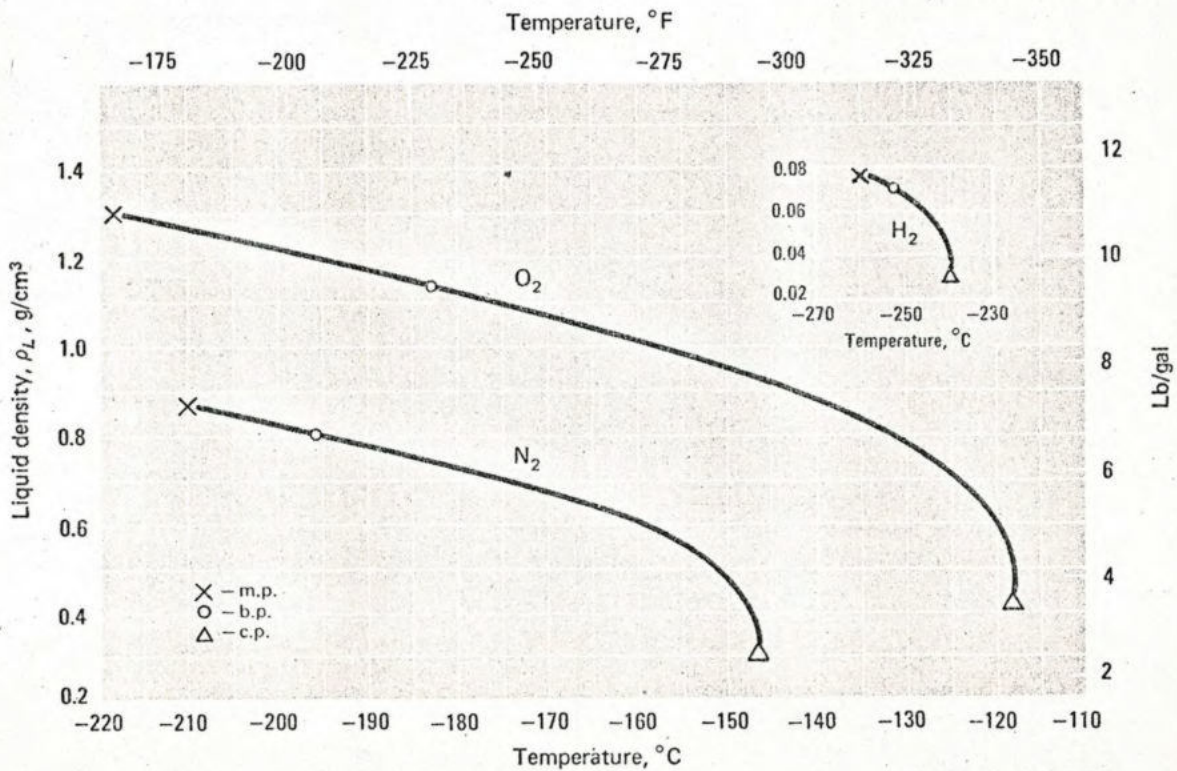
Fig. 8-4	Temperature Range		References
	m.p.-b.p.	b.p.-c.p.	
Hydrogen	■	■	19, 47, 284, 293, 302, 306, 307, 311, 321, 333, 335
Nitrogen	■	■	19, 43, 47, 300, 306, 321, 325, 331, 332
Oxygen	■	■	19, 47, 300, 303, 306, 321, 334

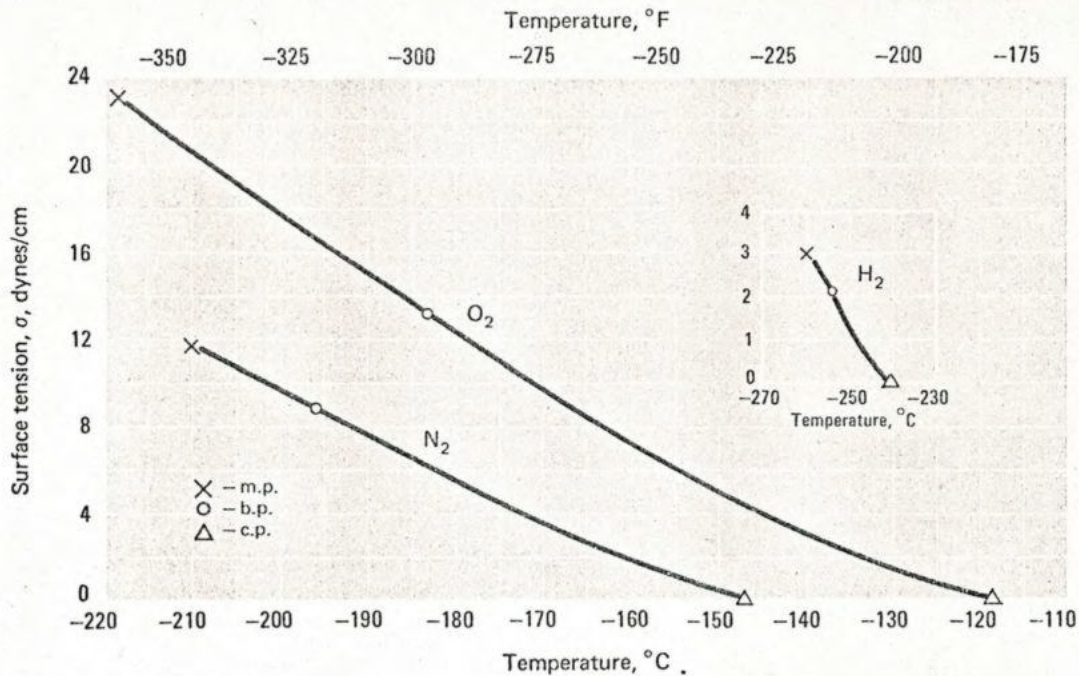
■ Laboratory data ■ Laboratory plus correlations □ All correlated data

Fig. 8-5	Temperature Range		References
	m.p.-b.p.	b.p.-c.p.	
Hydrogen	■	■	10, 43, 47, 285, 293, 301, 302, 304, 307, 314, 316, 319, 321, 333, 335
Nitrogen	■	■	10, 43, 47, 282, 300, 301, 315, 317, 321, 331, 332
Oxygen	■	■	10, 43, 47, 300, 301, 303, 306, 317, 319, 321, 324, 334

■ Laboratory data ■ Laboratory plus correlations □ All correlated data

Liquid Density — Fig. 8-5





Surface Tension - Fig. 8-6

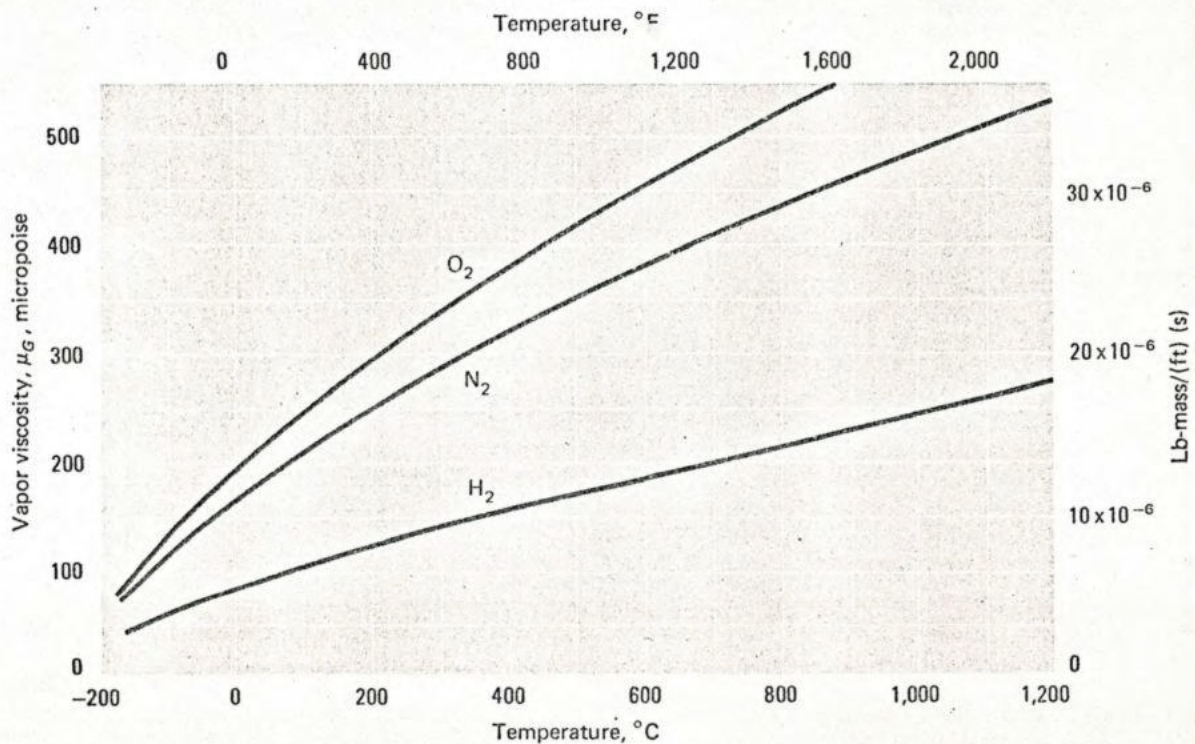
Fig. 8-6	Temperature Range		References
	m.p.-b.p.	b.p.-c.p.	
Hydrogen	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	47, 79, 265, 280, 293, 307, 333, 335
Nitrogen	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	47, 79, 310, 332
Oxygen	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	79, 303, 334

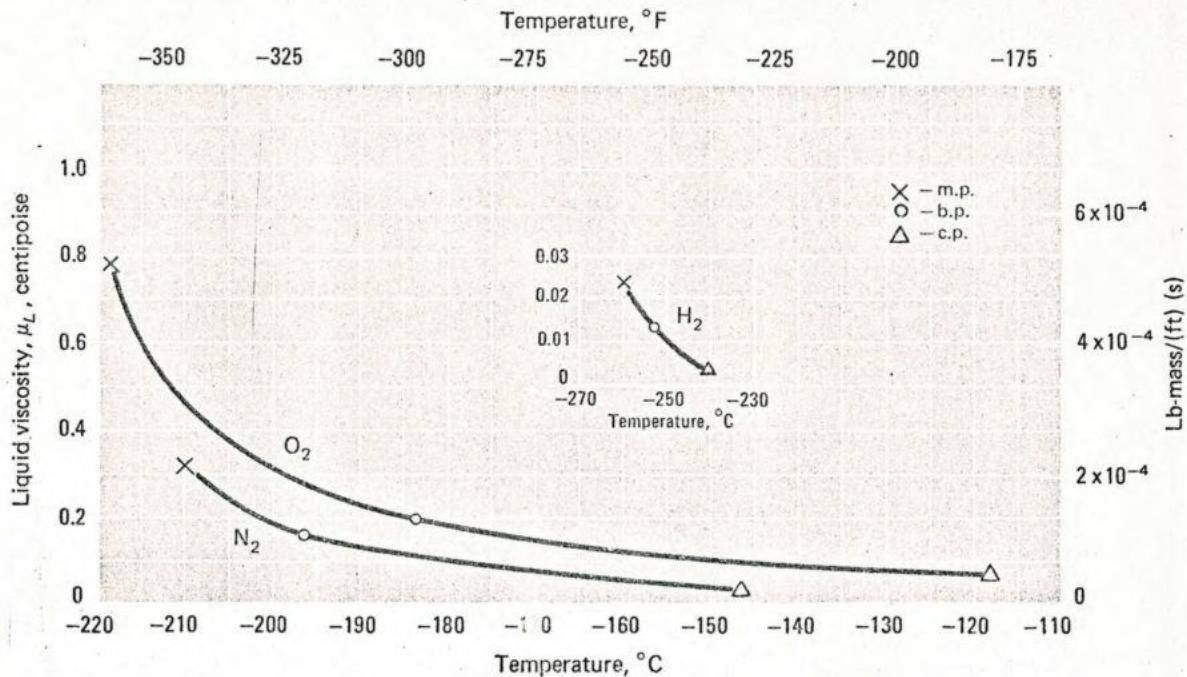
Laboratory data Laboratory plus correlations All correlated data

Fig. 8-7	Temperature Range, $^{\circ}\text{C}$			References
	0-500	500-1,000	1,000-1,500	
Hydrogen	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	2, 10, 18, 19, 47, 264, 269, 281, 286, 294, 306, 307, 312, 317, 336
Nitrogen	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	2, 10, 18, 19, 47, 270, 274, 281, 286, 291, 294, 297, 300, 306, 317, 326, 329, 330
Oxygen	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	2, 10, 18, 19, 47, 286, 294, 300, 303, 306, 317, 329, 330

Laboratory data Laboratory plus correlations All correlated data

Vapor Viscosity - Fig. 8-7





Liquid Viscosity — Fig. 8-8

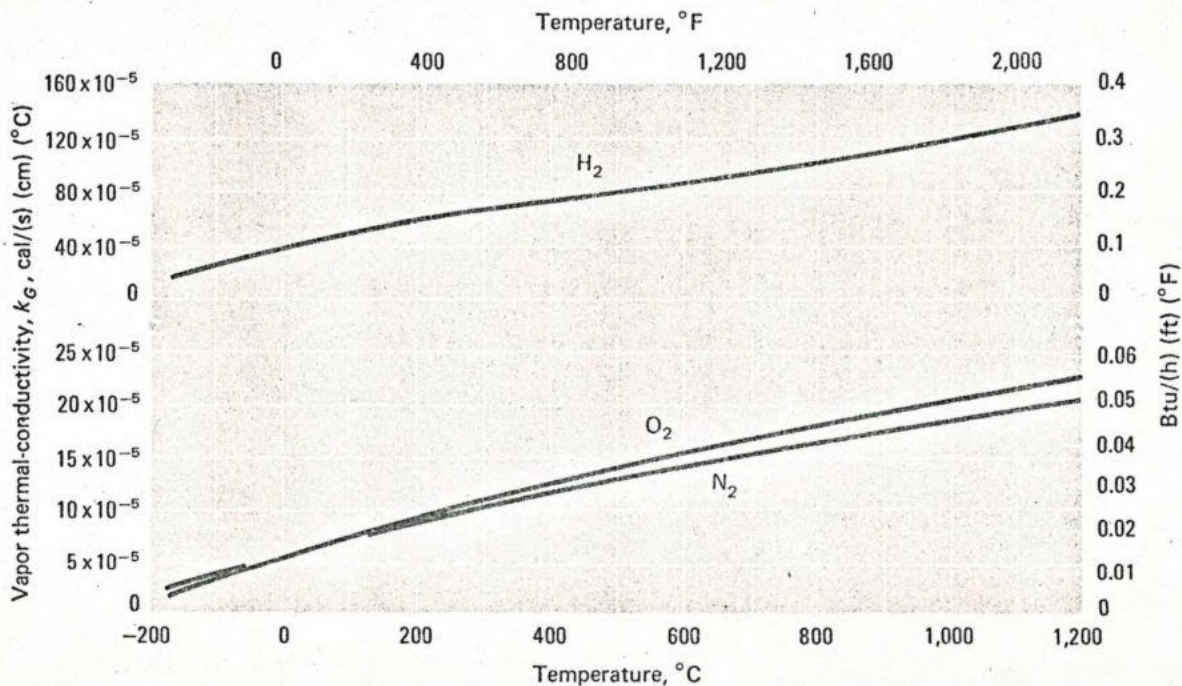
Fig. 8-8	Temperature Range		References
	m.p.—b.p.	b.p.—c.p.	
Hydrogen	☒	☒	47, 263, 273, 278, 280, 293, 305, 306, 307, 312, 317, 319, 353, 335
Nitrogen	☒	☒	43, 47, 270, 276, 278, 279, 290, 300, 306, 317, 319, 320, 332
Oxygen	☒	☒	47, 300, 303, 306, 317, 319, 320, 334*

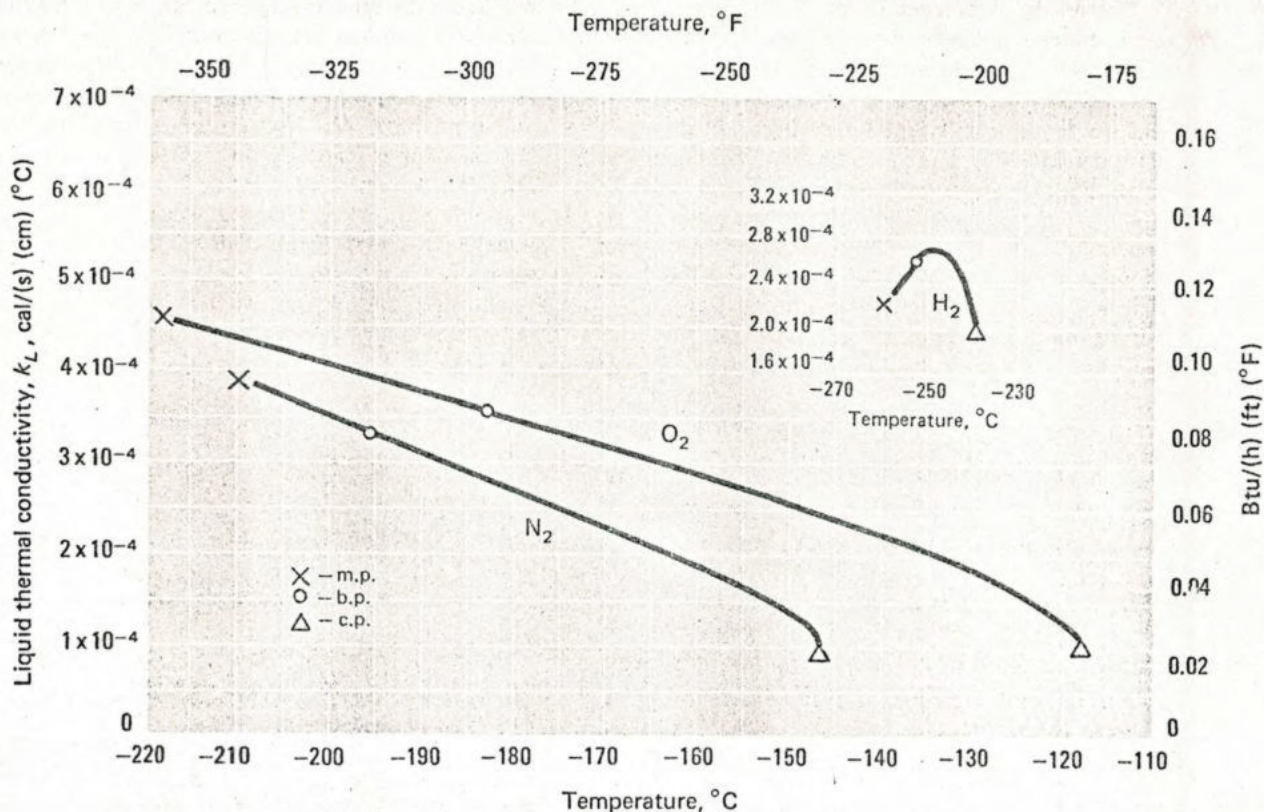
☒ Laboratory data ☒ Laboratory plus correlations ☐ All correlated data

Fig. 8-9	Temperature Range, °C			References
	0—500	500—1,000	1,000—1,500	
Hydrogen	☒	☒	☒	2, 18, 19, 44, 47, 272, 293, 304, 308, 307, 317, 318
Nitrogen	☒	☒	☒	2, 18, 19, 44, 47, 266, 267, 300, 306, 317, 318, 323, 328, 329, 330
Oxygen	☒	☒	☒	2, 18, 19, 44, 47, 300, 303, 306, 317, 327, 329, 330

☒ Laboratory data ☒ Laboratory plus correlations ☐ All correlated data

Vapor Thermal Conductivity — Fig. 8-9





Liquid Thermal Conductivity - Fig. 8-10

various literature sources. In most instances, deviations of reported results are less than 1% for hydrogen, nitrogen and oxygen.

Recent results of NBS investigators [303,331,332,333, 334,335] have been adapted for liquid heat-capacity. Results from several other sources generally agree with NBS data. Average deviations are less than 2%, 5% and 2.3%, respectively, for hydrogen, nitrogen and oxygen, for temperatures up to 80% of the critical one.

Density—Fig. 8-5

Laboratory density data over the full liquid state are extensive. They agree closely, with average deviations being less than 1%.

Surface Tension—Fig. 8-6

Surface-tension data were extended with the Othmer relation (Eq. 1-4, June 10 issue) to provide full liquid-phase coverage. Results from the Othmer plot and experimental data agreed closely; deviations from the least-squares fit were less than 1.5%.

Viscosity—Fig. 8-7, 8-8

Laboratory viscosity data for the gas phase have been critically reviewed [294,329]. The recommended smoothed values were selected because they agreed closely with extensive experimental data. Deviations were 3%, 2.5% and 6% or less, respectively, for hydrogen, nitrogen and oxygen. Recommended values also com-

Fig. 8-10	Temperature Range		References
	m.p.—b.p.	b.p.—c.p.	
Hydrogen	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	19, 47, 272, 287, 290, 293, 298, 304, 307, 317, 333, 335
Nitrogen	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	19, 47, 65, 288, 290, 299, 300, 303, 306, 316, 317, 328, 332
Oxygen	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	19, 47, 65, 288, 300, 317, 327, 334

Laboratory data Laboratory plus correlations All correlated data

pared quite favorably with Svehla estimates (Eq. 4-1, Sept. 30 issue, and Ref. 18, June 10) and with "Thermophysical Properties of Matter" (TPM) tabulated results (Ref. 19, June 10), which were both about 5% lower than the recommended values.

Liquid-viscosity data were extended by extrapolation (0.2-0.3, 0.5-3.3 and 0-0.5 $^{\circ}\text{C}$ for hydrogen, nitrogen and oxygen) to provide coverage of the full liquid phase. Since the extrapolation was small (i.e., a few tenths of a degree), each square in the key insert to the graph was fully darkened to reflect the extensive data coverage. Results from various sources agree with each other. Respective average deviations from the smoothed data fit are 2.6%, 3% and 4.5% for hydrogen, nitrogen and oxygen.

Thermal Conductivity—Fig. 8-9, 8-10

For gas-phase thermal conductivity, several NBS and TPM investigators [19,44,329] reviewed the experimental data and presented the recommended values adopted

here. The results from several sources are in agreement. The recommended values compare quite favorably with experimental data. Deviations in most cases are less than 5%.

Two sources of experimental data [298,304] are available for the liquid thermal conductivity of hydrogen. The data cover temperatures both above and below the boiling point. The complete liquid phase was covered by extrapolation (about 3°C) of the smoothed mean-data curve constructed from available data. Deviations from the mean were 10.7% or less for hydrogen data.

For nitrogen and oxygen, available experimental data

for liquid thermal conductivity from different sources cover most of the temperatures above and below the boiling point. Several NBS and TPM investigators [19,44,332,334] reviewed the data and recommended values adopted here. The recommended values describe the data quite favorably, with deviations in most instances of 5% or less. Testing of the corresponding-states correlation of Schaefer and Thodos (Eq. 3—2, Aug. 19 issue) with the recommended values indicated general agreement, with average deviations of 4.6% and 14.7% for nitrogen and oxygen. At the critical temperatures, a larger uncertainty is possible [19,44]. #

References

References 1 through 262 are listed in Parts 1 through 7 of this series.

263. Agrawal, G. M., and Thodos, G., *Physica*, **50**, p. 397 (1970).
 264. Barua, A. K., et al., *J. Chem. Phys.*, **41** (2), p. 374 (1964).
 265. Blagoy, Y. P., and Pashkov, V. V., *Soviet Physics JETP*, **22** (5), p. 999 (1966).
 266. Brain, T. J. S., *Int. J. Heat Mass Transfer*, **10**, p. 737 (1967).
 267. Briggs, D. G., et al., "Thermophysical Properties," 4th Symposium, p. 452, ASME (1968).
 268. Brower, G. T., and Thodos, G., *J. Chem. Eng. Data*, **13** (2), p. 262 (1968).
 269. Coremans, J. M. J., et al., *Physica*, **24**, p. 557 (1958).
 270. Dawe, R. A., and Smith, E. B., *J. Chem. Phys.*, **52** (2), p. 693 (1970).
 271. De Bock, A., et al., *Physica*, **34**, p. 49 (1967).
 272. Diller, D. E., and Roder, H. M., *Adv. Cryogenic Eng.*, **15**, p. 58 (1970).
 273. Diller, D. E., *J. Chem. Phys.*, **42** (6), p. 2089 (1965).
 274. DiPippo, R., and Kestin, J., "Thermophysical Properties," 4th Symposium, p. 304, ASME (1968).
 275. Edejer, M. P., and Thodos, G., *J. Chem. Eng. Data*, **12** (2), p. 206 (1967).
 276. Förster, S., *Cryogenics*, **3** (3), p. 176 (1963).
 277. Friedman, A. S., and White, D., *J. Am. Chem. Soc.*, **72**, p. 3931 (1950).
 278. Grocki, J. A., et al., *J. Chem. Phys.*, **51** (9), 3856 (1969).
 279. Greendonk, W., et al., *Physica*, **46**, p. 600 (1970).
 280. Grigorev, V. N., and Rudenko, N. S., *Soviet Physics JETP*, **20** (1), p. 63 (1965).
 281. Guevara, F. A., et al., *Phys. Fluids*, **12** (12), p. 2493 (1969).
 282. Herzberg, F., *Adv. Cryogenic Eng.*, **5**, p. 526 (1960).
 283. Jacobsen, R. T., et al., *Adv. Cryogenic Eng.*, **18**, p. 248 (1973).
 284. Johnston, H. L., et al., *J. Am. Chem. Soc.*, **72**, p. 3933 (1950).
 285. Johnston, H. L., et al., *J. Am. Chem. Soc.*, **76**, p. 1482 (1954).
 286. Johnston, H. L., and McCloskey, K. E., *J. Phy. Chem.*, **44**, p. 1038 (1940).
 287. Jones, I. W., *Int. J. Heat Mass Transfer*, **10**, p. 745 (1967).
 288. Kanitkar, D., and Thodos, G., "Thermophysical Properties," 4th Symposium, p. 286, ASME (1968).
 289. Kelley, K. K., and King, E. G., U.S. Bur. Mines, Bull. 592 (1961).
 290. Kerrisk, J. F., et al., *Adv. Cryogenic Eng.*, **9**, p. 188 (1964).
 291. Kestin, J., and Whitelaw, J. H., *Physica*, **29**, p. 335 (1963).
 292. Kestin, J., and Leidenfrost, W., *Physica*, **25**, p. 537 (1959).
 293. "Liquid Hydrogen," Pure and Applied Cryogenics, **5**, Pergamon Press, New York (1966).
 294. Maitland, G. C., and Smith, E. B., *J. Chem. Eng. Data*, **17**, (2), p. 150 (1972).
 295. Michels, A., et al., *Physica*, **24**, p. 659 (1958).
 296. Mullins, J. C., et al., *Adv. Cryogenic Eng.*, **8**, p. 126 (1963).
 297. Pew, K. J., et al., *Adv. Cryogenic Eng.*, **16**, p. 78 (1971).
 298. Powers, R. W., et al., *J. Am. Chem. Soc.*, **76**, p. 5972 (1954).
 299. Powers, R. W., et al., *J. Am. Chem. Soc.*, **76**, p. 5968 (1954).
 300. Rabinovich, V. A., and Vaserman, A. A., "Thermophysical Properties of Liquid Air and Its Components," No. 3, Israel Progr. Sci. Trans., Jerusalem (1970).
 301. Roder, H. M., et al., NBS Tech. Note 361 (revised), Oct. 1972.
 302. Roder, H. M. et al., NBS Monograph 94 (1965).
 303. Roder, H. M., and Weber, L. A., NASA SP-3071 (1972).
 304. Roder, H. M., and Diller, D. E., *J. Chem. Phys.*, **52** (11), 5928 (1970).
 305. Rudenko, H. S., and Konareva, V. G., *Russian J. Phy. Chem.*, **37** (12), p. 1493 (1963).
 306. Scott, R. B., "Cryogenic Engineering," Van Nostrand, New York, (1959).
 307. Scott, R. B., et al., "Technology and Uses of Liquid Hydrogen," Pergamon Press, New York (1964).
 308. Shupert, T. C., *Adv. Cryogenic Eng.*, **8**, p. 251 (1963).
 309. Silverberg, P. M., and Werzel, L. A., *J. Chem. Eng. Data*, **10** (4), p. 363 (1965).
 310. Sprow, F. B., and Prausnitz, J. M., *Trans. Faraday Soc.*, **62** (5), p. 1097 (1966).
 311. Smith, A. L., et al., *J. Am. Chem. Soc.*, **76**, p. 1486 (1954).
 312. Stiel, L. I., and Thodos, G., *Ind. Eng. Chem. Fundamentals*, **6** (3), p. 233 (1963).
 313. Stewart, R. B., *Adv. Cryogenic Eng.*, **17**, p. 8 (1972).
 314. Stewart, R. B., and Johnson, V. J., *Adv. Cryogenic Eng.*, **5**, p. 557 (1960).
 315. Street, W. B., and Staveley, L. A. K., *Adv. Cryogenic Eng.*, **13**, p. 363 (1968).
 316. Uhlir, A., Jr., *J. Chem. Phys.*, **20** (3), p. 463 (1952).
 317. Vance, R. W., and Duke, W. M., "Applied Cryogenic Engineering," Wiley, New York (1962).
 318. Van Dael, W., and Cauwenberger, H., *Physica*, **40**, p. 165 (1968).
 319. Van Itterbeek, A., and van Poemel, O., *Physica*, **8** (1), p. 133 (1941).
 320. Van Itterbeek, A., et al., *Physica*, **32**, p. 489 (1966).
 321. Van Itterbeek, A., and van Dael, W., *Adv. Cryogenic Eng.*, **9**, p. 207 (1964).
 322. Van Lammeren, J. A., *Physica*, **2**, p. 833 (1935).
 323. Walker, R. E., et al., *Phys. Fluids*, **3**, p. 482 (1960).
 324. Weber, L. A., *Adv. Cryogenic Eng.*, **15**, p. 50 (1970).
 325. Wiebe, R., and Brevoort, M. J., *J. Am. Chem. Soc.*, **52**, p. 622 (1930).
 326. Whitelaw, J. H., "Thermophysical Properties," 2nd Symposium, p. 521, ASME (1962).
 327. Ziebland, H., and Burton, J. T. A., *Brit. J. Appl. Phys.*, **6**, p. 416 (1955).
 328. Ziebland, H., and Burton, J. T. A., *Brit. J. Appl. Phys.*, **9**, p. 52 (1958).
 329. Hanley, H. J. M., and Ely, J. F., *J. Phys. Chem. Ref. Data*, **2** (4), p. 735 (1973).
 330. Hanley, H. J. M., and Childs, G. E., NBS Tech. Note 250 (Oct. 1966).
 331. Jacobsen, R. T., and Stewart, R. B., *J. Phys. Chem. Ref. Data*, **2** (4), p. 757 (1973).
 332. Jacobsen, R. T., et al., NBS Tech. Note 648 (Dec. 1973).
 333. McCarty, R. D., and Weber, L. A., NBS Tech. Note 617 (Apr. 1972).
 334. McCarty, R. D., and Weber, L. A., NBS Tech. Note 384 (July 1971).
 335. Roder, H. M., et al., NBS Tech. Note 641 (Oct. 1973).
 336. Roder, H. M., et al., NBS Tech. Note 625 (Oct. 1972).

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For other biographies:

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