

THE CRITICAL CONSTANTS OF INORGANIC SUBSTANCES

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I. Introduction

In 1953 Kobe and Lynn¹ reviewed the critical properties of elements and compounds. In 1968 Kudchadker, Alani, and Zwolinski² brought this review up to date for organic compounds, finding new or revised values for approximately 267 compounds. This present review was prepared to cover the literature from 1951 to December 1970 for elements and inorganic compounds. In the present work no deliberate attempt was made to search the literature before 1951, but when references were found to previously unreviewed work in this period they were added to the compilation. In the last few years much progress has occurred in both the expanded number of compounds for which critical data are available and in much more refined data for some of the important elementary gases. The Russians, notably Nisel'son and his coworkers, have measured critical properties for a large number of new metallic halides. The U. S. National Bureau of Standards has been engaged in the accurate definition of the critical state for a number of elementary gases. There have been a number of new "second

generation" experimental methods developed to investigate the region up to within 0.01° of the critical temperature. The two earlier reviews have thoroughly covered the theory and classical measurement of the critical region. It may be appropriate to discuss the "second generation" methods in this review.

Terms used in this paper follow.

<i>A</i>	constant in eq 14
<i>A'</i>	constant in eq 13
<i>A₁, A₂</i>	constants in eq 19
<i>B</i>	constant in eq 7, 17
<i>C_v</i>	heat capacity at constant volume
<i>E, F</i>	constants in eq 8
<i>H</i>	constant in eq 18
<i>L_v</i>	latent heat of vaporization
<i>M</i>	molecular weight
<i>P</i>	pressure in consistent units
<i>P_K</i>	vapor pressure in eq 8
<i>S</i>	constant in eq 18
<i>T</i>	temperature, degrees absolute
<i>V</i>	volume in consistent units
<i>X</i>	term defined in eq 4
<i>Z</i>	compressibility factor
<i>a</i>	constant in eq 3
<i>d</i>	density in consistent units
<i>g</i>	constant in eq 18
<i>n</i>	refractive index
<i>t</i>	temperature, °C
<i>α</i>	molar polarizability
<i>β</i>	constant in eq 7, 17
<i>β_p</i>	constant in eq 10
<i>ε</i>	dielectric constant
<i>θ</i>	relative temperature defined in eq 2

Subscripts

<i>T</i>	constant temperature
<i>c</i>	critical
<i>g</i>	gas
<i>l</i>	liquid
<i>r</i>	reduced
<i>v</i>	constant volume

II. Measurements in the Critical Region

As is well known, it is difficult to make precise measurements close to the critical point because of the large density gradient and high specific heats which exist there. There have been some second generation methods developed to circumvent or take advantage of the above-mentioned difficulties.

(1) K. A. Kobe and R. E. Lynn, *Chem. Rev.*, **52**, 117 (1953).

(2) A. P. Kudchadker, G. H. Alani, and B. J. Zwolinski, *ibid.*, **68**, 659 (1968).

A. REFRACTIVE INDEX MEASUREMENTS

Schmidt and coworkers^{3,4} among others have utilized measurements of refractive index in the gas and liquid phases to study the density gradients produced by gravity near the critical point. In this case the relationship between refractive index (n) and density (d) is given by

$$\frac{n^2 - 1}{n^2 + 1} \left(\frac{M}{d} \right) = \text{constant} \quad (1)$$

where M is molecular weight. A plot of reduced density (d_r) vs. height at various relative temperatures (θ)

$$\theta \equiv T - T_c \quad (2)$$

is prepared. The curve should exhibit a point of inflection at the midpoint of the chamber at the critical density and at the critical temperature. However, the exact shapes of these curves are a function of the mean density in the measurement chamber. An analysis is then made of the curves measured at various temperatures and mean densities in order to deduce the critical constants. One may compare Schmidt's⁴ values for the critical temperature of carbon dioxide (31.01°) and chlorodifluoromethane (28.715°) with the selected values of 31.0 (this paper) and 28.9 (Kudchadker, Alani, and Zwolinski²), respectively.

Alternatively, as in Edwards's⁵ work on determining the saturated liquid and vapor densities of ⁴He along the coexistence curve *via* refractive index measurements, one may treat such data differently. He has shown that his data correlate well using the equation

$$X^2/(1 - \ln X) = a(-\theta) \quad (3)$$

where

$$X \equiv (d_l - d_g)/(d_l - d_c) \quad (4)$$

As he points out, measurements can be made on a very thin slice (~1 mm) of fluid, thus minimizing density gradient complications.

Obviously the density data determined in this manner may also be analyzed in a manner similar to eq 7 described in section C (Dielectric Constant Measurements).

B. SPECIFIC HEAT AT CONSTANT VOLUME

Moldover and Little⁶ and Voronel and coworkers^{7,8} have demonstrated that the relationship between the specific heat at constant volume (C_v) and the temperature in the vicinity of the critical temperature is

$$C_v \propto \ln |\theta| \quad (5)$$

which describes a jump discontinuity in the specific heat vs. temperature curve at the critical temperature. Thus the critical temperature may be determined as the temperature of the discontinuity.

(3) E. H. W. Schmidt and K. Traube, *Progr. Int. Res. Thermodyn. Transp. Prop., Pap. Symp. Thermophys., 2nd, Princeton, N. J. 1962*, 193 (1962).

(4) M. S. Green and J. V. Sengers, "Critical Phenomena," National Bureau of Standards Miscellaneous Publication 273, U. S. Government Printing Office, Washington, D. C., 1966, pp 13-20.

(5) M. H. Edwards, ref 4, pp 82-85.

(6) M. R. Moldover and W. A. Little, ref 4, pp 79-82.

(7) M. I. Bagatskii, A. V. Voronel, and V. G. Gusak, *Sov. Phys. JETP*, **16**, 517 (1963).

(8) A. V. Voronel, V. G. Gorbunova, Yu. R. Chashkin, and V. V. Shechekochikhiva, *ibid.*, **23**, 597 (1966).

C. DIELECTRIC CONSTANT MEASUREMENTS

Another way to operate on very "thin" slices of fluid and thus minimize the effects of density gradients is to measure the dielectric constant between two closely spaced horizontal capacitor plates. The fluid density is given in terms of the dielectric constant by the Clausius-Mosotti equation

$$d = \frac{3M}{4\pi\alpha} \left(\frac{\epsilon - 1}{\epsilon + 2} \right) \quad (6)$$

where α is the molar polarizability and ϵ is the dielectric constant. The orthobaric densities may be correlated in a number of equivalent ways, depending on the precise form of the available data. Weber⁹ determined the densities of each phase at the same temperature and used the relationship

$$\left(\frac{d_l - d_g}{d_c} \right) = B \left[\frac{\theta}{T_c} \right]^\beta \quad (7)$$

III. Critical Constants and Vapor Pressures

Mention may be made here of a contribution by Edwards¹⁰ to the critical evaluation of some literature data on critical constants. He analyzed various sets of critical constants and vapor pressure determinations by using the Kirchoff equation

$$\log P_K = -E/T + F \quad (8)$$

and observing the shape and consistency of the deviation curve of

$$\text{devn} = P_K - P_{\text{obsd}} \quad (9)$$

as a function of temperature. This enables the use of accurate vapor pressure in the near-but-subcritical temperature range to help select the "best" values for critical temperature of the data available. For instance, in the case of ammonia, the critical temperature determination of Kopper¹¹ and the vapor pressure measurements of Beattie and Lawrence¹² proved to be the most consistent sets of data. This analysis helps in a rational choice of the most probable value for the critical temperature in this case in particular because Kobe and Lynn¹ found that the only other recourse was to average all the critical data on ammonia published since 1900.

IV. Evaluation and Selection Procedures

The criteria used in evaluating the published critical constant data were the same as those described by Kudchadker.² In each case the work was scrutinized in order to determine the probable purity of the sample and the probable accuracy of the measurements. Only in a very few cases was it necessary to depend on *Chemical Abstracts* for the information. In the cases of those compounds where several values were available, reasons are given in the text for the selections made. In the cases where only one set of properties has been published, an attempt has been made to deduce the accuracy. In the cases where no new data can be added to the reviews of Kobe and Lynn¹ or Kudchadker,² their selected values are retained. In

(9) L. A. Weber, *Advan. Cryog. Eng.*, **15**, 50 (1970).

(10) D. G. Edwards, "The Vapor Pressures of 30 Inorganic Liquids Between One Atmosphere and the Critical Point," University of California, Lawrence Radiation Laboratory, Livermore, Calif., June 17, 1964.

(11) H. Kopper, *Z. Phys. Chem., Abt. A*, **175**, 469 (1936).

(12) J. A. Beattie and C. K. Lawrence, *J. Amer. Chem. Soc.*, **52**, 6 (1930).

general in the case of the critical pressure no value has been recommended for a compound where the vapor pressure data need to be extrapolated for more than a few °K because of the uncertainty involved in such procedure. For the critical constants of the noble gases and the more important industrial gases, an attempt was made to secure the agreement of a number of researchers with an interest in this field. The author is grateful to the following people for their considered opinion:

- Dr. S. Angus, Director of Thermodynamic Tables Project Centre, Imperial College, London
 Dr. R. D. Goodwin, U. S. National Bureau of Standards, Boulder, Colo.
 Dr. A. Kreglewski, Texas A & M University
 Dr. H. Meyer, Duke University
 Dr. J. M. H. L. Sengers, U. S. National Bureau of Standards, Washington, D. C.
 Dr. L. A. Weber, U. S. National Bureau of Standards, Boulder, Colo.

V. Critical Review of Critical Properties

The key to the numbers recorded under the column labeled "Method" listed below is the same as that used by Kobe and Lynn¹ and Kudchadker² except that the last three methods have been added for the sake of convenience and refer to the discussion in section II.

Key	Method
1	Disappearance of the meniscus (usually the average value of the temperatures of disappearance and reappearance of the meniscus)
2	Disappearance of the meniscus upon a very slight volume increase (pressure decrease)
3	Disappearance of critical opalescence
4	Disappearance of droplets after the meniscus has broadened
5	Pressure-volume-temperature relations: $(\partial P/\partial V)_T = 0$
6	Disturbance of a balanced tube
7	Method of Ipatieff and Monroe (rotating bomb)
8	Method of Cailletet and Colaradeau
9	Plot of enthalpy vs. temperature
10	Break in the specific gravity curve
11	Change in dielectric constant
12	Equal viscosities of vapor and liquid
13	Calculation from some physical property
14	Survey
15	Method of Altschul
16	Extrapolation of vapor pressure curve
17	Calculation from vapor pressure equation
18	Plot of enthalpy vs. pressure
19	Law of rectilinear diameters
20	Refractive index measurements
21	Jump in specific heat at constant volume
22	Orthobaric densities from dielectric constant measurements

It will be noted that the metals Rb and Cs have been included in the section on elementary gases. This seems appropriate even though metals have strong cohesive forces (Rb and Cs are known to form weak dimers in the vapor state) and may be expected to have lower values of Z_c than the other elementary gases.

Similarly the halide section includes compounds associated by hydrogen bonding (hydrogen fluoride), compounds which exist as polymers (e.g., aluminum bromide), possibly unstable compounds (e.g., chlorine pentafluoride), as well as the non-polar covalent compounds (e.g., silicon tetrachloride). This variety of behavior is evidenced by unusual values of Z_c (see Table XVI). Aluminum chloride and bromide are known to exist as dimers and niobium pentafluoride is known to be a tetramer in the solid state. These facts offer possible explana-

tions for the very low values of Z_c for these compounds. Chlorine pentafluoride perhaps undergoes a dissociation ($\text{ClF}_5 \rightleftharpoons \text{ClF}_3 + \text{F}_2$) which could explain the high value of Z_c in this case.

A. NOBLE GASES (TABLE I)

1. Helium-4

Kobe and Lynn¹ reviewed the literature data to 1925. In 1958 the thermodynamic temperature scale was defined to 5.1 °K on the basis of the vapor pressure of ⁴He. In that case the value of critical pressure was taken to be 2.26 atm as given by Onnes,^{13,14} and the corresponding critical temperature was defined as 5.1994 °K.¹⁵

Edwards⁵ measured the orthobaric densities by refractive index measurements. Seventy-six experimental points were taken between 0.95 and 0.993 T_c . Density was measured on a horizontal slice of fluid only 1 mm deep which minimized hydrostatic head effects. Resolution of density was said to be of the order of 0.01 %.

The work of Moldover and Little⁶ has been described in section II.B. Temperatures were measured with a 0.1-W Ohmite carbon resistor calibrated against the vapor pressure of ⁴He using the T_{58} scale. Four separate runs gave $T_c = 5.189 \pm 0.001$ °K.

Roach and Douglass¹⁶ measured the dielectric constant (ϵ) of ⁴He between two closely spaced horizontal capacitor plates. The density of the helium was obtained by use of the Clausius-Mosotti relation. Pressures were measured with respect to a constant-pressure reference source which was regularly monitored by a mercury manometer 2 m high. Data were fitted to the equation

$$|d - d_c| \propto (P_c - P)^{2p} \quad (10)$$

by a method of least squares. The critical temperature was determined from the critical pressure according to the T_{58} temperature scale. They also analyzed Edwards⁵ data using the same techniques and derived the values given in the second entry for Roach and Douglass.¹⁶

The helium⁴ used by El Hadi and Durieux¹⁷ was held in contact with activated charcoal cooled to liquid nitrogen temperature at a pressure of about 90 cm. The sample was further purified by passing it through a copper capillary immersed in liquid helium. Liquid and vapor densities were directly measured in pycnometers. Temperatures were measured with a germanium thermometer calibrated against the vapor pressure of ⁴He between 1.2 and 5.2 °K. Vapor pressures were measured with a mercury manometer. They also reanalyzed the data of Edwards (second entry) using a value for the molar polarizability of 0.12427 cm³/mol instead of the value of 0.12454 used by Edwards.

The work reported for Vicentini-Missoni, Sengers, and Green¹⁸ is a scaled analysis of the PVT data of Roach and Douglass. The work reported for Sengers¹⁹ is a reanalysis of the orthobaric densities of Roach and Douglass.¹⁶

(13) H. K. Onnes, *Proc. Acad. Sci. Amsterdam*, **13**, 1093 (1911).

(14) H. K. Onnes, *ibid.*, **14**, 678 (1912).

(15) F. G. Brickwedde, *et al.*, *J. Res. Nat. Bur. Stand., Sect. A*, **64**, 1 (1960).

(16) P. R. Roach and D. H. Douglass, *Phys. Rev. Lett.*, **17**, 1083 (1966).

(17) Z. E. H. A. El Hadi and M. Durieux, *Physica*, **41**, 289 (1969).

(18) M. Vicentini-Missoni, J. M. H. L. Sengers, and M. S. Green, *J. Res. Nat. Bur. Stand., Sect. A*, **73**, 563 (1969).

(19) J. M. H. L. Sengers, private communication.

Table I
Noble Gases

Year	t_0 , °C	P_0 , atm	d_0 , g/cm ³	Investigators	Method ^a	Ref
1. Helium-4						
1911	-267.6		0.065	Onnes	13	13
1911	-267.85	2.26	0.066	Onnes	3	14
1915	-267.90	2.26		Onnes and Weber		<i>b</i>
1925			0.06930	Mathias, <i>et al.</i>	19	<i>c</i>
1958	-267.9506	2.26		Thermodynamic temp scale	See text	15
1965	-267.9576			Edwards	20	5
1965	-267.961			Moldover and Little	21	6
1966	-267.9610	2.2434	0.0701	Roach and Douglass	22	16
1966	-267.9623			Roach and Douglass	See text	16
1969			0.06976	El Hadi and Durieux	19	17
1969			0.06963	El Hadi and Durieux	See text	17
1969	-267.9611		0.0693	Vicentini-Missoni, Sengers, and Green	See text	18
1970	-267.9613		0.06895	Sengers	See text	19
1953	-267.9	2.26	0.0693	Kobe and Lynn		
Selected value	-267.9611	2.24	0.0698			
2. Helium-3						
1949	-269.82	1.15		Sydoriak and Sherman	5	<i>d</i>
1950	-269.84	1.13		Abraham, Osborne, and Weinstock	1	<i>e</i>
1950	-269.81	1.17		Abraham, Osborne, and Weinstock	5	<i>e</i>
1964	-269.826	1.149		Sydoriak and Sherman	5	20
1965			0.0418	Sherman	19	21
1965	-269.828			Edwards	See text	23
1967	-269.8412		0.04134	Zimmerman and Chase	22	24
1968	-269.841	1.134	0.0413	Bendiner, Elwell, and Meyer	22	25
1970	-269.8406		0.0414	Sengers	See text	19
1970	-269.8402		0.0414	Meyer	See text	26
1953	-269.82	1.15		Kobe and Lynn		1
Selected value	-269.841	1.13	0.0414			
3. Neon						
1917	-228.36	26.86		Onnes, Crommelin, and Cath	5	<i>f</i>
1923	-228.72			Crommelin	5	28
1923			0.4835	Mathias, Onnes, and Crommelin	19	<i>g</i>
1962	-228.75	27.19		Grilly	8	27
1953	-228.7	26.9	0.484	Kobe and Lynn		1
Selected value	-228.75	27.2	0.484			
4. Argon						
1910	-122.44	47.996	0.509	Crommelin	5	29
1912			0.53078	Mathias, Onnes, and Crommelin	19	29
1958	-122.29	48.34	0.5358	Michels, Levelt, and De Graaf	8, 17, 19	30
1963	-122.6			Bagatskii, Voronel, and Gusak	21	7
1965	-122.70			Voronel, Snigirev, and Chashkin	21	31
1967	-122.50	47.92		McCain and Ziegler	1	32
1968	-122.446	48.18		Pings and Teague	See text, 16	33
1970	-122.39	48.13	0.5359	Sengers	See text	19
1953	-122	48.0	0.531	Kobe and Lynn		1
Selected value	-122.4	48.1	0.533			
5. Krypton						
1937	-63.77	54.270		Meihuizen and Crommelin	5	36
1937			0.9085	Mathias, Crommelin, and Meihuizen	19	37
1937			0.9191	Mathias, Crommelin, and Meihuizen	19	37
1970	-63.69	54.48	0.918	Theeuwes and Bearman	16, 19	38
1953	-63.8	54.3	0.908	Kobe and Lynn		1
Selected value	-63.8	54.3	0.919			
6. Xenon						
1912	16.6	58.2	1.155	Patterson, Cripps and Gray	1, 15, 19	<i>h</i>
1951	16.65	57.89	1.09	Beattie, Barriault, and Brierly	5	<i>i</i>
1952	16.590		1.105	Weinberger and Schneider	1	40
1954	16.590	57.636	1.099	Habgood and Schneider	5, 19	41
1969	16.58		1.110	Vicentini-Missoni, Sengers, and Green	See text	18
1970	16.590		1.107	Sengers	See text	19
1953	16.59	58.0	1.105	Kobe and Lynn		1
Selected value	16.590	57.64	1.11			

Table I (Continued)

Year	t_c , °C	P_c , atm	d_c , g/cm ³	Investigators	Methods	Ref
7. Radon						
1909	104.5	62.4		Gray and Ramsay	1	42

^a The key to the methods in all the tables is in the text, p 73. ^b H. K. Onnes and S. Weber, *Proc. Acad. Sci. Amsterdam*, **18**, 493 (1916). ^c E. Mathias, C. A. Crommelin, H. K. Onnes, and J. C. Swallow, *ibid.*, **28**, 526 (1925). ^d S. G. Sydoriak, E. R. Grilly, and E. F. Hummel, *Phys. Rev.*, **75**, 303 (1949). ^e B. M. Abraham, D. W. Osborne, and B. Weinstock, *ibid.*, **80**, 366 (1950). ^f H. K. Onnes, C. A. Crommelin, and P. G. Cath, *Proc. Acad. Sci. Amsterdam*, **19**, 1058 (1917). ^g E. Mathias, C. A. Crommelin, and H. K. Onnes, *Commun. Kamerlingh Onnes Lab. Univ. Leiden*, **162b**, 11 (1923). ^h H. S. Patterson, R. S. Cripps, and R. W. Gray, *Proc. Roy. Soc., Ser. A*, **86**, 579 (1912). ⁱ J. A. Beattie, R. J. Barriault, and J. S. Brierly, *J. Chem. Phys.*, **19**, 1219 (1951).

There is good agreement among all of the most recent values (1965+) of critical temperature except that reported by Edwards. The selected value is an average one. The only modern measurement of critical pressure is that of Roach and Douglass and this value is selected. The direct measurement of the critical density by El Hadi and Durieux is to be preferred—it is rounded off to one less decimal place than was reported.

2. Helium-3

Kobe and Lynn¹ reviewed the work on this substance to 1953.

Sydoriak and Sherman²⁰ used a sample of ³He containing 0.041 mol % ⁴He (mass spectrometer reading) and corrected their PVT data for this impurity. Pressures were observed on oil and mercury manometers having inside diameters of 20 and 14.5 mm, respectively. Corresponding temperatures were measured by a ⁴He thermometer on the T_{68} scale.

Sherman^{21,22} measured 23 isochores of ³He with densities ranging from 0.015 to 0.066 g/cm³. Pressures were measured with a fused-quartz Bourdon-tube gauge having an accuracy of 0.05 mm. Temperatures were reduced to the T_{68} scale. The isochores were extrapolated to the vapor pressure curve measured by Sherman, Sydoriak, and Roberts²² to obtain the orthobaric densities.

Edwards²³ reanalyzed Sherman's orthobaric density data using an equation of the form

$$X^2/(1 - \ln X) = a(T_c - T) \quad (11)$$

where

$$X = (d_l - d_g)/(d_l + d_g) \quad (12)$$

Zimmerman and Chase²⁴ measured dielectric constants of ³He and analyzed the data as described in section II.C. Pressures were measured on a Texas-Instruments fused-quartz pressure gauge having a resolution of 3 μ . This gauge was calibrated by the manufacturer to a stated accuracy of 0.015% against a dead-weight tester. Temperature was determined using a ⁴He vapor pressure bulb on the T_{68} scale. A mass spectrometer analysis on the sample showed 0.035% ⁴He.

Bendiner, Elwell, and Meyer²⁵ fitted their liquid and vapor densities (derived from dielectric constant measurements) to the equations

$$d_c - d_g = A'(T_c - T) \quad (13)$$

$$d_l - d_c = A(T_c - T) \quad (14)$$

Sengers¹⁹ reanalyzed the data of Zimmerman and Chase.²⁴ The values quoted for Meyer²⁵ are for ³He with a 10-ppm impurity level.

The present consensus of opinion prefers the latter group of data (1967+, which has good internal agreement) and the selected values are average values from this group.

3. Neon

Kobe and Lynn¹ reviewed the data to 1923.

Grilly²⁷ obtained neon from Linde Air Products Co. The gas had a mass spectrometric analysis of 0.03% helium, 0.10% hydrogen, 0.08% nitrogen, and 0.002% oxygen. The helium and hydrogen were considered to be eliminated by pumping on the neon at $T < 20^\circ\text{K}$. Checks at various temperatures showed the pressure to be constant during isothermal condensation. Vapor pressures > 5 atm were measured with a Heise Bourdon gauge calibrated against a Consolidated piston gauge which in turn was calibrated against the vapor pressure of CO₂ at 0°C. The estimated maximum possible error in the Bourdon gauge measurement was ± 10 mm. Temperatures were measured with a Leeds and Northrup platinum resistance thermometer calibrated by the NBS. The resistance of the thermometer was measured with a Leeds and Northrup G-2 Mueller bridge which had been calibrated by the NBS. Pressure was measured as a function of temperature and amount of neon in the system for steps of 0.05° and 3%, respectively, near the critical region.

Agreement between Crommelin²⁸ and Grilly²⁷ on the critical temperature is good, and an average value of -228.74° is within the experimental error claimed by Grilly ($\pm 0.02^\circ$). This value is selected as the critical temperature. The selected critical pressure is that of Grilly, rounded off to one less significant figure.

4. Argon

Kobe and Lynn¹ reviewed the literature data to 1912.

Michels, Levelt, and De Graaff³⁰ used argon supplied by N. V. Philips Gloeilampenfabriek and shown by mass spec-

(20) S. G. Sydoriak and R. H. Sherman, *J. Res. Nat. Bur. Stand., Sect. A*, **68**, 547 (1964).

(21) R. H. Sherman, *Phys. Rev. Lett.*, **15**, 141 (1965).

(22) R. H. Sherman, S. G. Sydoriak, and T. R. Roberts, *J. Res. Nat. Bur. Stand., Sect. A*, **68**, 579 (1964).

(23) M. H. Edwards, *Phys. Rev. Lett.*, **15**, 348 (1965).

(24) G. O. Zimmerman and C. E. Chase, *ibid.*, **19**, 151 (1967).

(25) W. Bendiner, D. Elwell, and H. Meyer, *Phys. Lett. A*, **26**, 421 (1968).

(26) H. Meyer, private communication; B. Wallace and H. Meyer, *Phys. Rev. A*, **2**, 1593 (1970).

(27) E. R. Grilly, *Cryogenics*, **2**, 226 (1962).

(28) C. A. Crommelin, *Commun. Kamerlingh Onnes Lab. Univ. Leiden*, **162c**, 21 (1923).

(29) S. F. Pickering, *Nat. Bur. Stand. (U. S.), Sci. Pap.*, No. 541 (1926).

(30) A. Michels, J. M. Levelt, and W. De Graaff, *Physica*, **24**, 659 (1958).

trographical analysis to contain an impurity of a few hundredths of a per cent CH_4 . Temperatures were measured with a platinum resistance thermometer which had been calibrated at the triple point of water, the freezing point of mercury, the triple point of carbon dioxide, and the boiling point of oxygen. The values of P , PV , and d were corrected for gravitational effects.

The experimental method of Voronel and coworkers^{7, 31} was described in section II.B.

McCain and Ziegler³² used argon certified to be 99.999% pure, except for water. They passed this gas through a bed of Linde 5A molecular sieve. The accuracy of the temperature measurements was stated to be at least as good as $\pm 0.02^\circ\text{K}$. Pressures were measured with a Martin Decker precision test gauge which had been calibrated against a dead weight gauge.

Pings and Teague³³ used argon supplied by Linde Corp. and stated to have less than 20 ppm impurities. They measured the refractive index of the liquid and vapor phases as a function of temperature and inferred the critical temperature from the equality of the liquid and vapor refractive indices.

Edwards¹⁰ found the data of Michels, Levelt, and De Graaff to be more self-consistent than that of Crommelin.²⁹

The work of Sengers¹⁹ is a reanalysis of her own data in Michels, Levelt, and De Graaff. She suggests critical values of $-122.3 \pm 0.1^\circ$, 48.1 ± 0.02 atm, and 0.533 ± 0.003 g/cc. These values will encompass the majority of the data reported from 1910 onwards and seem to be the best estimates at this time. Kreglewski³⁴ and Angus³⁵ are in general agreement with this assessment although Angus' estimates of uncertainty are somewhat lower than those of Sengers.

5. Krypton

Kobe and Lynn¹ reviewed the literature data to 1937.

Theeuwes and Bearman³⁸ used Matheson research grade krypton with impurities stated to be 9 ppm N_2 , 2 ppm O_2 , and 15 ppm Xe. Temperatures were measured by a Rosemount Pt resistance thermometer calibrated by the NBS and a Dauphinee principle Guildine bridge and were estimated accurate to $\pm 0.01^\circ$. Pressures were measured with a Ruska Model 2450.1 deadweight gauge and with an estimated accuracy of $\pm 0.01\%$. The critical temperature and critical density were obtained graphically from a rectilinear diameter plot according to the method described by Rowlinson.³⁹ These authors did not wish to estimate an absolute accuracy for the critical temperature and critical density because of the errors inherent in the extrapolation of the rectilinear diameter plot.

Edwards¹⁰ found that the vapor pressure data and critical temperature of Meihuizen and Crommelin³⁶ form a consistent deviation curve and calculated a critical pressure of 54.31 atm.

The values of critical temperature and critical pressure of Meihuizen and Crommelin are retained as the selected values. The critical density reported by Kobe and Lynn¹ was from the

extrapolation of a straight-line diameter. However, Mathias, Crommelin, and Meihuizen³⁷ found that the diameter appeared to curve and that a cubic in temperature gave a better fit to the data. The extrapolation of this cubic equation gave a critical density of 0.9191 g/cm³ which is in very good agreement with the value of Theeuwes and Bearman.³⁸ Hence this value (rounded off to one less significant figure) is selected for the critical density.

6. Xenon

Kobe and Lynn¹ reviewed the literature data to 1952.

Habgood and Schneider⁴¹ used the same sample of xenon (<100 ppm Kr) as Weinberger and Schneider.⁴⁰ Temperatures were measured with a sensitivity of 0.0005° and an estimated absolute accuracy of $\pm 0.002^\circ\text{C}$ with a resistance thermometer and Mueller bridge. Pressures were measured with a sensitivity of ± 0.0003 atm and an estimated absolute accuracy of ± 0.005 atm with a piston gauge.

The work of Vicentini-Missoni, Sengers, and Green¹⁸ is a scaled analysis of Habgood and Schneider's PVT data. The work of Sengers¹⁹ is a reanalysis of Weinberger and Schneider's orthobaric densities.

The work of Weinberger and Schneider and Habgood and Schneider may be taken as definitive from the viewpoints of high precision and high sample purity (Beattie's sample of xenon contained 0.105 mol % Kr). The value of critical density of Habgood and Schneider, determined by use of the rectilinear diameter, is to be preferred.

Sengers¹⁹ suggests that the critical temperature reported by Weinberger and Schneider is good to $\pm 0.002^\circ$ and also suggests a value of 1.11 ± 0.01 g/cm³ for the critical density. She also suggests that the critical pressure reported by Habgood and Schneider is good to a few thousandths of an atmosphere. Her suggestions are adopted here.

7. Radon

Gray and Ramsay⁴² obtained radon from a solution of radium bromide containing metallic radium and stored it over fused potassium hydroxide. The radon was mixed with hydrogen and the mixture dried over quicklime. The radon was then condensed at liquid air temperatures and the hydrogen pumped off. The radon was then compressed in a modified Andrews' apparatus. The purity of the sample is not known, but it was stated that it contained hydrogen and helium. An estimate of the accuracy of this datum is impossible and it is merely recorded here as stated.

B. ELEMENTARY GASES (TABLE II)

1. Hydrogen (Normal)

There are no new data since Kobe and Lynn.¹

2. Hydrogen (Equilibrium)

The work of Hoge and Lassiter⁴³ was reviewed by Kobe and Lynn.¹

(31) A. V. Voronel, V. G. Snigirev, and Yu. R. Chashkin, *Sov. Phys. JETP*, **21**, 653 (1965).

(32) W. D. McCain and W. T. Ziegler, *J. Chem. Eng. Data*, **12**, 199 (1967).

(33) C. J. Pings and R. K. Teague, *Phys. Lett. A*, **26**, 496 (1968).

(34) A. Kreglewski, private communication.

(35) S. Angus, private communication.

(36) J. J. Meihuizen and C. A. Crommelin, *Physica*, **4**, 1 (1937).

(37) E. Mathias, C. A. Crommelin, and J. J. Meihuizen, *ibid.*, **4**, 200 (1937).

(38) F. Theeuwes and R. J. Bearman, *J. Chem. Thermodyn.*, **179** (1970).

(39) J. S. Rowlinson, "Liquids and Liquid Mixtures," Academic Press, New York, N. Y., 1959.

(40) M. A. Weinberger and W. G. Schneider, *Can. J. Chem.*, **30**, 422 (1952).

(41) H. W. Habgood and W. G. Schneider, *ibid.*, **32**, 98 (1954).

(42) R. W. Gray and W. Ramsay, *Trans. Chem. Soc. (London)*, **95**, 1073 (1909).

(43) H. J. Hoge and J. W. Lassiter, *J. Res. Nat. Bur. Stand.*, **47**, 75 (1951).

In the apparatus used by Roder and coworkers,⁴⁴ temperatures were measured by a platinum resistance thermometer calibrated by the NBS Temperature Physics section. This calibration was checked at the ice point and against the vapor pressure curve of high-purity nitrogen. Pressures were measured with a commercial, dual-range, precision deadweight gauge.

Goodwin⁴⁵ has reanalyzed the data of Hoge and Lassiter⁴³ and Roder.⁴⁴

Weber⁴⁶ has analyzed the index of refraction data of Diller.⁴⁷ Diller used ultrahigh purity hydrogen with a mass spectral analysis showing <1 ppm O₂, <5 ppm N₂, and <0.2 ppm total hydrocarbons. The presence of water as an impurity was characterized by a dew-point of -68°C. Temperatures were measured by a platinum resistance thermometer.

For the critical constants, the values of Hoge and Lassiter⁴³ and Roder⁴⁴ agree with each other within the estimated uncertainty of the former. For the critical pressure and critical density, Roder's values rounded off to one less significant figure are selected. For the critical temperature an average of the values of Roder⁴⁴ and Goodwin⁴⁵ is selected, again rounded off to one less significant figure.

3-5. Hydrogen Deuteride, Deuterium (Normal), and Deuterium (Equilibrium)

For these three substances there are no new data since Kobe and Lynn.¹

6 and 7. Rubidium and Cesium

Dillon, Nelson, and Swanson⁴⁹ measured orthobaric densities of cesium and rubidium by measuring γ radiation emanating from the vapor and liquid regions of the metals encapsulated in a molybdenum-tungsten alloy capsule. The metals had been irradiated in a thermal neutron flux. Critical temperatures were derived by use of the equation of Kordes⁵⁰

$$d_g d_l / [1/2(d_g + d_l)]^2 = t/t_c \quad (15)$$

where t = temperature in °C. A plot of the density data in this form on logarithmic coordinates extrapolates to the critical temperatures at

$$d_g d_l / [1/2(d_g + d_l)]^2 = 1.0 \quad (16)$$

Data were taken to 1650 and 1720° for cesium and rubidium, respectively.

The critical constants of Hochman and Bonilla⁵¹ were based on electrical conductivity measurements to 1650 and 1590° for cesium and rubidium, respectively.

Average values of the critical constants reported are selected since there is no way to select a "best" set.

(44) H. M. Roder, D. E. Diller, L. A. Weber, and R. D. Goodwin, *Cryogenics*, **3**, 16 (1963).

(45) R. D. Goodwin, *J. Res. Nat. Bur. Stand., Sect. A*, **74**, 221 (1969).

(46) L. A. Weber, private communication.

(47) D. E. Diller, *J. Chem. Phys.*, **49**, 3096 (1968).

(48) A. S. Friedman, D. White, and H. L. Johnston, *J. Amer. Chem. Soc.*, **73**, 1310 (1951).

(49) I. G. Dillon, P. A. Nelson, and B. S. Swanson, *J. Chem. Phys.*, **44**, 4229 (1966).

(50) E. Kordes, *Z. Electrochem.*, **57**, 73 (1953).

(51) J. M. Hochman and C. F. Bonilla, *Nucl. Sci. Eng.*, **22**, 434 (1965).

(52) E. Mathias, H. K. Onnes, and C. A. Crommelin, *Proc. Acad. Sci. Amsterdam*, **17**, 950 (1915).

8. Nitrogen

Kobe and Lynn¹ reviewed the data on this compound to 1951.

Voronel and coworkers⁹ determined that their sample of nitrogen contained 0.06-0.13% impurities, presumably argon.

Weber's⁵³ value is from a private communication and is as yet unpublished work.

There seems to be no reason to change the selected values of Kobe and Lynn¹ for critical temperature and critical pressure. The selected critical density has been arbitrarily chosen as the average of the values of Mathias, Onnes, and Crommelin,⁵² and Weber.⁵³

9. Phosphorus

The critical temperature reported by Marckwald and Helmholtz⁵⁴ is the only datum available.

10. Oxygen

Kobe and Lynn¹ reviewed the literature data to 1950. Kudchadker, Alani, and Zwolinski² reviewed the literature data to 1963.

Voronel and coworkers⁵⁶ obtained oxygen by the decomposition of chemically pure KMnO₄ with strict adherence to the methods of Hoge⁵⁵ so that a minimum purity of 99.99% could be expected. Measurements of specific heat were made at 0.04° intervals in the region of the critical temperature and the temperature of the jump discontinuity in specific heat was taken as the critical temperature.

Weber⁵⁷ used commercially available ultrapure oxygen with a nominal purity of 99.99% and passed it through a molecular sieve trap to remove water. Orthobaric densities were determined at 12 temperatures between 153.500 and 154.544°K by measurement of the dielectric constants of the liquid and vapor regions. The data were analyzed by means of the relationship

$$(d_l - d_g)/d_c = B[(T_c - T)/T_c]^\beta \quad (17)$$

and the values of d_c and T_c determined by iteration. $B = 3.5997 \pm 0.0196$ and $\beta = 0.351 \pm 0.001$. The thermometer and measuring system were said to have a total uncertainty of 0.01° and the densities to have an uncertainty of 0.1%. The critical pressure was determined from the vapor pressure data of Hoge⁵⁵ as correlated by Stewart⁵⁸ in a seventh power polynomial in temperature.

The critical temperatures of Weber and Voronel and coworkers are in very good agreement, and the average of the two values was selected as the most probable value. The critical pressure derived from Hoge by Weber is selected as is Weber's value for the critical density.

11. Ozone

Jenkins and Birdsall⁵⁹ prepared ozone from oxygen in an all-glass ozonizer. The oxygen was first passed through a heated

(53) L. A. Weber, *J. Chem. Thermodyn.*, in press (private communication).

(54) W. Marckwald and K. Helmholtz, *Z. Anorg. Chem.*, **124**, 81 (1922).

(55) H. J. Hoge, *J. Res. Nat. Bur. Stand.*, **44**, 321 (1950).

(56) A. V. Voronel, Yu. R. Chashkin, V. A. Popov, and V. G. Simkin, *Sov. Phys.-JETP*, **18**, 143 (1964).

(57) L. A. Weber, *Advan. Cryog. Eng.*, **15**, 50 (1969).

(58) R. B. Stewart, Ph.D. Thesis, University of Iowa, 1966.

(59) A. C. Jenkins and C. M. Birdsall, *J. Chem. Phys.*, **20**, 1158 (1952).

Table II
Elementary Gases

Year	$t_0, ^\circ\text{C}$	P_0, atm	$d_0, \text{g/cm}^3$	Investigators	Method	Ref
1. Hydrogen (Normal)						
1953	-239.9	12.80	0.0310	Kobe and Lynn		1
2. Hydrogen (Equilibrium)						
1951	-240.166	12.770	0.0314	Hoge and Lassiter	5	43
1963	-240.174	12.759	0.03142	Roder, Diller, Weber, and Goodwin	8, 19	44
1970	-240.197			Goodwin	See text	45
1970	-240.216			Weber	See text	46
Selected value	-240.17	12.76	0.0314			
3. Hydrogen Deuteride						
1951	-237.25	14.645	0.0482	Hoge and Lassiter	5	43
4. Deuterium (Equilibrium)						
1951	-234.90	16.282	0.0669	Hoge and Lassiter	5	43
5. Deuterium (Normal)						
1951	-234.8	16.432		Friedman, White, and Johnston	1	48
6. Rubidium						
1965	1820		0.346	Dillon, Nelson, and Swanson	See text, 19	49
1965	1838		0.334	Hochman and Bonilla	See text, 19	51
Selected value	1829		0.34			
7. Cesium						
1965	1847		0.428	Dillon, Nelson, and Swanson	See text, 19	49
1965	1783		0.451	Hochman and Bonilla	See text, 19	51
Selected value	1800		0.44			
8. Nitrogen						
1914	-147.13	33.490		Onnes, Dorsman, and Holst	1	<i>a</i>
1914			0.31096	Mathias, Onnes, and Crommelin	19	52
1915	-144.7	33.65		Cardoso	1	<i>b</i>
1951	-146.90	33.54		White, Friedman, and Johnston	1	<i>c</i>
1966	-146.96			Voronel, Gorbunova, Chashkin, and Shchekochikhiva	21	8
1970			0.315	Weber	See text	53
1953	-147.0	33.5	0.311	Kobe and Lynn		1
Selected value	-147.0	33.5	0.313			
9. Phosphorus						
1922	720.6			Marckwald and Helmholtz	1	54
10. Oxygen						
1911			0.4299	Mathias and Onnes	19	<i>d</i>
1914	-118.83	49.71		Onnes, Dorsman, and Holst	1	<i>e</i>
1915	-118.0	49.30	0.430	Cardoso	3	<i>f</i>
1950	-118.38	50.14	0.38	Hoge	5	55
1963	-118.15			Jones and Rowlinson	1	<i>g</i>
1964	-118.585			Voronel, Chashkin, Popov, and Simkin	21	56
1969	-118.574	49.77	0.4361	Weber	22	57
1953	-118.4	50.1	0.41	Kobe and Lynn		1
1968	-118.4	50.14	0.43	Kudchadker, Alani, and Zwolinski		2
Selected value	-118.570	49.77	0.436			
11. Ozone						
1922	-5	67	0.537	Riesenfeld and Schwab	1, 17, 19	61
1952	-12.1	54.7		Jenkins and Birdsall	1, 16	59
Selected value	-12.1	55	0.54			
12. Sulfur						
1953	1040	116		Kobe and Lynn		1
13. Fluorine						
1930	-129.1			Cady and Hildebrand	1	62
1970	-128.84	51.47	0.574	Prydz, Straty, and Timmerhaus	8, see text	63
Selected value	-128.84	51.47	0.574			
14. Chlorine						
1913	143.2			Estreicher and Schnerr	1	<i>h</i>
1915	144.0	76.1	0.573	Pellaton	1, 19	64
1966	144.0			Krichevskii, Tsekhanskaya, and Polyakova	1	65
1953	144	76	0.573	Kobe and Lynn		1

Table II (Continued)

Year	t_c , °C	P_c , atm	d_c , g/cm ³	Investigators	Method	Ref
15. Bromine						
1885	302		1.18	Nadejdine	?	66
1926	311	102		Scheffer and Voogd	1, 16	67
1968	315		1.26	Burriel-Lluna, Cragg, and Rowlinson	1, 19	68
1953	311	102	1.18	Kobe and Lynn		1
Selected value	311	102	1.26			
16. Iodine						
1902	512			Radice	1	69
1920	553			Rassow	1	70
1968	546		1.64	Burriel-Lluna, Cragg, and Rowlinson	1, 19	68
Selected value	546		1.64			
17. Mercury						
1932	1460	1587		Birch	See text	71

^a H. K. Onnes, C. Dorsman, and G. Holst, *Proc. Acad. Sci. Amsterdam*, **17**, 950 (1915). ^b E. Cardoso, *J. Chim. Phys.*, **13**, 312 (1915). ^c D. White, A. S. Friedman, and H. J. Johnston, *J. Amer. Chem. Soc.*, **73**, 5713 (1951). ^d E. Mathias and H. K. Onnes, *Proc. Acad. Sci. Amsterdam*, **13**, 939 (1911). ^e H. K. Onnes, C. Dorsman, and G. Holst, *ibid.*, **17**, 950 (1915). ^f E. Cardoso, *Arch. Sci. Phys. Nat.*, **39**, 400 (1915). ^g L. W. Jones and J. S. Rowlinson, *Trans. Faraday Soc.*, **59**, 1702 (1963). ^h T. Estreicher and A. Schnerr, *Z. Kompr. Fluss. Gase*, **15**, 161 (1913).

copper oxide filled tube to remove hydrocarbons, then to a KOH-filled tube, and a Dry Ice-acetone cold trap to remove CO₂ and water vapor. The mixture from the ozonizer was liquified at liquid oxygen temperature and oxygen was pumped off in a number of steps. The criterion of purity was a constant vapor pressure at -183° of 0.1 mm which closely checked the value reported by Spangenberg.⁶⁰ Temperatures were measured with Leeds and Northrup Duplex, glass-insulated, 30-gauge copper-constantan thermocouples calibrated at the mercury freezing point, the CO₂ sublimation point, and at liquid oxygen temperatures vs. a NBS calibrated L & N platinum resistance thermometer. Temperatures could be read to ±0.03 to ±0.05°. Vapor pressures were measured to -30° with a Pyrex glass sickle gauge sensitive to pressure changes to less than 1 psi. A vapor pressure equation of the form

$$\log P = g - (H/T) - ST \quad (18)$$

was extrapolated to the critical temperature (-12.1°). Three successive measurements of the temperature of the disappearance of the meniscus were recorded (-12.2, -12.2, -12.0°) before the sample was observed to decompose. A deep blue color near the critical point made observations of the meniscus difficult and no critical opalescence was seen.

No information on sample purity was given by Riesenfeld and Schwab.⁶¹ They observed critical temperatures from -23 to -5.0° and selected the highest as the most probable value.

The selected values of critical temperature and critical pressure are those of Jenkins and Birdsall, and the critical density of Riesenfeld and Schwab is the only datum available at this time.

12. Sulfur

There are no new data since Kobe and Lynn.¹

13. Fluorine

Cady and Hildebrand⁶² prepared fluorine by the electrolysis of fused potassium bifluoride. The fluorine from the generator

was then passed through a copper trap at 86°K to remove the less volatile impurities. Two attempts were made to determine the critical temperature in glass ampoules. The fluorine apparently reacted with the glass, and the two trials gave observed critical temperatures of 143.3 and 144.1°K. The authors stated that the critical temperature was approximately 144°K. Temperatures were measured by a thermocouple and stated to be correct to ±0.05°K.

Prydz, Straty, and Timmerhaus⁶³ used fluorine of 99.99% purity supplied by Argonne National Laboratory. Temperatures were measured with a platinum resistance thermometer calibrated by the National Bureau of Standards according to the IPTS-48 and NBS-1955 scale above and below 90°K, respectively. Pressures were measured on an oil dead-weight gauge which was separated from the fluorine by an intermediate nitrogen system using two differential pressure transducers.

Experimental PVT isochores were extrapolated to their intersection with an accurate vapor pressure equation to obtain saturated liquid and vapor densities at temperatures (T). These densities were fitted to the equation

$$(T_c - T)/T = |(d - d_c)/d_c|^3 \left(A_1 \ln d + \sum_{i=2}^9 A_i d^{i-2} \right) \quad (19)$$

(developed by Goodwin⁴⁵) by the method of weighted least squares.

The critical values of Prydz, Straty, and Timmerhaus are selected.

14. Chlorine

The only experimental measurement since the summary by Kobe and Lynn¹ has been a critical temperature determination by Krichevskii, Tsekhanskaya, and Polyakova.⁶⁵ They prepared chlorine by the thermal dissociation of gold chloride. Temperatures were measured with a thermometer with scale divisions of 0.01°.

(60) A. L. Spangenberg, *Z. Phys. Chem.*, **119**, 419 (1926).

(61) E. H. Riesenfeld and G. M. Schwab, *Z. Phys.*, **11**, 12 (1922).

(62) G. H. Cady and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **52**, 3839 (1930).

(63) R. Prydz, G. C. Straty, and K. D. Timmerhaus, *J. Chem. Phys.*, **53**, 2359 (1970).

(64) M. Pellaton, *J. Chim. Phys.*, **13**, 426 (1915).

(65) I. R. Krichevskii, Y. V. Tsekhanskaya, and Z. A. Polyakova, *Dokl. Akad. Nauk SSSR*, **166**, 897 (1966).

Edwards¹⁰ found that a critical temperature of 144.12° and the vapor pressure data of Pellaton⁶⁴ gave the most consistent fit. However, Angus⁴¹ is presently reanalyzing the data on chlorine and suggests that the first decimal place is still in doubt. Thus there seems to be no reason to alter the choice of Kobe and Lynn.¹

15. Bromine

Burriel-Lluna, Cragg, and Rowlinson⁶⁸ used an Analar sample of high purity. Orthobaric densities and the end of the two-phase regions were determined by measuring the densities of the liquid and vapor regions of a sealed tube by absorption of γ radiation from ¹³⁴Cs. Temperatures were measured by a Pt, Pt-10% Rh thermocouple calibrated against the melting point of Zn and used with a thermoelectric free potentiometer, Diesselhorst Pattern Type 3589 (H. Tinsley and Co.), with a sensitivity of 1 μ V. A rectilinear diameter in the quadratic form was used to determine the critical density.

Edwards¹⁰ prefers the data of Scheffer and Voogd⁶⁷ over that of Nadejdine.⁶⁶ A deviation curve for vapor pressure using an input value of $T_c = 311^\circ$ and calculating a $P_c = 102$ atm is consistent.

The values of critical temperature and critical pressure remain as selected by Kobe and Lynn.¹ The critical density is calculated from the rectilinear diameter of Burriel-Lluna, Cragg, and Rowlinson using a critical temperature of 311°.

16. Iodine

Kobe and Lynn¹ reviewed the work of Radice⁶⁹ and Rassow.⁷⁰

Burriel-Lluna, Cragg, and Rowlinson⁶⁸ used an Analar sample of high purity. A discussion of their experimental technique may be found in the previous section on bromine.

The values of critical temperature and critical density of Burriel-Lluna, Cragg, and Rowlinson are selected.

17. Mercury

Birch⁷¹ determined the critical temperature and critical pressure of mercury by measuring the continuous variation of electrical resistance with temperature at constant pressure. If the pressure was low enough to permit boiling, there was a sharp increase in electrical resistance. In this way the boiling curve was followed up to a pressure (1640 atm) at which the increase in resistance was no longer so abrupt which served as an indication of the critical point.

C. DEUTERIDES (TABLE III)

Kopper¹¹ used the following methods of preparation: the deuterium halides were prepared by the reaction of the corresponding phosphorus trihalide with 99.2% D₂O; D₂S and D₂Se were prepared by the reaction of the corresponding aluminum compound with 99.2% D₂O; ND₃ and PD₃ were prepared by the reaction of magnesium nitride and magnesium phosphide

(66) "International Critical Tables," Vol. III, McGraw-Hill, New York, N. Y., 1931, p 201.

(67) F. E. C. Scheffer and M. Voogd, *Recl. Trav. Chim. Pays-Bas*, **45**, 214 (1926).

(68) J. A. Burriel-Lluna, C. B. Cragg, and J. S. Rowlinson, *An. Real Soc. Espan. Fis. Quim. (Madrid)*, **64**, 1 (1968).

(69) Radice, Doctoral Thesis, Geneva, 1899; Landolt-Bernstein, "Tabellen," Vol. I, J. Springer, Berlin, 1923, p 256.

(70) H. von Rassow, *Z. Anorg. Chem.*, **114**, 117 (1920).

(71) F. Birch, *Phys. Rev.*, **41**, 641 (1932).

Table III

Deuterides

Year	t_c , °C	Investigators	Method	Ref
1936	132.3	1. Nitrogen Trideuteride	1	11
		Kopper		
1936	50.4	2. Phosphorus Trideuteride	1	11
		Kopper		
1936	98.9	3. Arsenic Trideuteride	1	11
		Kopper		

with 99.2% D₂O; and AsD₃ was prepared from aluminum arsenide and D₂O. He does not state the method of purification but stresses that the samples he used were rigorously purified for the purpose of measuring the Raman spectra of the compounds. These Raman spectra compounds were distilled into the capillary tubes which were 1 cm long. Temperatures were measured with an Anschutz thermometer with 0.2° scale divisions. His estimate of error in critical temperature is $\pm 0.3^\circ$. He also measured the critical properties of the corresponding hydrogen compounds which he prepared in analogous ways, and these may be found under the appropriate heading.

D. NITROGEN COMPOUNDS (TABLE IV)

1. Ammonia

There are no new data on critical constants for ammonia since 1950, but Kopper's¹¹ value of critical temperature is to be added to the list. Edwards¹⁰ finds that Kopper's t_c is most consistent with the vapor pressure data of Beattie and Lawrence⁷² and calculates a critical pressure of 112.53 atm. These values are selected as most probable. The value for critical density selected by Kobe and Lynn¹ is retained.

2-4. Hydrazine, Hydrogen Cyanide, and Cyanogen

There are no new data for these three substances since Kobe and Lynn.¹

The low value of Z_c for hydrogen cyanide (see Table XVI) is probably due to the fact that this is a strongly hydrogen-bonding type compound such as hydrogen fluoride.

5. Trifluoramine oxide

NOF₃ was prepared⁷³ by allowing NF₃ and oxygen to react in an electric discharge tube. The NOF₃ was purified chromatographically with 1 m of 33% perfluorotributylamine and 2 m of Kel-F tetramer supported on Chromosorb P. They found the weight per cent of fluorine and nitrogen to be 66.2 and 16.0, respectively, compared with the calculated values of 65.5 and 16.1. They also found the molecular weight to be 86.6 compared with the calculated 87.0. Temperatures were measured with a platinum resistance thermometer. The meniscus disappeared at 29.8° and reappeared at 29.1°. The selected value of critical temperature is taken as that of the disappearance of the meniscus.

(72) J. A. Beattie and C. K. Lawrence, *J. Amer. Chem. Soc.*, **52**, 6 (1930).

(73) W. B. Fox, J. S. MacKenzie, E. R. McCarthy, J. R. Holmes, R. F. Stahl, and R. Juurik, *Inorg. Chem.*, **7**, 2064 (1968).

Table IV
Nitrogen Compounds

Year	t_c , °C	P_c , atm	d_c , g/cm ³	Investigators	Method	Ref
			1. Ammonia			
1936	132.5			Kopper	1	11
1953	132.3	111.3	0.235	Kobe and Lynn		1
			2. Hydrazine			
1953	380	145		Kobe and Lynn		1
			3. Hydrogen Cyanide			
1953	183.5	53.2	0.195	Kobe and Lynn		1
			4. Cyanogen			
1953	127	59		Kobe and Lynn		1
			5. Trifluoramine Oxide			
1968	29.5		0.593	Fox, <i>et al.</i>	1, 19	73

E. CHALCOGENIDES

1. Oxides (Table V)

a. Water

Kudchadker, Alani, and Zwolinski² selected the critical properties recommended by the Sixth International Conference on the Properties of Steam in October 1963, New York, N. Y.

Blank⁷⁴ used a sample which was shown by spectral analysis to contain less than 5 mg of total impurities per kilogram of sample. Pressures were measured by a dead-weight gauge, and temperatures were measured by platinum resistance thermometers. Both measuring devices were calibrated by the Physikalisch-Technischen Bundesanstalt Braunschweig. A horizontal visual cell was used for the observance of the disappearance and appearance of the meniscus, and the critical point was passed with rates of temperature change of about 0.01–0.03°/hr.

Sengers¹⁹ considers the data of Blank to be the best available for critical temperature and critical pressure, and these are selected as most probable. The critical density still has a large uncertainty (Sengers suggests several per cent) and would be better rounded off to two decimal places at the present time.

b. Heavy Water

Oliver and Grisard⁷⁶ obtained their D₂O from Consolidated Mining and Smelting Co. of Canada Ltd., Trail, B. C. The sample was analyzed as 99.87 wt % D₂O. Temperatures were measured by a platinum resistance thermometer and G-2 Mueller bridge and estimated accurate to ±0.01°.

The experimental work of Blank⁷⁴ was discussed in the preceding section. The sample of heavy water had 2.7% of normal water and other impurities less than 5 mg/kg. The measured critical temperature was corrected for the normal water impurity.

Riesenfeld and Chang⁷⁵ obtained two samples of heavy water from Norsk Hydro-Elektrisk, Kvalstofaktiselskab, Oslo. The purities of these samples were 98.0 and 99.1 mol % D₂O, the impurity being H₂O. The samples were distilled under vacuum to remove air. Critical temperatures were determined for each of these samples, three other mixtures of D₂O and H₂O (22.1, 45.6, and 70.9 mol % D₂O), and pure H₂O. An extrapolation of the critical properties to 100% D₂O was then performed.

The data of Oliver and Grisard and Blank for the critical temperature are in good agreement and an average value is selected. The directly measured critical pressure of Blank is selected. The critical density of Riesenfeld and Chang is the only datum available.

c. Carbon Monoxide

This compound was reviewed by Kudchadker,² and there has been no new reported work.

d. Carbon Dioxide

Kobe and Lynn¹ and Kudchadker² reviewed this compound. The only new experimental datum since then is Straub's.⁸¹ His experimental procedure was that reviewed in section III.A under a discussion of the work of Schmidt. The work reported for Vicentini-Missoni, Sengers, and Green¹⁸ is a reanalysis of the work of Michels, Blaisse, and Michels.⁸⁰

The picture on the critical temperature is by no means as clear as indicated by Kudchadker,² who based his analysis primarily on Michels' work and its agreement with the newer values. The reanalysis¹⁸ of Michels' work gives a critical temperature which appears to agree with that of Onnes and Fabius,⁷⁷ Hein,⁷⁸ and Kennedy and Meyers.⁷⁹ Also, according to Sengers¹⁹ there are problems with Michels' scale of temperatures. His scale is not IPTS-27 or -48 and is in fact unrecognizable. For these reasons, the selected value of critical temperature reverts to the value (and the number of significant figures) selected by Kobe and Lynn.¹ The critical pressure is rounded off to 72.8 atm and the critical density remains as that selected by Kobe and Lynn and Kudchadker.

e. Nitrous Oxide

Kobe and Lynn¹ reviewed the literature to 1929.

(74) F. Blank, *Waerme-Stoffuebertrag.*, 2, 53 (1969).

(75) E. H. Riesenfeld and T. L. Chang, *Z. Phys. Chem., Abt. B*, 30, 61 (1935).

(76) G. D. Oliver and J. W. Grisard, *J. Amer. Chem. Soc.*, 78, 561 (1956).

(77) H. K. Onnes and G. H. Fabius, *Commun. Kamerlingh Onnes Lab., Univ. Leiden*, No. 98 (1906).

(78) P. Hein, *Z. Phys. Chem.*, 86, 385 (1913).

(79) H. T. Kennedy and C. H. Meyers, *Amer. Soc. Heating, Refrig. Aircond. Engr.*, 15, 125 (1928).

(80) A. Michels, B. Blaisse, and C. Michels, *Proc. Roy. Soc., Ser. A*, 60, 358 (1937).

(81) J. Straub, *Chem. Ing. Tech. Z.*, 39, 191 (1967); *Chem. Abstr.*, 67, 25865g (1967).

Table V

Oxides

Year	$t_0, ^\circ\text{C}$	P_0, atm	$d_0, \text{g/cm}^3$	Investigators	Method	Ref
a. Water						
1969	373.91	217.56		Blank	1	74
1953	374.2	218.3	0.32	Kobe and Lynn		1
1968	374.15	218.3	0.315	Kudchadker, Alani, and Zwolinski		2
Selected value	373.91	217.6	0.32			
b. Heavy Water						
1935	371.5	218.6	0.363	Riesefeld and Chang	1, 19	75
1956	370.8	215.70		Oliver and Grisard	1, 16	76
1956	370.9			Oliver and Grisard	8	76
1969	370.66	213.75		Blank	1	74
Selected value	370.8	213.8	0.36			
c. Carbon Monoxide						
1953	-140	34.5	0.301	Kobe and Lynn		1
1968	-140.23	34.53	0.301	Kudchadker, Alani, and Zwolinski		2
d. Carbon Dioxide						
1906	30.985		0.460	Onnes and Fabius	1	77
1908	31.10	73.00	0.459	Dorsman	?	29
1908	31.26			Bradley, Brown, and Hale	1	<i>a</i>
1912	31.0	72.85		Cardoso and Bell	3	<i>b</i>
1913	30.97			Hein	1	78
1917			0.4597	Keyes and Kennedy	19	<i>c</i>
1926	31.10	72.95		Meyers and Van Dusen	1, 16	<i>d</i>
1927			0.4683	Lowry and Erickson	19	<i>e</i>
1928	30.96			Kennedy and Meyers	1	79
1937	31.04	72.85	0.468	Michels, Blaisse, and Michels	5	80
1953		72.6		Cook	16	<i>f</i>
1953	31.04			Lorentzen	20	<i>g</i>
1954	31.08			Palmer	1	<i>h</i>
1954	31.01	72.78	0.463	Schmidt and Thomas	1, 16, 20	<i>j</i>
1956	31.01			Ambrose	1	<i>k</i>
1956	31.045	72.839	0.474	Wentorf	1	<i>l</i>
1967	31.03			Straub	20	81
1969	30.96			Vicentini-Missoni, Sengers, and Green	<i>i</i>	18
1953	31.0	72.9	0.468	Kobe and Lynn		1
1968	31.04	72.85	0.468	Kudchadker, Alani, and Swolinski		2
Selected value	31.0	72.8	0.468			
e. Nitrous Oxide						
1894	38.8	77.5	0.454	Villard	?	<i>m</i>
1897	36	71.9		Kuenan	1	<i>n</i>
1912	36.5	71.65		Cardoso and Arni	3	<i>o</i>
1929			0.459	Quinn and Wernimont	19	<i>p</i>
1953	36.4	71.4	0.452	Cook	1, 19	82
1953		71.12		Cook	16	82
1956	36.434	71.596	0.4525	Couch and Kobe	5, 16, 19	83
1965	36.585			Schmidt	20	4
1967	36.416			Straub	20	81
1970	36.417			Sengers	<i>i</i>	19
1953	36.5	71.7	0.457	Kobe and Lynn		1
Selected value	36.42	71.5	0.452			
f. Nitric Oxide						
1953	-93	64	0.52(?)	Kobe and Lynn		1
g. Dinitrogen Tetroxide						
1885	171.2			Nadejdine	1	84
1913	158.2	100		Scheffer and Treub	1, 16	84
1952		100	0.550	Reamer and Sage	16, 19	85
1953	158	100	0.56	Kobe and Lynn		1
Selected value	158	100	0.55			
h. Sulfur Dioxide						
1926	157.5	77.79		Cardoso and Fiorentino	1	86
1927			0.524	Cardoso and Sorrentino	19	87
1931	157.8			Bond and Williams	6	88
1961	157.5	77.808	0.525	Kang, Hirth, Kobe, and McKetta	5, 19	89

Table V (Continued)

Year	$t_c, ^\circ\text{C}$	P_c, atm	$d_c, \text{g/cm}^3$	Investigators	Method	Ref
1953	157.5	77.8	0.524	Kobe and Lynn		1
Selected value	157.5	77.81	0.525			
i. Sulfur Trioxide						
1923	218.2	83.8	0.633	Berthoud	1, 19	90
1963	217.7	80.8		Abercromley and Tiley	1, 16	91
Selected value	217.7	81	0.63			
j. Rhenium Oxide						
1969	669.0		1.45	Nisel'son, <i>et al.</i>	1, 19	92

^a W. P. Bradley, A. W. Brown, and C. F. Hale, *Phys. Rev.*, **19**, 258 (1904). ^b E. Cardoso and R. Bell, *J. Chim. Phys.*, **10**, 497 (1912). ^c F. G. Keyes and H. T. Kennedy, *Refriger. Eng.*, **3**, 32 (April 1927). ^d C. H. Meyers and H. Von Dusen, *J. Res. Nat. Bur. Stand.*, **10**, 38 (1935). ^e H. H. Lowry, and W. R. Erickson, *J. Amer. Chem. Soc.*, **49**, 2729 (1927). ^f D. Cook, *Trans. Faraday Soc.*, **49**, 716 (1953). ^g H. L. Lorentzen, *Acta Chem. Scand.*, **7**, 1335 (1953). ^h H. B. Palmer, *J. Chem. Phys.*, **22**, 625 (1954). ⁱ See text. ^j E. Schmidt and W. Thomas, *Forsch. Geb. Ingenieurw.*, **20B**, 151 (1954). ^k D. Ambrose, *Trans. Faraday Soc.*, **52**, 772 (1956). ^l R. H. Wentorf, *J. Chem. Phys.*, **24**, 607 (1956). ^m M. P. Villard, *Ann. Chim. Phys.*, **10**, 387 (1897). ⁿ J. P. Kuenan, *Phil. Mag.*, **44**, 174 (1897). ^o E. Cardoso and E. Arni, *J. Chim. Phys.*, **10**, 504 (1912). ^p E. L. Quinn and G. Wernimont, *J. Amer. Chem. Soc.*, **51**, 2002 (1929).

Cook⁸² used commercial anesthetic grade N₂O supplied by British Oxygen Co. and stated to contain less than 21 mg/m³ of CO₂ and less than 22 mg/m³ of H₂O. The nitrous oxide was distilled three times between two glass traps using liquid nitrogen as a refrigerant. Sample purity was indicated by a change of 0.03 atm in vapor pressure between the dew point and the bubble point at 25°. Temperatures were read on mercury-in-glass thermometers graduated to 0.01° which had been calibrated by the National Physical Laboratory. Pressures were measured on a Budenberg dead weight gauge which had been calibrated against the vapor pressure of pure CO₂ at the ice point as recommended by Bridgman. In the critical region temperature was changed at the rate of 0.01°/hr. The observed critical pressure was 71.4 atm, and the critical pressure calculated by extrapolation of a log P vs. $1/T$ plot was 71.12 atm.

Couch and Kobe⁸³ obtained pharmaceutical grade nitrous oxide from Stuart Oxygen Co. which was stated to be 99.7% pure with nitrogen as the principle impurity. This material was vacuum distilled at liquid nitrogen temperature and its final purity was estimated to be 99.998% on the basis of change in vapor pressure on isothermal condensation. Temperature was measured to $\pm 0.002^\circ$ with a calibrated platinum resistance thermometer. Pressures were measured with a dead weight gauge calibrated against the vapor pressure of CO₂. Volume was measured with an estimated accuracy of ± 0.005 ml.

The work of Schmidt⁴ and Straub⁸¹ is described in section II.A.

The work of Sengers¹⁹ is a reanalysis of Schmidt's orthobaric density data.

The values of critical temperature of Sengers, Straub, and Couch and Kobe are in good agreement, and average value is selected. The values of critical pressure and critical density of Cook and Couch and Kobe are in good agreement and again average values are selected.

f. Nitric Oxide

There have been no new data reported since Kobe and Lynn.¹

g. Dinitrogen Tetroxide

There have been no data added since 1952, but it does appear as if some of the previously reported values are not experi-

(82) D. Cook, *Trans. Faraday Soc.*, **49**, 716 (1953).

(83) E. F. Couch and K. A. Kobe, *J. Chem. Eng. Data*, **6**, 229 (1961).

mental. Edwards¹⁰ says that the values of critical temperature and critical pressure attributed to Baume and Robert¹ were apparently taken from the "International Critical Tables." It is questionable that the critical density attributed to Bennewitz and Windisch¹ is reliable since it was estimated from a generalized Joule-Thompson curve. Edwards¹⁰ calculates a value of $P_c = 99.66$ atm from the vapor pressure data of Schlinger and Sage and the critical temperature of Scheffer and Treub.⁸⁴ There are no changes in the values of critical temperature and critical pressure selected by Kobe and Lynn.¹ The critical density is taken from the datum of Reamer and Sage.⁸⁵ The high value of Z_c (see Table XVI) is probably due to the fact that gaseous dinitrogen tetroxide decomposes to NO₂ at elevated temperatures.

h. Sulfur Dioxide

Kobe and Lynn¹ reviewed the literature references to 1927.

The method of Bond and Williams⁸⁸ is based on the disturbance of a balanced tube and is thoroughly discussed by Kobe and Lynn.¹

Kang, *et al.*,⁸⁹ used sulfur dioxide supplied by the Tennessee Corp., Atlanta, Ga., with the specification of 99.9975% purity. Further purification raised the minimum purity to 99.998% according to a mass spectrometer analysis. Temperatures were measured with a platinum resistance thermometer whose resistance was measured on a G-2 Mueller bridge. Pressures were measured with a Pratt and Whitney dead weight gauge calibrated against the vapor pressure of CO₂ at 0°.

Edwards¹⁰ calculates a critical pressure of 77.810 atm at a critical temperature of 157.50°.

The critical temperatures of Cardoso and Fiorentino⁸⁶ and Kang agree, and this value is the selected one. Kang's value of critical pressure, rounded off to one less significant figure, is selected. The critical densities of Cardoso and Sorrentino⁸⁷ and Kang are within experimental error and the selection of Kobe and Lynn¹ is retained.

(84) F. E. C. Scheffer and J. P. Treub, *Z. Phys. Chem.*, **81**, 308 (1912).

(85) H. H. Reamer and B. H. Sage, *Ind. Eng. Chem.*, **44**, 185 (1952).

(86) E. Cardoso and V. Fiorentino, *J. Chim. Phys.*, **23**, 841 (1926).

(87) E. Cardoso and E. Sorrentino, *ibid.*, **24**, 77 (1927).

(88) P. A. Bond and D. A. Williams, *J. Amer. Chem. Soc.*, **53**, 34 (1931).

(89) T. L. Kang, L. J. Hirth, K. A. Kobe, and J. J. McKetta, *J. Chem. Eng. Data*, **6**, 220 (1961).

Table VI

Sulfides

Year	$t_c, ^\circ\text{C}$	P_c, atm	$d_c, \text{g/cm}^3$	Investigators	Method	Ref
a. Hydrogen Sulfide						
1910	99.6	88.3		Scheffer	1	<i>a</i>
1910	100.43			Estreicher and Schnerr	1	29
1912	100.43	89.05		Cardoso and Arni	3	<i>b</i>
1921	100.4	88.90		Cardoso	3	93
1936	100.1			Kopper	1	11
1950	100.4	88.9	0.3488	Reamer, Sage, and Lacey	5	94
1953	99.92	88.203	0.3461	Kay and Rambosek	5	95
1953	100.4	88.9	0.349	Kobe and Lynn		1
Selected value	100.0	88.2	0.346			
b. Deuterium Sulfide						
1936	99.1			Kopper	1	11
c. Carbon Disulfide						
1953	279	78	0.44	Kobe and Lynn		1

^a F. E. C. Scheffer, *Z. Phys. Chem.*, **71**, 695 (1910). ^b E. Cardoso and E. Arni, *J. Chim. Phys.*, **10**, 504 (1912).

i. Sulfur Trioxide

Kobe and Lynn¹ reviewed the work of Berthoud.⁹⁰

Abercromley and Tiley⁹¹ obtained SO₃ from Imperial Smelting Corp. which had <0.05% SO₂ as an impurity and triply distilled it *in vacuo* to a SO₂ content <0.005%. The moisture content was inferred from stability of the SO₃ toward polymerization and was thought certainly less than 0.1% and possibly less than 0.01%. The sample ampoules were 3–5 cm long and were heated and cooled at the rate of 0.2°/hr. The temperature range between the disappearance and appearance of the meniscus was 0.1°. Pressures were measured on a Bourdon gauge which was calibrated against a dead weight gauge.

Edwards¹⁰ calculates a critical pressure of 81.44 atm using the data of Abercromley and Tiley.

An average value of the critical temperatures of Berthoud and Abercromley and Tiley, rounded off to the nearest degree, is virtually within the quoted accuracy of Abercromley and Tiley ($\pm 0.2^\circ$) and is the selected value. An average value of the critical pressure of Abercromley and Tiley and Edwards,¹⁰ rounded off to the nearest atmosphere, is selected as the most probable value.

j. Rhenium Oxide

The sample was prepared⁹² by the oxidation of powdered rhenium metal with gaseous oxygen and purified by rectification in a sieve plate column operated at atmospheric pressure. The sample contained less than 10⁻⁴% (each) of Na, K, Ca, Mo, and W. Temperatures were measured with a calibrated chromel–alumel thermocouple with a claimed accuracy of $\pm 0.5^\circ$.

2. Sulfides (Table VI)

a. Hydrogen Sulfide

Kobe and Lynn¹ reviewed the literature data to 1950, except for the work of Kopper.¹¹ Experimental details of Kopper's

work may be found in the discussion for deuterium compounds (section V.C).

Kay and Rambosek⁹⁵ used a commercial sample of H₂S which was stated to be of 99.78 mol % purity. This sample was bubbled through water and then through a solution of barium hydroxide maintained at 0°C. It was then passed over Drierite, charcoal, and P₂O₅. The sample was then deaerated by distilling it back and forth from one cold trap to another, discarding the first fraction and a residual fraction each time. Twelve such distillations were carried out. Purity was tested by measuring the vapor pressure during the isothermal condensation, the differences between dew and bubble point being 2.45 psi at 165.72°F. Pressures were measured by a dead weight gauge calibrated against the vapor pressure of CO₂ at 0°. Temperatures were measured by copper–constantan thermocouples which had been calibrated against a Pt resistance thermometer which had itself been calibrated by the NBS.

Edwards¹⁰ has found that the most consistent set of vapor pressure and critical constants is that of Kay and Rambosek and that the data of Cardoso⁹³ were inconsistent.

There are two sets of data here, that of Cardoso⁹³ and Reamer, Sage, and Lacey⁹⁴ on one hand and that of Kopper¹¹ and Kay and Rambosek⁹⁴ on the other. It would seem that Kay and Rambosek took more care in drying the H₂S than Reamer, Sage, and Lacey. Of the two direct observations of the critical temperatures, Kopper's method of the disappearance of the meniscus is probably more accurate than Cardoso's disappearance of critical opalescence. Hence the critical temperature is selected as the average value of Kopper and Kay and Rambosek, and the latter's values of critical pressure and critical density are also selected.

b. Deuterium Sulfide

Kopper's¹¹ work is described in section V.C.

c. Carbon Disulfide

There has been no new work reported since Kobe and Lynn.¹

(90) A. Berthoud, *Helv. Chim. Acta*, **5**, 513 (1922).

(91) D. C. Abercromley and P. F. Tiley, *J. Chem. Soc.*, 4902 (1963).

(92) L. A. Nisev'son, R. K. Nikolaev, I. I. Vasilevskaya, and A. G. Vasil'eva, *Russ. J. Inorg. Chem.*, **14**, 595 (1969).

(93) E. Cardoso, *Gazz. Chim. Ital.*, **51**, 153 (1921).

(94) H. H. Reamer, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **42**, 140 (1950).

(95) W. B. Kay and G. M. Rambosek, *ibid.*, **45**, 221 (1953).

Table VII

Selenides

Year	$t_c, ^\circ\text{C}$	P_c, atm	$d_c, \text{g/cm}^3$	Investigators	Method	Ref
a. Hydrogen Selenide						
1953	138	88		Kobe and Lynn		1
b. Deuterium Selenide						
1936	139.2			Kopper	1	11

Table VIII

Mixed Chalcogenides

Year	$t_c, ^\circ\text{C}$	P_c, atm	$d_c, \text{g/cm}^3$	Investigators	Method	Ref
Carbonyl Sulfide						
1881	105			Ilosvay	1	96
1901	105	65		Hempel	?	97
1951	102.2			Partington and Neville	1	98
1953	105	61		Kobe and Lynn		1
Selected value	102	58	0.44			

3. Selenides (Table VII)

a. Hydrogen Selenide

There has been no new work reported since Kobe and Lynn.¹

b. Deuterium Selenide

Kopper's¹¹ work is described in section V.C.

4. Mixed (Table VIII)

a. Carbonyl Sulfide

Kobe and Lynn¹ reviewed the data of Ilosvay⁹⁶ and Hempel.⁹⁷

Partington and Neville⁹⁸ prepared carbonyl sulfide from Bender's salt by the action of dilute acid. The impure sample was passed through a cold trap at 0°, 30% sodium hydroxide, concentrated sulfuric acid, and finally a cold trap at -55° to remove traces of alcohol. It was evacuated at -55° and then distilled through a column of phosphorus pentoxide with the center fraction being saved. Finally it was redistilled into storage bulbs, the center fraction again being retained. Temperatures in the critical region were measured with a mercury thermometer, calibrated at the freezing and boiling points of water and against a vapor pressure thermometer containing carbon dioxide. They stated that the appearance of the meniscus was more distinct than was the disappearance of the meniscus.

The carbonyl sulfide used by Ilosvay was obtained by treating an aqueous solution of potassium butyl thiocarbonate with dilute sulfuric acid and purifying the sample by passing it through concentrated sodium hydroxide, sulfuric acid, and triethylphosphine.

Kobe and Lynn¹ considered that Hempel's sample was relatively impure and selected the value for critical pressure (61 atm) estimated from the vapor pressure of Stock and Kuss⁹⁹ and reported in the "International Critical Tables."¹⁰⁰

(96) I. N. Ilosvay, *Bull. Soc. Chim. Belg.*, **37**, 294 (1881).

(97) W. Hempel, *Z. Anorg. Chem.*, **14**, 865 (1901).

(98) J. R. Partington and H. H. Neville, *J. Phys. Colloid Chem.*, **55**, 1550 (1951).

(99) A. Stock and E. Kuss, *Ber.*, **50**, 159 (1917).

(100) Reference 66, p 748.

The critical temperature of Partington and Neville, rounded off to three figures, is selected as being the most reliable because of a more careful purification procedure. No better vapor pressure data are available and so the critical pressure is estimated at 102° from the vapor pressure data in the "International Critical Tables" and rounded off to the nearest atmosphere. A least-squares fit of the orthobaric density data of Partington and Neville to the linear form of the rectilinear diameter gives a value of the critical density of 101° at 0.44 to the nearest two significant figures.

F. HALIDES

1. Fluorides (Table IX)

a. Hydrogen Fluoride

Kobe and Lynn¹ reviewed the work of Bond and Williams.⁸⁸

Franck and Spalthoff¹⁰¹ distilled hydrogen fluoride in a silver vessel. The water content of the purified sample, as indicated by conductivity measurements, was less than 0.05% (mole). Temperatures were measured with a platinum resistance thermometer. Pressures were measured with a Bourdon gauge which had been calibrated by the Physikalisch-Technischen Bundesanstalt-Eichung.

The data of Franck and Spalthoff were obtained by direct measurements and are probably more accurate than those of Bond and Williams and are therefore selected.

The unusually low value of Z_c (see Table XVI) is possibly due to the fact that this compound is of the strongly hydrogen-bonding type.

b and c. Boron Trifluoride and Silicon Tetrafluoride

No new work has been reported on these two substances since Kobe and Lynn.¹

d. Tetrafluorohydrazine

The work of Colburn and Kennedy¹⁰² was reviewed by Kudchadker.²

(101) E. U. Franck and W. Spalthoff, *Z. Phys. Chem.*, **8**, 255 (1956).

(102) C. B. Colburn and A. Kennedy, *J. Amer. Chem. Soc.*, **80**, 5004 (1958).

Table IX

Fluorides

Year	$t_c, ^\circ C$	P_c, atm	$d_c, g/cm^3$	Investigators	Method	Ref
a. Hydrogen Fluoride						
1931	230.2			Bond and Williams	6	88
1956	188	64.0	0.29	Franck and Spalthoff	1, 19	101
Selected value	188	64	0.29			
b. Boron Trifluoride						
1953	-12.3	49.2		Kobe and Lynn		1
c. Silicon Tetrafluoride						
1953	-14.1	36.7		Kobe and Lynn		1
d. Tetrafluorohydrazine						
1958	36	77		Colburn and Kennedy	1, 17	102
1964	36.2	36.6		Kuznetsova, Egorova, and Pankratov	1	103
1964		33.6		Kuznetsova, Egorova, and Pankratov	16	103
Selected value	36.2	37				
e. <i>cis</i> -Difluorodiazine						
1959	-1			Colburn, <i>et al.</i>	?	104
f. <i>trans</i> -Difluorodiazine						
1959	-13			Colburn, <i>et al.</i>	?	104
g. Nitrogen Trifluoride						
1968	-39.3	44.7		Kudchadker, Alani, and Zwolinski		2
h. Difluoramine						
1959	130			Kudchadker, Alani, and Zwolinski		2
i. Phosphorus Trifluoride						
1939	-2.05	42.69		Booth and Bozarth	1	105
j. Oxygen Fluoride						
1952	-58.0			Anderson, <i>et al.</i>	1	107
k. Sulfur Tetrafluoride						
1960	90.9			Tulloch, <i>et al.</i>	1	108
l. Sulfur Hexafluoride						
1951	45.555		0.7517	Atack and Schneider	5	<i>a</i>
1951	45.547	37.113		MacCormack and Schneider	1	109
1951	45.5	36.8	0.727	Miller, Verdelli, and Gall	1, 16, 19	<i>b</i>
1955	45.58	37.10	0.734	Clegg, Rowlinson, and Sutton	1, 19	110
1956	45.642	37.193	0.725	Wentorf	1, 5	<i>c</i>
1960	45.55	37.04		Otto and Thomas	1	<i>d</i>
1966	45.63		0.741	Khodeeva	1, 19	111
1968	45.560	37.093	0.738	Markarevich, Sokolova, and Sorina	1, 19	112
1953	45.55	37.11	0.752	Kobe and Lynn		1
1968	45.55	37.11	0.734	Kudchadker, Alani, and Zwolinski		2
Selected value	45.55	37.10	0.736			
m. Niobium Pentafluoride						
1967	464	62	1.21	Pitt	8, 19	113
n. Uranium Hexafluoride						
1953	245			Llewellyn	1	114
1953	230.2	45.5		Oliver, Milton, and Grisard	8	115
1958	232.5		1.41	Brokaw	8, 19	116
1958	232.6			Whybrew, Tayman, and Kokulis	1	116
Selected value	232.5	46	1.41			

^a D. Atack and W. G. Schneider, *J. Phys. Colloid Chem.*, **55**, 532 (1951). ^b H. C. Miller, L. S. Verdelli, and J. F. Gall, *Ind. Eng. Chem.*, **43**, 1126 (1951). ^c R. H. Wentorf, *J. Chem. Phys.*, **24**, 607 (1956). ^d J. Otto and W. Thomas, *Z. Phys. Chem. (Frankfurt am Main)*, **23**, 84 (1960).

Kuznetsova, Egorova, and Pankratov¹⁰³ prepared N_2F_4 by reaction of NF_3 with mercury (99.99% pure). The reaction products were distilled three times at low temperatures. Spectrographic analysis using a IKS-14 spectrograph and chromatographic analysis using a molecular sieve column showed

(103) T. V. Kuznetsova, L. F. Egorova, and A. V. Pankratov, *Russ. J. Phys. Chem.*, **38**, 1014 (1964).

no impurities. Temperatures were measured with pentane and mercury thermometers having 0.1° divisions and by copper-constantan thermocouples. The critical pressure was measured with a standard manometer, the accuracy being ± 0.08 atm.

The critical temperatures reported by both sets of investigators agree quite well. The critical pressure of Colburn and Kennedy is contradictory to their vapor pressure equation

$[\log P_{\text{mm}} = (-692/T) + 6.33]$ because if one substitutes $T = T_c = 309^\circ\text{K}$ into equation, one predicts $P_c = 16$ atm.

The selected value of critical temperature is that of Kuznetsova, Egorova, and Pankratov, and the selected value of critical pressure is that of the same work, rounded off to the nearest atmosphere.

e and f. *cis*- and *trans*-Difluorodiazine¹⁰⁴

The difluorodiazines were prepared from the electrolysis of ammonium bifluoride. The *trans* isomer was purified by chromatography to an estimated purity of 99.7%. The *cis* isomer was purified by low temperature distillation to a minimum purity of 97.5% with a maximum impurity of 2.1%. Analysis was by mass spectroscopy. The method of measurement of the critical temperature was not described.

g and h. Nitrogen Trifluoride and Difluoramine

These compounds were reviewed by Kudchadker, Alani, and Zwolinski,² and no new data are available.

i. Phosphorus Trifluoride¹⁰⁵

This compound was prepared by fluorination of phosphorus trichloride. A large sample was distilled and the middle portion of the pure fraction used for the critical property measurements. Temperatures were measured¹⁰⁶ by a platinum resistance thermometer which had been calibrated at the boiling point of oxygen, the sublimation point of carbon dioxide, the freezing point of mercury, and the ice point and the normal boiling point of water. Pressures were measured by a dead weight gauge.

j. Oxygen Fluoride¹⁰⁷

OF_2 was prepared by treating fluorine with 3% NaOH solution. Primary purification was accomplished by cooling the sample with liquid O_2 and aspirating with a water pump. Final purification was done by distillation in a 3-ft. glass column tightly packed with $1/8$ -in. single turn glass helices. Distillation was carried out until the temperature was constant at -144° , one-fourth of the remaining liquid was then distilled and discarded, and one-half of the remainder was distilled and collected. Two iodometric analyses indicated 99.60 and 100.02% purity. An infrared analysis showed less than 0.1% SiF_4 and 0.002% CF_4 as the only impurities. Temperatures were measured with a five junction copper-constantan thermocouple and a potentiometer accurate to $10 \mu\text{V}$. All observations of both the disappearance and the appearance of the meniscus occurred within 0.1° .

k. Sulfur Tetrafluoride¹⁰⁸

No statement was given as to the source or the purity of the sulfur tetrafluoride. This is the only literature datum available.

l. Sulfur hexafluoride

Kudchadker, Alani, and Zwolinski² reviewed the data on this compound to 1960.

Khodeeva¹¹¹ used sulfur hexafluoride prepared by G. Sorina and which is apparently the same material used by Markarevich, Sokolova, and Sorina.¹¹² Temperatures were measured with a Beckmann thermometer with 0.01° divisions.

The sulfur hexafluoride used by Markarevich, Sokolova, and Sorina¹¹² was stated to be 99.995% pure. Temperatures were measured with a Beckmann thermometer with 0.01° divisions and stated to be accurate to 0.02° . Pressures were measured with a Type MOP-60 dead weight gauge to within 0.005 atm. Observations of the critical properties were made in a horizontal molybdenum glass tube of 9–10-mm internal diameter.

The values of t_c and P_c of Markarevich, Sokolova, and Sorina are in excellent agreement with the selected values of Kobe and Lynn¹ and Kudchadker, Alani, and Zwolinski.² The selected value of critical temperature remains the same, and the critical pressure is taken as the average value of McCormack and Schneider,¹⁰⁹ Clegg, Rowlinson, and Sutton,¹¹⁰ and Markarevich, Sokolova, and Sorina. The critical density is taken to be the average of the data of Clegg, Rowlinson, and Sutton and Markarevich, Sokolova, and Sorina, both of whom used the method of the rectilinear diameter.

m. Niobium Pentafluoride¹¹³

NbF_5 was prepared by reaction of 99+ % pure niobium with F_2 in a nickel vessel at 400° . The concentrations of B, Mn, Ni, Ca, Cu, Mg, and Si were determined by X-ray spectroscopy with the first three elements being present in less than 0.1 wt % and the last four elements being present in less than 0.01 wt %. Temperatures were measured with a chromel–alumel thermocouple and pressures were measured on a 0–3000 psi gauge.

n. Uranium Hexafluoride

Llewellyn¹¹⁴ purified UF_6 by adding carefully dried and degassed potassium fluoride to remove hydrogen fluoride. The chief impurities were then SiF_4 and freshly liberated HF. The UF_6 was then repeatedly distilled into reservoirs at -20° . An experimental determination of molecular weight gave 352 ± 1 compared with the calculated 352.1.

Oliver, Milton, and Grisard¹¹⁵ stated that the purity of their samples was estimated to be 99.75 mol % by mass spectra analysis that showed 0.01% fluorocarbon and 0.24% other volatiles and emission spectra that showed 0.005% nonvolatile impurities. Temperatures were measured with a certified platinum resistance thermometer. Pressures were compared against the vapor pressure of water (temperature measured with a certified platinum resistance thermometer), using helium as a buffer.

Whybrew, Tayman, and Kokulis¹¹⁶ used UF_6 prepared

(109) K. E. McCormack and W. G. Schneider, *Can. J. Chem.*, **29**, 699 (1951).

(110) H. P. Clegg, J. S. Rowlinson, and J. R. Sutton, *Trans. Faraday Soc.*, **51**, 1327 (1955).

(111) S. M. Khodeeva, *Russ. J. Phys. Chem.*, **40**, 1061 (1966).

(112) L. A. Markarevich, E. S. Sokolova, and G. A. Sorina, *ibid.*, **42**, 10 (1968).

(113) W. W. Pitt, *U. S. At. Energy Comm.*, ORNL-7M-1683, CRSTI (1967).

(114) D. R. Llewellyn, *J. Chem. Soc.*, 28 (1953).

(115) G. D. Oliver, H. T. Milton, and J. W. Grisard, *J. Amer. Chem. Soc.*, **75**, 2827 (1953).

(116) P. H. Abelson, Ed., *U. S. At. Energy Comm.*, TID-5229 (1958).

(117) E. Mathias, "Le point critique des corps purs," Paris, 1904.

(118) C. Dorsman, Dissertation, Amsterdam, 1908.

(104) C. B. Colburn, F. A. Johnson, A. Kennedy, K. McCallum, L. C. Metzger, and C. D. Parker, *J. Amer. Chem. Soc.*, **81**, 6397 (1959).

(105) H. S. Booth and A. R. Bozarth, *ibid.*, **61**, 2927 (1939).

(106) H. S. Booth and C. F. Swinehart, *ibid.*, **57**, 1337 (1935).

(107) R. Anderson, J. G. Schnizlein, R. C. Toole, and T. D. O'Brien, *J. Phys. Colloid Chem.*, **56**, 233 (1952).

(108) C. W. Tullock, F. S. Fawcett, W. C. Smith, and D. D. Coffman, *J. Amer. Chem. Soc.*, **82**, 539 (1960).

Table X

Chlorides

Year	t_0 , °C	P_0 , atm	d_0 , g/cm ³	Investigators	Method	Ref
a. Hydrogen Chloride						
1904			0.462	Mathias	19	117
1908	51.0	81.5	0.423	Dorsman	1	118
1912	51.4	81.55		Cardoso and Germann	3	119
1913	51.4			Estreicher and Schnerr	1	<i>a</i>
1913	51.1	80.49		Drozdowski and Pietrzak	?	<i>b</i>
1936	51.0			Kopper	1	11
1962	51.5	81.5	0.45	Franck, Brose, and Mangold	16	120
1962	51.54	82.0		Thomas	1	121
1953	51.4	81.5	0.42	Kobe and Lynn		1
Selected value	51.5	82.0	0.45			
b. Deuterium Chloride						
1936	50.3			Kopper	1	11
c. Boron Trichloride						
1953	178.8	38.2		Kobe and Lynn		1
d. Aluminum Trichloride						
1914	356.4			Rotinjanz and Suchodski	1	122
1969	352.5	26	0.510	Denisova and Baskova	1, 19	123
Selected value	352.5	26	0.510			
e. Trichlorosilane						
1967	206.0			Nisel'son, Sokolova, and Lapidus	1, 19	124
f. Silicon Tetrachloride						
1861	230.0			Mendelejeff	1	125
1927	233.6			Parker and Robinson	1	126
1958		37.1		Menzer	15	127
1967	234.0		0.521	Nisel'son, Sokolova, and Lapidus	1, 19	124
1953	233			Kobe and Lynn		1
Selected value	234	37	0.521			
g. Germanium Tetrachloride						
1887	276.9	38		Nilson and Patterson	1	128
1967	279.0		0.65	Nisel'son, Sokolova, and Pugachevich	1, 19	129
Selected value	279	38	0.65			
h. Stannic Chloride						
1953	318.7	37.0	0.742	Kobe and Lynn		1
i. Phosphorus Trichloride						
1883	285.5			Powlewski	1	130
1965	290.0		0.520	Nisel'son, Mogucheveva and Sokolova	1, 19	130
Selected value	290		0.52			
j. Arsenic Trichloride						
1965	318.3		0.720	Nisel'son, Mogucheveva, and Sokolova	1, 19	130
k. Antimony Trichloride						
1914	524			Rotinjanz and Suchodski	1	122
1939	523		0.814	Zhuravlev	1, 19	131
1965	520.9		0.842	Nisel'son, Mogucheveva, and Sokolova	1, 19	130
Selected value	521		0.84			
l. Bismuth Chloride						
1964	905	118.1 ± 4	1.210	Johnson and Cubicciotti	1, 19	132
m. Titanium Tetrachloride						
1958		45.7		Menzer	15	127
1967	365.0		0.565	Nisel'son and Tret'yakova	1, 19	133
Selected value	365	46	0.56			
n. Zirconium Tetrachloride						
1961	499		1.33	Nisel'son	1, 19	134
1962	503.5		0.76	Nisel'son and Sokolova	1, 19	135
1967	505.0	56.9	0.730	Denisova, <i>et al.</i>	1, 19	136
Selected value	505	56.9	0.730			
o. Hafnium Tetrachloride						
1961	445		0.905	Nisel'son	1, 19	134
1962	452.5		1.06	Nisel'son and Sokolova	1, 19	135

Table X (Continued)

Year	$t_c, ^\circ\text{C}$	P_c, atm	$d_c, \text{g/cm}^3$	Investigators	Method	Ref
1967	449.2	57.0	1.05	Denisova, <i>et al.</i>	1, 19	136
Selected value	450	57.0	1.05			
				p. Niobium Pentachloride		
1964	534		0.68	Nisel'son, Pustil'nik, and Sokolova	1, 19	138
				q. Tantalum Pentachloride		
1964	494		0.89	Nisel'son, Pustil'nik, and Sokolova	1, 19	138
				r. Molybdenum Pentachloride		
1965	577.0		0.74	Nisel'son and Sokolova	1, 19	139
				s. Tungsten Hexachloride		
1965	650.0		0.94	Nisel'son and Sokolova	1, 19	139
				t. Mercuric Chloride		
1914	703			Rotinjanz and Suchodski	1	140
1920	704			Rassow	1	70
1966	699		1.555	Johnson, Silva, and Cubicciotti	1, 19	141
Selected value	700		1.56			

^a T. Estreicher and A. Schnerr, *Z. Kompr. Fluss. Gase*, **15**, 161 (1913). ^b E. Drozdowski and J. Pietrzak, *Bull. Int. Acad. Sci. Cracovie*, **4A**, 219 (1913).

from the fluorination of UF_4 . The UF_6 was contained in a metal tube and viewed by an X-ray apparatus and fluorescent screen. The meniscus was seen at 232.4° and not seen at 232.6° at a density of 1.47 g/cm^3 .

Brokow¹¹⁶ presumably used the same UF_6 as Whybrew, Tayman, and Kokulis.

Llewellyn's value for the critical temperature appears to be erroneous. If one looks at the P vs. T plot given by Oliver, Milton, and Grisard it appears, from the sharpness at which the single phase curve departs from the vapor pressure curve, that they were at a density considerably greater than critical (their only datum) and hence one would expect an indicated temperature lower than the critical value. Therefore, the value of 232.5° of Brokow, which fits in the range between the observation and nonobservation of the meniscus of Whybrew, Tayman, and Kokulis, is selected as the critical temperature.

2. Chlorides (Table X)

a. Hydrogen Chloride

Kobe and Lynn¹ discarded the data published before 1908 and selected the data of Cardoso and Germann¹¹⁹ for the critical temperature and pressure and the datum of Dorsman,¹¹⁸ rounded off to two figures, for the critical density.

The hydrogen chloride used by Franck, Brose, and Mangold¹²⁰ was supplied by BASF, Ludwigshafen, and stated by the manufacturer to be 99.9% pure with the remaining 0.2% (*sic*) inert gases predominantly hydrogen. This material was condensed into a small steel cylinder and the gas phase pumped off repeatedly until the vapor pressures at 0.6 and 20.7° agreed with the data of Cardoso and Germann within 0.4 atm. Specific heat and PVT data were obtained and orthobaric densities were derived from breaks in the curves of specific heat and pressure as functions of temperature. Temperatures for the specific heat data were measured with a calibrated platinum resistance thermometer and temperatures for the

PVT data were measured with calibrated Pt-PtRh thermocouples. Pressures were measured with Bourdon gauges calibrated against a dead weight gauge and stated to be correct to 1.5%.

Thomas¹²¹ used hydrogen chloride supplied by the same manufacturer as in the preceding. This material was stated to be 99.7% (wt) pure with the impurities being hydrogen, nitrogen, and carbon monoxide. The sample was fractionally distilled several times and then frozen in liquid air, and the residual vapor and gas were pumped off. The sample introduced to the Pyrex sample bomb was dried by passing it through a tube cooled by a solid CO_2 -alcohol mixture. The HCl was then frozen with liquid air and subjected to evacuation to a pressure of nearly 0.1 mm, reheated, refrozen, and reevacuated, this process being repeated several times. Vapor pressures were measured to 49° and the $\log P = A - [B/(T + C)]$ equation extrapolated to the visually determined critical temperature of 51.54° . The critical temperature was determined at a sample density of 0.42 g/cm^3 .

Edwards¹⁰ concludes that the data of Thomas gives the best deviation curve for the vapor pressure and calculates a critical pressure 82.07 atm at a critical temperature of 51.54° . The critical densities of Mathias¹¹⁷ and Franck, Brose, and Mangold agree within experimental error. The data of Thomas are selected for the critical temperature and critical pressure, and the datum of Franck, Brose, and Mangold is selected as the critical density.

b. Deuterium Chloride

Kopper's¹¹ work is described in section V.C.

c. Boron Trichloride

No new work has been reported since Kobe and Lynn.¹

d. Aluminum Trichloride

Rotinjanz and Suchodski¹²² measured temperatures with a Pt-PtRh thermocouple calibrated at the ice point, boiling

(119) E. Cardoso and A. F. O. Germann, *J. Chim. Phys.*, **10**, 517 (1912).

(120) *Progr. Intern. Res. Thermodyn. Transp. Prop., Pap. Symp. Thermophys., 2nd, Princeton, N. J., 1962*, 159 (1962).

(121) Reference 120, p 166.

(122) L. Rotinjanz and W. Suchodski, *Z. Phys. Chem.*, **87**, 635 (1914).

point of water, and the melting points of zinc, antimony, and silver.

Denisova and Baskova¹²³ used "chemically pure" anhydrous aluminum trichloride and further purified it by two to three vacuum sublimations in the presence of granulated zinc or aluminum filings. The maximum impurity content was stated to be 0.001%. Experimental details may be found in the discussion of zirconium tetrachloride under Denisova, *et al.*

The newer results of Denisova and Baskova are selected as the most probable values.

e. Trichlorosilane¹²⁴

The trichlorosilane used in this work was purified by high-efficiency distillation with a midcut of the purest fraction being the final sample. Experimental details were those reported under zirconium tetrachloride (Nisel'son and Sokolova¹³⁵) except that the sample tubes could be rotated during observations of the critical region, to minimize gravitational effects.

f. Silicon Tetrachloride

Kobe and Lynn¹ rejected the data of Mendelejeff¹²⁵ on the basis of impurity of sample.

Parker and Robinson¹²⁶ prepared silicon tetrachloride by chlorination of ferrosilicon. The crude sample was purified by distillation, stored over sodium amalgam for 2 months, and fractionally distilled under vacuum before use.

The article by Menzer¹²⁷ gave no details other than that the critical pressure was determined by the method of Altschul.

The work of Nisel'son, Sokolova, and Lapidus¹²⁴ is discussed in the preceding section.

The critical temperatures measured by Parker and Robinson and by Nisel'son, Sokolova, and Lapidus agree within experimental accuracy and so the selected value for critical temperature is taken as the average of the two results.

g. Germanium Tetrachloride

The work of Nilson and Patterson¹²⁸ was reviewed by Kobe and Lynn.¹

Nisel'son, Sokolova, and Pugachevich¹²⁹ purified germanium tetrachloride by rectification on an efficient column, a center cut of the purest fraction being used. Near the critical region the furnace containing the block and ampoule was rotated by a special device to reduce gravitational effects. Otherwise the experimental details are those of Nisel'son and Sokolova,¹³⁵ discussed under zirconium tetrachloride.

The critical temperature datum of Nisel'son, Sokolova, and Pugachevich is selected as more is known about their work than the much earlier work on this compound.

h. Stannic Chloride

No new work has been reported since Kobe and Lynn.¹

(123) N. D. Denisova and A. P. Baskova, *Russ. J. Phys. Chem.*, **43**, 1317 (1969).

(124) L. A. Nisel'son, T. D. Sokolova, and I. I. Lapidus, *Russ. J. Inorg. Chem.*, **12**, 752 (1967).

(125) D. Mendelejeff, *Justus Liebig's Ann. Chem.*, **119**, 1 (1861).

(126) T. W. Parker and D. L. Robinson, *J. Chem. Soc.*, 1977 (1927).

(127) W. Menzer, *Naturwissenschaften*, **45**, 126 (1958).

(128) L. F. Nilson and O. Patterson, *Z. Phys. Chem.*, **1**, 27 (1887).

(129) L. A. Nisel'son, T. D. Sokolova, and P. P. Pugachevich, *Russ. J. Inorg. Chem.*, **12**, 306 (1967).

i. Phosphorus Trichloride

Nisel'son, Mogucheva, and Sokolova¹³⁰ prepared PCl_3 by the chlorination of phosphorus and purified the sample by fractional distillation. Details of their experimental procedure may be found in the discussion for zirconium tetrachloride. The reference to Powlewsky was found in this article.

The critical values of Nisel'son, Mogucheva, and Sokolova are selected as the most probable.

j. Arsenic Trichloride

Nisel'son, Mogucheva, and Sokolova¹³⁰ prepared arsenic trichloride by chlorinating arsenic and purified the sample by fractional distillation. For a discussion of their experimental technique see the section under zirconium tetrachloride.

k. Antimony Trichloride

For a discussion of the technique of Rotinjanz and Suchodski,¹²² see the discussion under aluminum trichloride.

Zhuravlev¹³¹ prepared antimony trichloride by the reaction of chlorine with metallic antimony. The sample was then subjected to three distillations and one sublimation. The product was constant boiling at 224.0° (under atmospheric pressure).

Nisel'son, Mogucheva, and Sokolova¹³⁰ prepared antimony trichloride by the chlorination of antimony and purified it by fractional distillation. For their experimental technique, see the discussion under zirconium tetrachloride.

The newer experimental data of Nisel'son, Mogucheva, and Sokolova are selected for antimony trichloride.

l. Bismuth Chloride

Johnson and Cubicciotti¹³² prepurified bismuth chloride by distillation under an atmosphere of HCl. It was then distilled into quartz tubes in an atmosphere of dry HCl and inert gas. The tubes were then evacuated to remove residual gas and sealed off under vacuum. Temperatures were measured by a Pt-PtRh thermocouple which was compared with another Pt-PtRh thermocouple calibrated by the NBS. In the critical region high heat losses from the sample tubes precluded continual observation of the meniscus. Thus temperatures were recorded when the meniscus was absent and present, and an average value was taken as the critical temperature. This is one reason for the rather high uncertainty of the stated value. Vapor pressures above 250 psi were measured with a Bourdon gauge which could be read to 0.1 atm and were recorded up to 902°. A vapor pressure equation of the form $\log P = A - B/T$ was then extrapolated to the critical temperature.

m. Titanium Tetrachloride

The article by Menzer¹²⁷ gave no details other than that the critical pressure was determined by the method of Altschul.

The TiCl_4 used by Nisel'son and Tret'yakova¹³³ was purified by high frequency rectification. For experimental details, see the discussion for zirconium tetrachloride under Nisel'son and Sokolova.¹³⁵

(130) L. A. Nisel'son, V. V. Mogucheva, and T. D. Sokolova, *ibid.*, **10**, 320 (1965).

(131) D. I. Zhuravlev, *Zh. Fiz. Khim.*, **13**, 684 (1939).

(132) (a) J. W. Johnson, and D. Cubicciotti, *J. Phys. Chem.*, **68**, 2235 (1964); (b) *ibid.*, **69**, 3916 (1965).

(133) L. A. Nisel'son and K. V. Tret'yakova, *Russ. J. Inorg. Chem.*, **12**, 452 (1967).

n. Zirconium Tetrachloride

Nisel'son¹³⁴ and Nisel'son and Sokolova¹³⁵ prepared the halide from elemental zirconium which originally contained less than 0.05% Hf and other impurities (Al, Fe, Ti) each less than or equal to 0.01%. The metal was then reacted with dry halogen and the tetrahalide purified by resublimation in sealed ampoules containing filings of Armco iron. During the resublimation, the middle 85–90% of the charge was collected. Nisel'son and Sokolova measured temperatures with a chromel–alumel thermocouple which had been calibrated at the melting points of Zn (419.5°) and Al (659.6°), all of >99.99% purity. Temperatures are believed accurate to $\pm 0.05^\circ$. Ampoules 2–3 cm long were used to reduce gravitational effects in the critical region.

Denisova, Safronov, Pustil'nik, and Bystrova¹³⁶ prepared and purified zirconium tetrachloride in the same manner as Nisel'son. It was stated that the final halide contained iron, silicon, titanium, and aluminum at the 0.001% level. Temperatures were measured¹³⁷ with chromel–alumel thermocouples to a stated accuracy of $\pm 0.5^\circ$. Pressures were measured with a Type MOP-60 dead weight gauge. The visual tube was mounted horizontally (i.d. 9–10 mm) to minimize gravitational effects.

In selecting values for the critical temperature and the critical density, slightly more weight is assigned to the work of Denisova, *et al.*, because their equipment was better designed to minimize gravitational effects.

o. Hafnium Tetrachloride

Nisel'son and Sokolova¹³⁵ prepared HfCl₄ by chlorination of metallic hafnium which itself was made by calciothermic reduction of hafnium dioxide and contained ~ 0.3 –0.2% ZrO₂, the other impurities in the metal being ~ 0.01 %. The chlorination was by dry chlorine in a quartz tube under an atmosphere of pure dry argon. The HfCl₄ was purified by resublimation in sealed ampoules from filings of Armco iron, the latter assisting in the removal of iron impurities by converting it to the less volatile bivalent form. During the sublimation the center fraction amounting to 85–90% of the charge was retained. Experimental details were discussed under zirconium tetrachloride.

Denisova, Safronov, Pustil'nik, and Bystrova¹³⁶ prepared hafnium tetrachloride by the chlorination of metallic hafnium containing less than 0.5% of zirconium. The sample was purified by fourfold sublimation in evacuated and sealed glass ampoules. The concentration of iron, silicon, titanium, aluminum, and other impurities was at the 0.001% level. Experimental details were discussed under zirconium tetrachloride.

In selecting values for critical temperature and critical density slightly more weight is assigned to the latter's¹³⁶ work because their equipment was better designed to minimize gravitational effects.

p. Niobium Pentachloride¹³⁸

Niobium pentachloride was purified by distillation and the fraction collected contained less than 0.2% impurities. For

details of the experimental apparatus for determining the critical properties see the discussion for zirconium tetrachloride under Nisel'son and Sokolova.¹³⁵

q. Tantalum Pentachloride¹³⁸

Tantalum pentachloride was purified by distillation, and the fraction which was retained contained less than 0.02% impurities. Experimental details for the critical property determination are given in the discussion for zirconium tetrachloride under Nisel'son and Sokolova.¹³⁵

r. Molybdenum Pentachloride¹³⁹

Nisel'son and Sokolova prepared MoCl₅ by chlorination of molybdenum and purified the sample by rectification on a sieve-plate column. They stated that the main impurities had a concentration below the sensitivity of their analytical methods, quoted as "hundredths and thousandths of 1%." For the experimental details of the methods used by these authors, see the discussion of zirconium tetrachloride. The values of critical constants of MoCl₅ were regarded as somewhat provisional by the authors because of low thermal stability at high temperatures.

s. Tungsten Hexachloride¹³⁹

For details of the purification of WCl₆, see the discussion for molybdenum pentachloride. For details of the determination of the critical properties, see the discussion for zirconium tetrachloride under Nisel'son and Sokolova.¹³⁵

t. Mercuric Chloride

The experimental method of Rotinjanz and Suchodski¹⁴⁰ is discussed in part d of this section.

No details of purity were given by Rassow.⁷⁰

In the work of Johnson, Silva, and Cubicciotti,¹⁴¹ analyzed reagent HgCl₂ was recrystallized from a 0.05 N HCl solution, and the crystals were dried in a vacuum desiccator with continuous pumping for 72 hr with an ultimate pressure of 5×10^{-3} mm for the last 24 hr. A chemical analysis showed 73.8% Hg and 26.13% Cl as compared with theoretical values of 73.88 and 26.12%, respectively. The measured melting point was $280.7 \pm 0.5^\circ$.

There is remarkably good agreement among all the values of critical temperature considering the difficulties inherent in working at such elevated temperatures. The selected value is an "average" of the reported data with somewhat more weight on the more modern work of Johnson, Silva, and Cubicciotti.

3. Bromides (Table XI)

a. Hydrogen Bromide

No new work has been reported since Kobe and Lynn,¹ but the work of Kopper¹¹ needs to be added to the tabulation. Kopper's work is discussed in section V.C.

Edwards¹⁰ found that the set of data by Drozdowski and Pietrzak¹⁴² was the most self-consistent, and hence their values

(134) L. A. Nisel'son, *ibid.*, 6, 635 (1961).

(135) L. A. Nisel'son and T. D. Sokolova, *ibid.*, 7, 1382 (1962).

(136) N. D. Denisova, E. K. Safronov, A. I. Pustil'nik, and O. N. Bystrova, *Russ. J. Phys. Chem.*, 41, 30 (1967).

(137) G. A. Sorina and G. D. Efreanova, *ibid.*, 40, 143 (1966).

(138) L. A. Nisel'son, A. I. Pustil'nik, and T. D. Sokolova, *Russ. J. Inorg. Chem.*, 9, 574 (1964).

(139) L. A. Nisel'son and T. D. Sokolova, *ibid.*, 10, 9 (1965).

(140) L. Rotinjanz and W. Suchodski, *Z. Phys. Chem.*, 87, 253 (1914).

(141) J. W. Johnson, W. J. Silva, and D. Cubicciotti, *J. Phys. Chem.*, 70, 1169 (1966).

(142) E. Drozdowski and J. Pietrzak, *Bull. Int. Acad. Sci. Cracovie*, 4A, 219 (1913).

Table XI

Bromides

Year	t_0 , °C	P_0 , atm	d_0 , g/cm ³	Investigators	Method	Ref
a. Hydrogen Bromide						
1896	90.8			Estreicher	1	<i>a</i>
1913	91.07			Estreicher and Schnerr	1	<i>b</i>
1913	90.00	84.44		Drozdowski and Pietrzak	?	142
1919	89.80	84.00		Moles	3, 17	<i>c</i>
1936	89.9			Kopper	1	11
1953	90.0	84.0		Kobe and Lynn	1	1
Selected value	90.0	84.4				
b. Deuterium Bromide						
1936	88.8			Kopper	1	11
c. Boron Tribromide						
1953	300		0.90	Kobe and Lynn		1
d. Aluminum Tribromide						
1914	499			Rotinjanz and Suchodski	1	122
1937	495	26.7	0.8775	Zhuravlev	1, 16, 19	143
1968	490	28.5	0.8605	Johnson, Silva, and Cubicciotti	1, 16, 19	144
Selected value	490	28.5	0.860			
e. Tribromosilane						
1967	336.0			Nisel'son, Sokolova, and Lapidus	1	124
f. Silicon Tetrabromide						
1967	390.0			Nisel'son, Sokolova, and Lapidus	1	124
g. Antimony Tribromide						
1914	631.4			Rotinjanz and Suchodski	1	122
h. Bismuth Bromide						
1965	945		1.487	Johnson, Cubicciotti, and Silva	1, 16, 19	145
i. Zirconium Tetrabromide						
1962	532		0.97	Nisel'son and Sokolova	1, 19	135
j. Hafnium Tetrabromide						
1962	473		1.20	Nisel'son and Sokolova	1, 19	135
k. Niobium Pentabromide						
1964	736.0		1.05	Nisel'son and Sokolova	1, 19	146
l. Tantalum Pentabromide						
1964	700.0		1.26	Nisel'son and Sokolova	1, 19	146
m. Mercuric Bromide						
1914	738			Rotinjanz and Suchodski	1	140
1920	738			Rassow	1	70

^a T. Estreicher, *Z. Phys. Chem.*, **20**, 605 (1896). ^b T. Estreicher and A. Schnerr, *Z. Komps. Fluss. Gase*, **15**, 161 (1913). ^c E. Moles, *J. Chim. Phys.*, **17**, 419 (1919).

are selected, rounded off to one less significant figure than reported.

b. Deuterium Bromide

Kopper's¹¹ work is discussed in section V.C.

c. Boron Tribromide

No new work has been reported since Kobe and Lynn.¹

d. Aluminum Tribromide

The work of Rotinjanz and Suchodski¹²² is discussed in section V.F.3.d.

Zhuravlev¹⁴³ extrapolated a vapor pressure equation of the form $\log P = A + B/T$ from 490 to 495°. The rectilinear diameter was expressed in a quadratic form.

(143) D. I. Zhuravlev, *Zh. Fiz. Khim.*, **10**, 325 (1937).

Johnson, Silva, and Cubicciotti¹⁴⁴ used Fisher certified reagent AlBr₃. This material was evacuated overnight at room temperature and then sublimated at 70° through a sintered glass filter until one-half the original material was collected; then the remainder was discarded. A bromine analysis indicated 89.95% bromine compared with the theoretical value of 89.88%.

e and f. Tribromosilane¹²⁴ and Silicon Tetrabromide¹²⁴

The work of Nisel'son, Sokolova, and Lapidus¹²⁴ is discussed in section V.F.2.e.

g. Antimony Tribromide

The work of Rotinjanz and Suchodski¹²² is discussed in section V.F.2.d.

(144) J. W. Johnson, W. J. Silva, and D. Cubicciotti, *J. Phys. Chem.*, **72**, 1664 (1968).

Table XII

Iodides

Year	t_c , °C	P_c , atm	d_c , g/cm ³	Investigators	Method	Ref
a. Hydrogen Iodide						
1896	150.5			Estreicher	1	<i>a</i>
1913	150.8			Estreicher and Schnerr	1	<i>b</i>
1913	150.0	80.8		Drozdowski and Pietrzak	?	142
1936	150.7			Kopper	1	11
1953	150	81		Kobe and Lynn	1	1
Selected value	150.7	82				
b. Deuterium Iodide						
1936	148.6			Kopper	1	11
c. Aluminum Triiodide						
1914	682			Rotinjan and Suchodski	1	122
d. Antimony Triiodide						
1914	828			Rotinjan and Suchodski	1	122
e. Zirconium Tetraiodide						
1962	686		1.13	Nisel'son and Sokolova	1, 19	146
f. Hafnium Tetraiodide						
1962	643		1.30	Nisel'son and Sokolova	1, 19	146
g. Mercuric Iodide						
1914	799			Rotinjan and Suchodski	1	140
1920	797			Rassow	1	70
Selected value	798					

^a T. Estreicher, *Z. Phys. Chem.*, **20**, 605 (1896). ^b T. Estreicher and A. Schnerr, *Z. Kamps. Fluss. Gase*, **15**, 161 (1913).

Table XIII

Mixed Halides

Year	t_c , °C	P_c , atm	d_c , g/cm ³	Investigators	Method	Ref
a. Chlorine Pentafluoride						
1968	143.0			Rogers, <i>et al.</i>	1	147
1968	142.6	51.9	0.565	Rogers, <i>et al.</i>	8, 16, 19	147
Selected value	143	52	0.56			
b. Chlorotrifluorosilane						
1953	34.5	34.2		Kobe and Lynn		1
c. Dichlorodifluorosilane						
1953	95.8	34.5		Kobe and Lynn		1
d. Trichlorofluorosilane						
1953	165.3	35.3		Kobe and Lynn		1
e. Nitrogen Chloride Difluoride						
1968	64.3	50.8		Kuznetsova, Egorova, and Pankratov	1, 16	148
f. Difluoromonochlorophosphine						
1939	89.17	44.61		Booth and Bozarth	1	105
g. Monofluorodichlorophosphine						
1939	189.84	49.3		Booth and Bozarth	1	105

h. Bismuth Bromide¹⁴⁵

Bismuth bromide was prepurified by three distillations under an oxygen atmosphere and then distilled into quartz tubes under a dry oxygen atmosphere, the oxygen then being removed by evacuation. The rest of the experimental details are discussed in section V.F.2.e.

i-l. Zirconium Tetrabromide,¹⁴⁶ Hafnium Tetrabromide,¹⁴⁶ Niobium Pentabromide,¹⁴⁶ and Tantalum Pentabromide¹⁴⁶

The work of Nisel'son and Sokolova^{146,146} is discussed in section V.F.2.n.

(145) J. W. Johnson, D. Cubicciotti, and W. J. Silva, *ibid.*, **69**, 1989 (1965).

(146) L. A. Nisel'son and T. D. Sokolova, *Russ. J. Inorg. Chem.*, **9**, 1117 (1964).

Table XIV

Oxyhalides

Year	$t_c, ^\circ\text{C}$	P_c, atm	$d_c, \text{g/cm}^3$	Investigators	Method	Re
				1. Nitryl Fluoride		
1955	76.3			Hetherington and Robinson	1	149
				2. Phosgene		
1953	182	56	0.52	Kobe and Lynn		1
				3. Nitrosyl Chloride		
1910	167			Briner and Pylkoff	1	150
				4. Vanadium Oxychloride		
1967	363.5		0.600	Nisel'son and Tret'yakova	1, 19	133
				5. Tungsten Oxide Tetrachloride		
1967	509		1.01	Nisel'son, Nikolaev, and Onshanskaya	1, 19	151
				6. Rhenium Oxide Tetrachloride		
1967	508.5		0.95	Nisel'son, Nikolaev, and Onshanskaya	1, 19	151
				7. Perchloryl Fluoride		
1955	95.9		0.637	Engelbrecht and Atzwanger	1, 19	152
1957	95.18	53.0		Jarry	1, 17	153
1968	95.2	53.0		Kudchadker, Alani, and Zwolinski		2
Selected value	95.2	53.0	0.637			

m. Mercuric Bromide

Rotinjanz and Suchodski¹²² obtained mercuric bromide from Kahlbaum and repurified it by vacuum resublimation. Other experimental details are given under section V.F.2.d.

No details of sample purity are given by Rassow.⁷⁰

4. Iodides (Table XII)

a. Hydrogen Iodide

No new work has been reported since Kobe and Lynn,¹ but Kopper's¹¹ datum needs to be added to the tabulation. Kopper's work is discussed in section V.C.

Edwards¹⁰ finds the vapor pressure data of Drozdowski and Pietrzak¹⁴² inconsistent in the critical region. Using Kopper's value for critical temperature, he estimates a critical pressure of 81.9 atm. Kopper's value for critical temperature and Edwards' calculated critical pressure (rounded off to the nearest atmosphere) are selected as the most probable.

b. Deuterium Iodide¹¹

Kopper's work is discussed in section V.C.

c and d. Aluminum Triiodide¹²² and Antimony Triiodide¹²²

The work of Rotinjanz and Suchodski is discussed in section V.F.2.d.

e and f. Zirconium Tetraiodide¹⁴⁶ and Hafnium Tetraiodide¹⁴⁶

The work of Nisel'son and Sokolova is discussed in section V.F.2.n.

g. Mercuric Iodide

Rotinjanz and Suchodski¹⁴⁰ obtained their sample from Kahlbaum and repurified it by vacuum resublimations. They

encountered difficulty in seeing the meniscus because of the deep reddish-brown color of this compound.

No details of sample purity were given by Rassow.⁸⁴

An average value of the two datum points, which is within the uncertainty stated by Rotinjanz and Suchodski ($\pm 3^\circ$), is selected as the probable critical temperature.

5. Mixed (Table XIII)

a. Chlorine Pentafluoride¹⁴⁷

Chlorine pentafluoride was prepared by the fluorination of alkali metal chlorotetrafluorides and passed over sodium fluoride to remove HF. A sample assay showed greater than 99% (wt) of ClF₅ in the final material. Temperatures were measured with a chromel-alumel thermocouple calibrated at the freezing and boiling points of water. Pressures were measured with Strathan pressure transducers calibrated with a Heise Bourdon gauge. Vapor pressures were measured to 140.1° and an extrapolation of log *P* vs. 1/*T* was made to the critical temperature of 142.6°.

b-d. Chlorotrifluorosilane, Dichlorodifluorosilane, and Trichlorofluorosilane

No new work has been reported on these substances since Kobe and Lynn.¹

e. Nitrogen Chloride Difluoride¹⁴⁸

Kuznetsova, Egorova, and Pankratov prepared ClNF₂ by joint fluorination and chlorination of sodium azide. The compound was rectified and then purified chromatographically on a preparative column. Chromatographic, spectroscopic, and mass spectroscopic analysis of the purified material showed 100% ClNF₂. The sample was repurified chromatographically

(147) H. H. Rogers, M. T. Constantine, J. Quaglino, H. E. Dubb, and N. N. Ogimachi, *J. Chem. Eng. Data*, **13**, 307 (1968).

(148) T. V. Kuznetsova, L. F. Egorova, and A. V. Pankratov, *Russ. J. Inorg. Chem.*, **13**, 1189 (1968).

Table XV
Miscellaneous

Year	t_c , °C	P_c , atm	d_c , g/cm ³	Investigators	Method	Ref
1. Diborane						
1948	16.7	39.5		Newkirk	1	154
1958	16.6			Paridon, MacWood, and Hu	See text	155
Selected value	16.6	40				
2. Phosphine						
1887	54.0	70.5		Skinner	1	<i>a</i>
1898	52.8	64.0		Leduc and Sacerdote	1	<i>b</i>
1906	51.3	64.5		Briner	1	<i>c</i>
1936	51.9			Kopper	1	11
1953	51.3	64.5		Kobe and Lynn		1
Selected value	51.6	64.5				
3. Phosphonium Chloride						
1953	49.1	72.7		Kobe and Lynn		1
4. Phosphonitrilic Fluoride						
a. Trimer						
1963	187.7			Cheng and McCoubrey	1	156
b. Tetramer						
1963	223.2			Cheng and McCoubrey	1	156
c. Pentamer						
1962	250.8			Cheng and McCoubrey	1	156
5. Arsine						
1936	99.9			Kopper	1	11

^a S. Skinner, *Proc. Roy. Soc.*, **42**, 283 (1887). ^b M. A. Leduc, *Ann. Chim. Phys.*, **15**, 1 (1898). ^c J. Briner, *J. Chim. Phys.*, **4**, 476 (1906).

immediately before use because of gradual decomposition to N₂F₄ and Cl₂.

f. Phosphorus(III) Chloride Difluoride¹⁰⁵

This compound was prepared by the fluorination of phosphorus trichloride and purified by fractional distillation in an automatic column. A chemical analysis showed 33.88% (wt) chlorine and 29.49% (wt) phosphorus compound with calculated values of 33.94 and 29.69%, respectively.

Experimental details are discussed in section V.F.1.i.

g. Phosphorus(III) Dichloride Fluoride¹⁰⁵

This compound was prepared by the fluorination of phosphorus trichloride and purified by fractional distillation. Experimental details are given in section V.F.1.i.

G. OXYHALIDES (TABLE XIV)

1. Nitryl Fluoride¹⁴⁹

Hetherington and Robinson prepared NO₂F by fluorinating sodium nitrite and fractionating the sample several times under vacuum to remove the volatile impurities. It was stored and fractionated again immediately before use and kept in the apparatus for the shortest possible time. Temperature measurement was stated to be accurate to ±0.2°, but no details were given.

2. Phosgene

No new work has been reported since Kobe and Lynn.¹

3. Nitrosyl Chloride¹⁵⁰

NOCl was prepared by reaction of Cl₂ with NO and by reaction of nitrosyl sulfate with sodium chloride. It was purified by a series of recrystallizations and fractional distillations and passed through "pentoxide" to remove water. An analysis showed 65.51% chlorine which is the same as the calculated percentage. The measured normal boiling point was -5.5°. Observation of the meniscus was made difficult by the appearance of a dark color at high temperatures. The error in measurement of T_c is thus given as ±2°.

4. Vanadium Oxychloride¹³³

VOCl₃ was purified by high frequency rectification. For experimental details see the discussion for zirconium tetrachloride, section V.F.2.n, under Nisel'son and Sokolova.¹³⁵

5. Tungsten Oxide Tetrachloride¹⁵¹

WOCl₄ was prepared by the reaction of WO₃ and WCl₅ and was purified in a sieve plate column with the final central fraction having impurities below the 0.001% level. Experimental data may be found in the discussion for zirconium tetrachloride, section V.F.2.n, under Nisel'son and Sokolova.¹³⁵

6. Rhenium Oxide Tetrachloride¹⁵¹

ReOCl₄ was prepared by the reaction of ReCl₅ with dry oxygen and purified in a sieve plate column with the final central fraction having impurities below the 0.001% level. Experimental

(150) M. E. Briner and Z. Pytkoff, *J. Chim. Phys.*, **10**, 640 (1912).

(151) L. A. Nisel'son, R. K. Nikolaev, and Z. N. Onshanskaya, *Russ. J. Inorg. Chem.*, **12**, 453 (1967).

(149) G. Hetherington and P. L. Robinson, *J. Chem. Soc.*, 2230 (1955).

Table XVI
Summary of Selected Critical Properties^a

Formula	Substance	Mol wt	Critical temperature				Critical pressure Atm	Critical pressure lb _f /in. ²	Critical density g/cm ³	Critical density lb _m /ft ³	Critical volume		Z _c
			°K	°C	°R	°F					l./g-mol	ft ³ /lb-mol	
A. Noble Gases													
⁴ He	Helium-4	4.0026	5.1889	-267.9611	9.3400	-450.3300	2.24	32.9	0.0698	4.358	0.0573	0.9185	0.301
³ He	Helium-3	3.0009	3.309	-269.841	5.956	-453.714	1.13	16.6	0.0414	2.58	0.0725	1.161	0.302
Ne	Neon	20.183	44.40	-228.75	79.92	-379.75	27.2	400	0.484	30.2	0.0417	0.668	0.311
Ar	Argon	39.948	150.8	-122.4	271.4	-188.3	48.1	707	0.533	33.3	0.0749	1.20	0.291
Kr	Krypton	83.80	209.4	-63.8	376.8	-82.9	54.3	798	0.919	57.4	0.0912	1.46	0.287
Xe	Xenon	131.30	289.733	16.583	521.519	61.849	57.64	847.1	1.11	69.3	0.118	1.89	0.286
Rn	Radon	222	377	104	679	219	62	911					
B. Elementary Gases													
H ₂	Hydrogen (normal)	2.0159	33.2	-239.9	59.8	-399.9	12.80	188.1	0.0310	1.935	0.0650	1.042	0.305
H ₂	Hydrogen (equilibrium)	2.0159	32.98	-240.17	59.36	-400.31	12.76	187.5	0.0314	1.960	0.0642	1.028	0.303
HD	Hydrogen deuteride	3.024	36.0	-237.2	64.7	-395.0	14.6	215	0.0482	3.009	0.0628	1.005	0.310
D ₂	Deuterium (normal)	4.032	38.4	-234.8	69.0	-390.7	16.4	241					
D ₂	Deuterium (equilibrium)	4.032	38.2	-234.9	68.8	-390.9	16.3	240	0.0669	4.177	0.0603	0.965	0.314
Rb	Rubidium	85.47	2105	1832	3789	3329			0.34	21	0.25	4.0	
Ce	Cesium	132.905	2079	1806	3742	3282			0.44	27	0.30	4.8	
N ₂	Nitrogen	28.013	126.2	-147.0	227.1	-232.6	33.5	429	0.313	19.5	0.0895	1.43	0.290
P	Phosphorus	30.974	994	721	1789	1329							
O ₂	Oxygen	31.999	154.58	-118.57	278.24	-181.43	49.77	731.4	0.436	27.2	0.0734	1.18	0.288
O ₃	Ozone	47.998	261.0	-12.1	469.9	10.2	55	808	0.54	34	0.089	1.4	0.23
S	Sulfur	32.064	1314	1041	2365	1905	116	1705					
F ₂	Fluorine	37.997	144.30	-128.85	259.74	-199.93	51.47	756.4	0.574	35.8	0.0662	1.06	0.288
Cl ₂	Chlorine	70.906	417	144	751	291	76	1117	0.573	35.8	0.124	1.98	0.275
Br ₂	Bromine	159.818	584	311	1051	591	102	1499	1.26	78.7	0.127	2.03	0.270
I ₂	Iodine	253.809	819	546	1474	1014			1.64	102	0.155	2.48	
Hg	Mercury	200.59	1735	1462	3123	2663	1587	23322					
C. Deuterides													
ND ₃	Nitrogen trideuteride	20.052	405.6	132.4	730.0	270.3							
PD ₃	Phosphorus trideuteride	37.022	323.6	50.4	582.4	122.7							
AsD ₃	Arsenic trideuteride	80.970	372.0	98.9	669.7	210.0							
D. Nitrogen Compounds													
NH ₃	Ammonia	17.03	405.6	132.4	730.0	270.3	111.3	1636	0.235	14.7	0.0725	1.16	0.242
N ₂ H ₄	Hydrazine	32.05	653	380	1176	716	145	2131					
HCN	Hydrogen cyanide	27.03	456.8	183.6	822.2	362.5	53.2	782	0.195	12.2	0.139	2.22	0.197
C ₂ N ₂	Cyanogen	52.04	400	127	720	260	59	867					
NOF ₃	Trifluoramine oxide	87.00	302.6	29.5	544.8	85.1			0.593	37.0	0.169	2.70	
E. Chalcogenides													
1. Oxides													
H ₂ O	Water	18.015	647.14	373.99	1164.85	705.18	217.6	3198	0.32	20	0.056	0.90	0.23
D ₂ O	Heavy water	20.031	644.0	370.8	1159.1	699.4	213.8	3142	0.36	22	0.056	0.89	0.23
CO	Carbon monoxide	28.011	132.91	-140.24	239.2	-220.47	34.53	507.4	0.301	18.8	0.0931	1.49	0.295
CO ₂	Carbon dioxide	44.010	304.2	31.0	547.5	87.8	72.8	1070	0.468	29.2	0.0940	1.51	0.274

N ₂ O	Nitrous oxide	44.013	309.56	36.41	557.21	97.54	71.5	1051	0.452	28.2	0.0974	1.56	0.274
NO	Nitric oxide	30.006	180	-93	324	-136	64	940	0.52	32	0.058	0.92	0.25
N ₂ O ₄	Dinitrogen tetroxide	92.011	431	158	776	316	100	1470	0.55	34	0.17	2.7	0.47
SO ₂	Sulfur dioxide	64.06	430.8	157.6	775.4	315.4	77.81	1144	0.525	32.8	0.122	1.95	0.268
SO ₃	Sulfur trioxide	80.06	491.0	217.8	883.7	424.0	81	1190	0.63	39	0.13	2.0	0.26
Re ₂ O ₇	Rhenium oxide	484.4	942	669	1696	1236			1.45	90.5	0.334	5.35	
2. Sulfides													
H ₂ S	Hydrogen sulfide	34.08	373.2	100.0	671.7	212.0	88.2	1296	0.346	21.6	0.0985	1.58	0.284
D ₂ S	Deuterium sulfide	36.09	372.2	99.1	670.0	210.3							
CS ₂	Carbon disulfide	71.64	552	279	994	534	78	1146	0.44	27	0.16	2.6	0.28
3. Selenides													
H ₂ Se	Hydrogen selenide	81.01	411	138	740	280	88	1293					
D ₂ Se	Deuterium selenide	83.02	412.4	139.2	742.2	282.5							
4. Mixed													
COS	Carbonyl sulfide	60.07	375	102	675	215	58	852	0.44	27	0.14	2.2	0.26
F. Halides													
1. Fluorides													
HF	Hydrogen fluoride	20.01	461	188	830	370	64	940	0.29	18	0.069	1.1	0.12
BF ₃	Boron trifluoride	67.81	260.8	-12.3	469.5	9.8	49.2	723					
SiF ₄	Silicon tetrafluoride	104.08	259.0	-14.1	466.3	6.6	36.7	539					
N ₂ F ₄	Tetrafluorohydrazine	104.01	309.4	36.2	556.8	97.1	37	544					
N ₂ F ₂	<i>cis</i> -Difluorodiazine	66.01	272	-1	490	30							
N ₂ F ₂	<i>trans</i> -Difluorodiazine	66.01	260	-13	468	8							
NF ₃	Nitrogen trifluoride	71.00	234.0	-39.2	421.1	-38.7	44.7	657					
HNF ₂	Difluoramine	53.01	403	130	725	265							
PF ₃	Phosphorus trifluoride	87.97	271.2	-2.0	488.1	28.4	42.7	628					
OF ₂	Oxygen fluoride	54.00	215.2	-58.0	387.3	-72.4							
SF ₄	Sulfur tetrafluoride	108.06	364.0	90.9	655.3	195.6							
SF ₆	Sulfur hexafluoride	146.05	318.69	45.54	573.64	113.97	37.10	545.2	0.736	45.9	0.198	3.18	0.267
NbF ₅	Niobium pentafluoride	187.90	737	464	1327	867	62	911	1.21	75.5	0.155	2.49	0.16
UF ₆	Uranium hexafluoride	352.02	505.8	232.6	910.4	450.7	46	676	1.41	88.0	0.250	4.00	0.28
2. Chlorides													
HCl	Hydrogen chloride	36.46	324.6	51.5	584.4	124.7	82.0	1205	0.45	28	0.081	1.3	0.25
DCl	Deuterium chloride	37.47	323.4	50.3	582.2	122.5							
BCl ₃	Boron trichloride	117.17	452.0	178.8	813.5	353.8	38.2	561					
AlCl ₃	Aluminum trichloride	133.34	629	356	1132	672	26	382	0.510	31.8	0.261	4.19	0.13
SiHCl ₃	Trichlorosilane	135.45	479	206	862	402							
SiCl ₄	Silicon tetrachloride	169.90	507	234	913	453	37	544	0.521	32.5	0.326	5.23	0.29
GeCl ₄	Germanium tetrachloride	214.41	552	279	994	534	38	558	0.65	41	0.33	5.3	0.28
SnCl ₄	Stannic chloride	260.50	592.0	318.8	1065.5	605.8	37.0	544	0.742	46.3	0.351	5.62	0.267
PCl ₃	Phosphorus trichloride	137.33	563	290	1014	554			0.52	32	0.26	4.2	
AsCl ₃	Arsenic trichloride	181.28	591	318	1064	604			0.720	44.9	0.252	4.03	
SbCl ₃	Antimony trichloride	228.11	794	521	1429	969			0.84	52	0.27	4.3	
BiCl ₃	Bismuth chloride	315.34	1179	906	2122	1662	118	1734	1.21	75.5	0.261	4.17	0.32
TiCl ₄	Titanium tetrachloride	189.71	638	365	1149	689	46	676	0.56	35	0.34	5.4	0.30
ZrCl ₄	Zirconium tetrachloride	233.03	778	505	1401	941	56.9	836	0.730	45.6	0.319	5.11	0.284

Table XVI (Continued)

Formula	Substance	Mol wt	Critical temperature				Critical pressure		Critical density		Critical volume		Z _c
			°K	°C	°R	°F	Atm	lb _i /in. ²	g/cm ³	lb _m /ft ³	l./g-mol	ft ³ /lb-mol	
2. Chlorides (Continued)													
HfCl ₄	Hafnium tetrachloride	320.30	723	450	1302	842	57.0	838	1.05	65.6	0.304	4.88	0.292
NbCl ₅	Niobium pentachloride	270.17	807	534	1453	993			0.68	42	0.40	6.4	
TaCl ₅	Tantalum pentachloride	358.21	767	494	1381	921			0.89	56	0.40	6.4	
MoCl ₅	Molybdenum pentachloride	273.21	850	577	1530	1070			0.74	46	0.37	5.9	
WCl ₆	Tungsten hexachloride	396.57	923	650	1662	1202			0.94	59	0.42	6.8	
HgCl ₂	Mercuric chloride	271.50	973	700	1752	1292			1.56	97.4	0.174	2.79	
3. Bromides													
HBr	Hydrogen bromide	80.92	363.2	90.0	653.7	194.0	84.4	1240					
DBr	Deuterium bromide	81.93	362.0	88.8	651.5	191.8							
BBr ₃	Boron tribromide	250.54	573	300	1032	572			0.90	56	0.28	4.5	
AlBr ₃	Aluminum tribromide	266.71	763	490	1374	914	28.5	419	0.860	53.7	0.310	4.97	0.141
SiHBr ₃	Tribromosilane	268.82	609	336	1096	636							
SiBr ₄	Silicon tetrabromide	347.72	663	390	1194	734							
SbBr ₃	Antimony tribromide	361.48	904	631	1627	1167							
BiBr ₃	Bismuth bromide	448.71	1219	946	2194	1734			1.49	93.0	0.301	4.82	
ZrBr ₄	Zirconium tetrabromide	410.86	805	532	1449	989			0.97	61	0.42	6.8	
HfBr ₄	Hafnium tetrabromide	498.13	746	473	1343	883			1.20	74.9	0.415	6.65	
NbBr ₅	Niobium pentabromide	492.46	1010	737	1818	1358			1.05	65.6	0.469	7.51	
TaBr ₅	Tantalum pentabromide	580.49	974	701	1753	1293			1.26	78.7	0.461	7.38	
HgBr ₂	Mercuric bromide	360.41	1012	739	1822	1362							
4. Iodides													
HI	Hydrogen iodide	127.91	424.0	150.8	763.1	303.4	82	1205					
DI	Deuterium iodide	128.92	421.8	148.6	759.2	299.5							
AlI ₃	Aluminum triiodide	407.69	955	682	1719	1259							
SbI ₃	Antimony triiodide	502.46	1102	829	1984	1524							
ZrI ₄	Zirconium tetraiodide	598.84	960	687	1728	1268			1.13	70.5	0.530	8.49	
HfI ₄	Hafnium tetraiodide	686.11	916	643	1649	1189			1.30	81.1	0.528	8.45	
HgI ₂	Mercuric iodide	454.90	1072	799	1930	1470							
5. Mixed													
ClF ₅	Chlorine pentafluoride	130.44	416	143	749	289	52	764	0.56	35	0.23	3.7	0.35
SiF ₃ Cl	Chlorotrifluorosilane	120.53	307.6	34.5	553.8	94.1	34.2	503					
SiF ₂ Cl ₂	Dichlorodifluorosilane	136.99	369.0	95.8	664.1	204.4	34.5	507					
SiFCl ₃	Trichlorofluorosilane	153.44	438.6	165.4	789.4	329.7	35.3	519					
NCIF ₂	Nitrogen chloride difluoride	87.46	337.4	64.3	607.4	147.7	50.8	747					
PF ₂ Cl	Phosphorus(III) chloride difluoride	104.42	362.4	89.2	652.2	192.5	44.6	655					
PFCl ₂	Phosphorus(III) dichloride fluoride	120.88	463.0	189.8	833.3	373.6	49	720					
G. Oxyhalides													
NOF	Nitryl fluoride	65.00	349.4	76.3	629.0	169.3							
COCl ₂	Phosgene	98.92	455	182	819	359	56	823	0.52	32	0.19	3.0	0.28
NOCl	Nitrosyl chloride	65.46	440	167	792	332							
VOCl	Vanadium oxychloride	173.30	636	363	1145	685			0.60	37	0.29	4.6	

WOCl ₄	341.66	782	509	1408	948	1.01	63.0	0.338	5.42	
ReOCl ₄	344.0	781	508	1406	946	0.95	59	0.36	5.8	
ClO ₃ F	102.45	368.4	95.2	663.0	203.3	0.637	39.8	0.161	2.58	0.282
H. Miscellaneous										
B ₂ H ₆	26.67	289.8	16.6	521.6	61.9		40		588	
PH ₃	34.00	324.8	51.6	584.6	124.9		64.5		948	
PH ₂ Cl	70.46	322.2	49.1	580.0	120.3		72.7		1068	
(PNF ₂) ₃	248.93	461.0	187.8	829.7	370.0					
(PNF ₂) ₄	331.91	496.4	223.2	893.4	433.7					
(PNF ₂) ₅	414.88	524.0	250.8	943.1	483.4					
AsH ₃	77.95	373.0	99.9	671.5	211.8					

^a °K = °C + 273.15, °F = (1.8)°C + 32, °R = °F + 459.67, 1 atm = 14.696 lb/in.², 1 g/cm³ = 62.48 lb/ft³, R = 82.056 cm³ atm/(deg mol).

details are discussed under zirconium tetrachloride, section V.F.2.n, under Nisel'son and Sokolova.¹³⁶

7. Perchloryl Fluoride

Englebrecht and Atzwanger¹⁵² prepared a sample of ClO₃F for the critical property determinations by reaction of potassium chlorate with elemental fluorine. Purification was achieved by passing the effluent gases from the fluorination repeatedly through a solution of 10% NaOH and 5% Na₂S₂O₈ and then drying them over NaOH pellets and P₂O₅. Temperatures were measured with a copper-constantan thermocouple calibrated against the ice point, solid CO₂, and boiling O₂.

Kudchaker, Alani, and Zwolinski² reviewed the work of Jarry,¹⁵³ and their selected value of critical temperature and critical pressure are retained.

H. MISCELLANEOUS (TABLE XV)

1. Diborane

Newkirk¹⁵⁴ used an original sample of diborane which analyzed 99.8% diborane and 0.2% noncondensables. This was then frozen in a thin layer, pumped on to remove the noncondensables, and distilled into capillary tubes. Temperatures in the measurement cell were changed at the rate of 2°/hr. Results were extrapolated to zero time to correct for slow decomposition of the diborane and gave a critical temperature of 16.63°. This value was averaged with another run (16.94) to give the final corrected value that was reported.

Paridon, MacWood, and Hu¹⁵⁵ used diborane of 99.91 mol % purity. They measured the latent heat of vaporization to 280°K and smoothed the data by fitting it to the equation

$$L_v = 546.2(T_c - T)^{0.39} \text{ cal mol}^{-1} \quad (20)$$

where $T_c = 289.7^\circ\text{K}$.

There is good agreement (within experimental error) between the critical temperatures of both workers, particularly if one uses the zero time value of Newkirk (16.63°), and thus 16.6° is selected as the most probable value of critical temperature.

2. Phosphine

No new work has been reported since Kobe and Lynn,¹ but Kopper's¹¹ datum needs to be added to the tabulation. Kopper's work is discussed in section V.C.

There is no reason to change the selected values of Kobe and Lynn.¹

3. Phosphonium Chloride

No new work has been reported since Kobe and Lynn.¹

4. Phosphonitrilic Fluoride Mers¹⁵⁶

Samples of the trimer, tetramer, and pentamer of phosphonitrilic fluoride were supplied by Albright and Wilson (Mfg.)

(152) A. Engelbrecht and H. Atzwanger, *J. Inorg. Nucl. Chem.*, **2**, 348 (1956).

(153) R. L. Jarry, *J. Phys. Chem.*, **61**, 498 (1957).

(154) A. E. Newkirk, *J. Amer. Chem. Soc.*, **70**, 1978 (1948).

(155) L. J. Paridon, G. E. MacWood, and J.-H. Hu, *J. Phys. Chem.*, **63**, 1998 (1959).

(156) D. C.-H. Cheng and J. C. McCoubrey, *J. Chem. Soc.*, 4993 (1963).

Ltd. and were shown by ir analysis to be pure apart from soluble nitrobenzene. The latter was removed by bulb-to-bulb fractionation *in vacuo*. There was a slight decomposition noted with the pentamer, and T_c was obtained by extrapolation to zero time. Temperatures were measured on a mercury-in-glass thermometer checked against an NPL calibrated thermometer and against a calibrated thermocouple. The tubes were 5 cm in length and temperature was varied at the rate of 0.01 °/min.

5. Arsine

Kopper's¹¹ work is discussed in section V.C.

VI. Summary Table (Table XVI)

The selected critical properties are summarized in Table XVI. An estimate of probable errors involved (except for those specifically mentioned in the text) is one to ten units in the last significant figure reported in Table XVI. However, the errors in rubidium, cesium, and mercury may be higher than this general estimate.

Temperatures above 13.81°K can be regarded as being de-

fined on IPTS-68, the necessary corrections from IPTS-48 having been made using the tables of Douglas.¹⁵⁷

VII. Correlation and Prediction

Methods for the correlation and prediction of critical constants have been discussed by Reid and Sherwood¹⁵⁸ and Kudchadker, Alani, and Zwolinski,² and there is a new book on this subject by Fishtine¹⁵⁹ to be published in the near future. Therefore, there seems to be no real need to cover this subject in the present article.

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(157) T. B. Douglas, *J. Res. Nat. Bur. Stand., Sect. A*, **73**, 451 (1969).

(158) R. C. Reid and T. K. Sherwood, "The Properties of Gases and Liquids," McGraw-Hill, New York, N. Y., 1966.

(159) S. H. Fishtine, private communication.