The Critical Constants of the Elements

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The critical temperatures available in the literature for seventeen elements constitute the basis of this study for predicting critical temperatures from normal boiling points. When not available, the normal boiling point can be estimated from vapor-pressure data. The extension of the vapor-pressure data beyond the normal boiling point establishes the critical pressure from the estimated critical temperature.

In accordance with this procedure, critical temperatures and pressures have been predicted for thirty-six elements included in the periodic table from lithium to uranium. These critical constants constitute the core of this study and have been used to calculate both van der Waals' constants. These constants, when plotted against their atomic numbers, produce correlations that may permit the further prediction of van der Waals' constants for other elements.

A simple relationship between the critical volume and the volume van der Waals' constant is found to exist and is presented as a basis for predicting the critical volume of elements.

Considerable attention has been directed in the literature to the prediction of critical constants for organic compounds. In this respect Riedel (*49, 50, 51*) and Lydersen (*27*) present methods of calculating the critical temperatures, pressures, and volumes from group contributions, the normal boiling points, and the molecular weights of these substances. Another approach has been demonstrated (*67, 68*) for the calculation of van der Waals' constants which are used to predict the critical constants of aliphatic hydrocarbons from molecular structural considerations.

Because modern technology requires information on the state of materials at elevated temperatures and pressures, it is necessary to learn about hitherto unexplored areas, such as the high-temperature and pressure regions. In order to fill in some of the existing voids, the study of the critical state of the elements was undertaken without restrictions of temperature and pressure. In this study procedures were adopted that permitted the extension of meager vapor-pressure information obtained at moderate conditions into the critical region.

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CRITICAL TEMPERATURE

Experimental critical temperatures are limited primarily to those reported by Kobe and Lynn (*31*). In addition, values reported by Hoge and Lassiter (*26*) for hydrogen deuteride and deuterium, by Cady and Hildebrand (*9*) for fluorine, and by Marckwald and Helmholtz (*37*) for phosphorus constitute present knowledge of the critical temperatures of the elements. These critical temperatures are presented in Table 1 along with their corresponding normal boiling points. The following relationship between the normal boiling point and the critical temperature was proposed by Guldberg in 1890 for simple molecules containing one and two atoms (*21*):

$$\frac{T_b}{T_c} = 0.567 \qquad (1)$$

In 1942 Meissner and Redding (*42*) presented the following relationship for all the elements:

$$T_c = 1.70T_b - 2.0 \qquad (2)$$

The available critical temperatures and corresponding normal boiling points of the elements presented in Table 1 have been correlated on logarithmic scales to produce the relationship of Figure 1. With the exception of helium, the sixteen elements correlate linearly to define the critical temperature as

$$T_c = 1.4732T_b^{1.0313} \qquad (3)$$

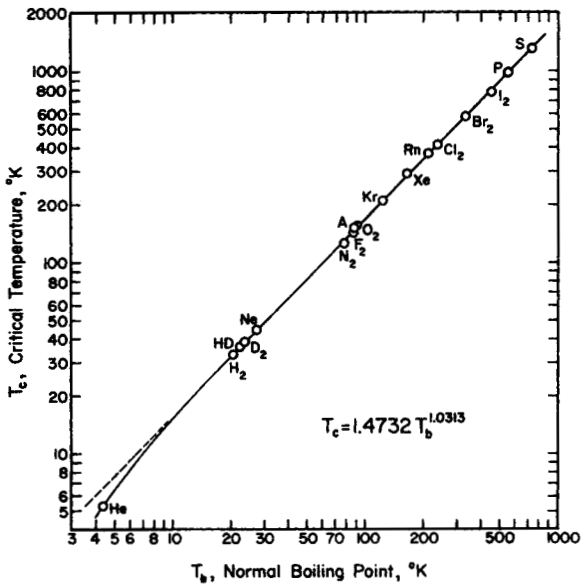

Fig. 1. Relationship of critical temperatures and normal boiling points for the elements.

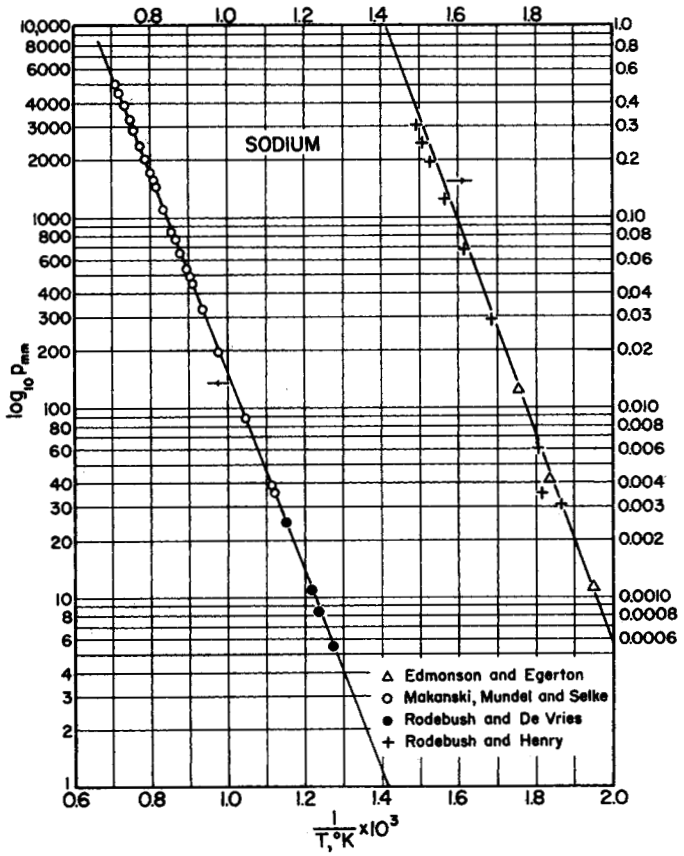

Fig. 2. Vapor-pressure function of sodium.

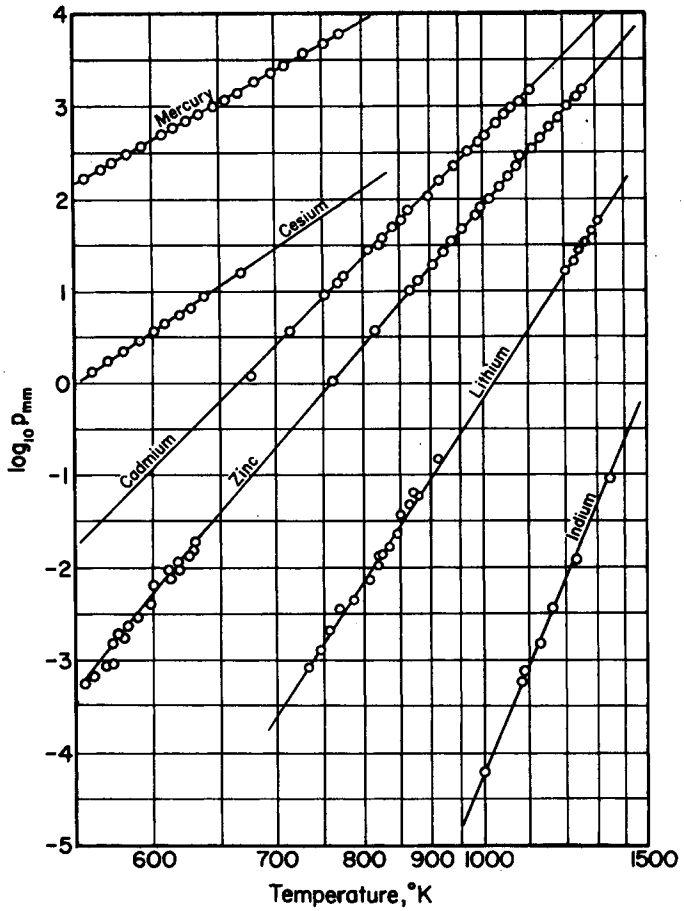

Fig. 3. Vapor-pressure relationships for low-boiling metals.

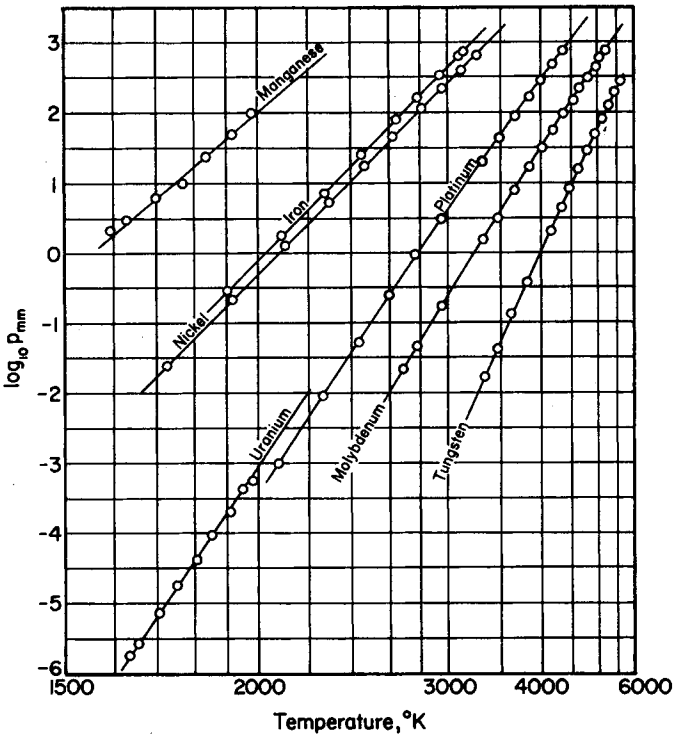

Fig. 4. Vapor-pressure relationships for high-boiling metals.

Values calculated with Equation (3) are found to have a mean deviation of 1.38% from the experimental values reported in Table 1 for elements ranging from hydrogen to phosphorus and sulfur. In view of this close agreement, Equation (3) appears to be reliable and has been assumed applicable to the elements.

With Equation (3) the prediction of the critical temperature is readily made for those elements for which normal boiling points are available. For several elements this value is either not reported or agreed upon by different sources. This condition necessitated a critical review of vapor-pressure data available in the literature to establish not only dependable normal boiling points but also information that would enable the extension of the vapor-pressure function above its normal boiling point.

INTERPRETATION OF VAPOR-PRESSURE DATA

Vapor-pressure data reported in the literature for high-boiling elements are limited to the low-pressure range. The correlation of these data on a logarithmic pressure scale vs. reciprocal absolute temperature does not necessarily produce a straight-line relationship, and consequently the extension of this function up to and past the normal boiling point becomes unreliable. Therefore the direct use of vapor-pressure data alone cannot be relied upon to extend a knowledge of normal boiling points and critical pressures. In view of these limitations, the use of a vapor-pressure reference-state correlation has been adopted. This method of plotting was introduced by Cox (*12*) and later more fully discussed by Othmer (*45*).

The elements for which extensive information is lacking can be roughly classified as those of intermediate and low volatility. In order to correlate the vapor-pressure data of these elements properly, two reference-state plots have been utilized, with the vapor-pressure data of sodium used to construct the plot for elements of intermediate volatility and those of copper used to establish the low-volatility plot.

SODIUM

The current interest in sodium as a heat transfer medium for nuclear reactors has accelerated the determination of properties for this element. As a result vapor-pressure data have been determined for temperatures as high as 1400°K. and pressures up to 6.4 atm. (*36*). The vapor-pressure data for sodium available in the literature (*14, 36, 52, 56*) are presented in Figure 2 and indicate a curvature in the low-pressure region. The vapor-pressure function for pressures above 10 mm. of mercury is linear, and the straight-line portion has been assumed to extend up to the critical point. For this portion of the curve the vapor-pressure of sodium can be defined as

$$\log p = 7.41417 - \frac{5{,}242}{T} \qquad (4)$$

A reference-state plot based on sodium has been constructed by considering the coexisting vapor pressures of the substance and of sodium at the same temperature. In accordance with this approach, the vapor-pressure behavior for a number of elements has been translated to a Cox-Othmer type of chart as presented in Figure 3. In this figure the abscissa has been translated directly to temperatures corresponding to the vapor pressures of sodium. Only vapor-pressure curves of representative elements have been included in this plot. The complete listing of references selected for this study is presented in Table 2.

COPPER

In an approach similar to that used for sodium, the data of Edwards, Johnston, and Ditmars (*15*), Harteck (*23*), Hersch (*25*), and Marshall, Dornte, and Norton (*38*) have been utilized in conjunction with the normal boiling

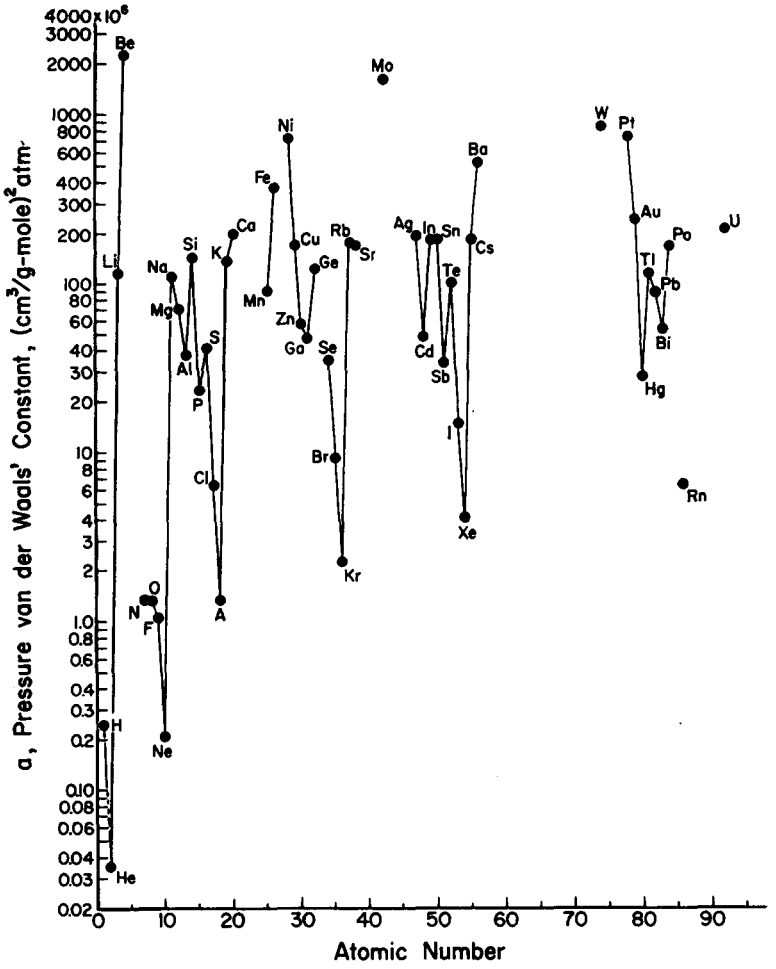

Fig. 5. Relationship of pressure van der Waals' constant and atomic number of the elements.

point reported by Brewer (*47*). On the basis of this information the vapor-pressure relationship for copper below its normal boiling point becomes

$$\log p = 8.464 - \frac{16{,}352}{T} + 0.036 \log T \qquad (5)$$

For the selection of vapor-pressure data those of Jones, Langmuir, and Mackay (*30*) have not been used to produce Equation (5). Their data for copper on a log p vs. $1/T$ plot produce a curve that is essentially parallel to that obtained with Equation (5). This equation produces a vapor-pressure function having a slight curvature which becomes insignificant in the vicinity of the normal boiling point. This vapor-pressure function from the normal boiling point, 2,868°K., to the critical point has been assumed to be linear and to have the slope calculated from Equation (5) at 2,868°K. This straight-line portion of the vapor-pressure function for copper has been found to be

$$\log p = 8.600 - \frac{16{,}402}{T} \qquad (6)$$

Equations (5) and (6) permit the calculation of exacting vapor pressures for the construction of a plot similar to Figure 3 in which the available vapor pressures of the elements having low volatilities have been correlated.

Vapor-pressure data for certain high-boiling metals are reported by Jones, Langmuir, and Mackay (*30*). This group indirectly establishes vapor pressures by heating the substance in vacuum and accounting for the rate of evaporation (33). Using this method, Jones, Langmuir, and Mackay established the vapor pressures for copper, iron, nickel, platinum, molybdenum, and tungsten. A slight discrepancy has been found between the values reported by the Langmuir group and those calculated from Equation (5) for copper. In view of this disagreement with copper, it is reasonable to assume that this difference also exists in the vapor-pressure data reported for iron, nickel, platinum, molybdenum, and tungsten. Consequently the vapor-pressure data of Jones, Langmuir, and Mackay have been translated to make them consistent with Equation (5). As a result of this correction, normal boiling points have been obtained that are in closer agreement with those reported in the current literature (*47*) for these elements.

The information resulting from the data of Langmuir and associates has been utilized to produce the vapor-pressure relationships presented in Figure 4. The abscissa of this figure has been generated from the vapor pressures of copper resulting from Equations (5) and (6). In addition to the data for iron, nickel, platinum, molybdenum, and tungsten, relationships are also presented in Figure 4 for manganese and uranium.

CRITICAL PRESSURE

The reference plots of Figures 3 and 4 include curves that are essentially

Table 1. Comparison of Experimental and Calculated Critical Values

	Critical constants (experimental)				Van der Waals' constants		Calculated values	
	T_b, °K.	T_c, °K.	P_c, atm.	v_c, cc./g. mole	$a \times 10^{-6}$, (cc./g.-mole)² atm.	b, cc./g.-mole	T_c, °K.	v_c, cc./g. mole
Hydrogen	20.5	33.3	12.80	65.0	0.246	26.68	33.2	62.2
Hydrogen deuteride	22.1	35.91	14.64	62.8	0.250	25.16	35.94	58.7
Deuterium	23.6	38.26	16.28	60.3	0.255	24.10	38.45	56.2
Helium	4.3	5.3	2.26	57.8	0.0353	24.05		56.1
Nitrogen	77.4	126.2	33.5	90.1	1.350	38.64	130.6	90.2
Oxygen	90.0	154.8	50.1	74.4	1.359	31.69	152.6	73.9
Fluorine	86.2	144	55		1.071	26.85	146	62.6
Neon	27.3	44.5	26.9	41.7	2.091	16.97	44.6	39.6
Phosphorus	553	993.8	120.8		23.22	84.38	987.2	196.9
Sulfur	718	1,313	116		42.21	116.10	1,299	270.9
Chlorine	238.6	417	76.1	124	6.491	56.20	417	131.1
Argon	87.6	151	48.0	75.2	1.349	32.27	148	75.3
Bromine	331.9	584	102	144	9.498	58.73	586	137.0
Krypton	121.4	209.4	54.3	92.2	2.294	39.56	207.8	92.3
Iodine	457.5	785	116		15.09	69.41	816	162.0
Xenon	164.1	289.75	58.0	118.8	4.116	51.24	283.59	119.6
Radon	211	377.16	62.0		6.517	62.40	367.53	145.6

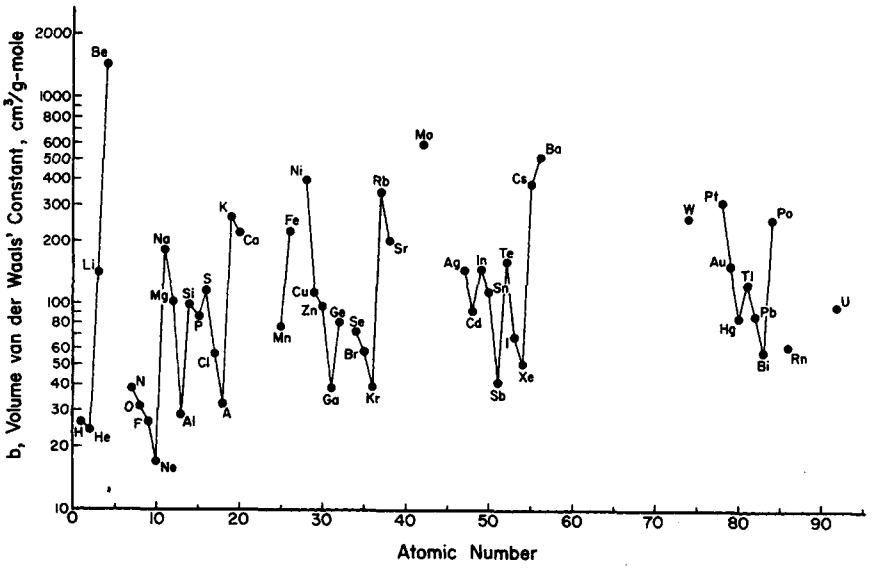

Fig. 6. Relationship of volume van der Waals' constant and atomic number of the elements.

TABLE 2. SUMMARY OF CALCULATED CRITICAL CONSTANTS FOR SOME ELEMENTS

	Calculated critical constants				
	T_b, °K.	T_c, °K.	P_c, atm.	v_c, cc./g.-mole	References used
Sodium reference plot					
Lithium	1,598	2,966	215	329.7	*24, 39*
Sodium	1,156	2,124	116	437.6	*14, 36, 52, 56*
Potassium	1,026	1,878	72.6	618.2	*19, 32, 35*
Rubidium	982	1,795	52.4	818.7	*22, 62*
Cesium	964	1,760	46.7	900.7	*2, 22, 32, 66*
Beryllium	3,243	6,153	47.2	3,115	*3*
Magnesium	1,373	2,535	254	238.5	*11, 24, 34, 58, 61*
Calcium	1,755	3,267	151	517.1	*24*
Strontium	1,647	3,059	155	471.7	*24*
Barium	1,961	3,663	72.3	1,211	*24*
Aluminum	2,520	4,744	1,695	67.0	*3, 6*
Gallium	2,418	4,546	1,208	89.9	*23*
Indium	2,331	4,377	301	347.5	*1*
Thallium	1,730	3,219	263	292.5	*11, 20, 34*
Silicon	2,739	5,159	530	232.6	*3, 59*
Germanium	2,982	5,642	715	188.6	*63, 65*
Tin	3,067	5,809	524	264.9	*64*
Lead	1,878	3,584	416	205.9	*17, 28, 70*
Antimony	1,610	2,989	740	96.7	*57*
Bismuth	1,764	3,284	574	136.7	*10, 57, 71*
Selenium	962	1,757	249	168.6	*7, 44, 46*
Tellurium	1,264	2,329	148	376.1	*7*
Polonium	1,239	2,281	90	605.7	*8*
Gold	2,938	5,557	371	358.0	*57, 60*
Zinc	1,180	2,169	229	226.4	*3, 4, 11, 29, 41, 53, 69*
Cadmium	1,039	1,903	209	217.6	*4, 16, 18, 29, 34, 55*
Mercury	630	1,135	134	202.4	*13, 43, 54*
Copper reference plot					
Molybdenum	5,165	9,880	169	1,399	*30*
Tungsten	5,950	11,500	445	618	*30*
Manganese	2,305	4,327	561	184	*3*
Iron	3,147	5,966	271	526	*30*
Nickel	3,315	6,294	158	952	*30*
Platinum	4,323	8,280	267	741	*30*
Copper	2,868	5,421	493	263	*15, 23, 25, 38, 47*
Silver	2,532	4,767	336	339	*23*
Uranium	3,946	7,533	778	231	*48*

linear; hence their extension to atmospheric pressure establishes the normal boiling point. The prediction of the critical temperature is then made with Equation (3) and the estimated normal boiling point. The further extension of the vapor-pressure functions in Figures 3 and 4 beyond the normal boiling point and up to the predicted critical temperature locates the critical pressure. This approach was utilized for the prediction of critical pressures of thirty-six additional elements for which a limited number of vapor-pressure data were available. These predicted critical temperatures and pressures are presented in Table 2.

The critical temperatures and pressures reported in the literature for the elements are summarized in Table 1, those predicted from this study, in Table 2. These critical values have been used to calculate both van der Waals' constants a and b from the relationships

$$a = \frac{27R^2T_c^2}{64P_c} \tag{7}$$

and

$$b = \frac{RT_c}{8P_c} \tag{8}$$

The resulting van der Waals' constants, when correlated with their atomic numbers, produce the relationships of Figures 5 and 6. These van der Waals' constant correlations exhibit a typical periodic variation similar to those already available for molecular volume and normal boiling point.

CRITICAL VOLUME

The critical volume defined in terms of the volume van der Waals' constant has been theoretically derived to be

$$v_c = 3b \tag{9}$$

For the critical volumes of hydrocarbons (*67, 68*), the ratio of v_c/b was not found to be equal to 3 but varied with the nature and size of the hydrocarbon molecule.

The volume van der Waals' constant for the elements of Table 1, when divided into the experimental critical volume, produced essentially constant ratios. For the elements for which complete information was available, the ratio v_c/b was found to be as follows:

	v_c/b
Hydrogen	2.43
Hydrogen deuteride	2.50
Deuterium	2.50
Helium	2.40
Nitrogen	2.33
Oxygen	2.35
Neon	2.36
Chlorine	2.20
Argon	2.33

Bromine	2.46
Krypton	2.33
Xenon	2.32

Since helium, hydrogen, and to some extent neon possess quantum effects, their ratios have been excluded to produce an average value of $v_c/b = 2.335$ for the remaining seven elements. This ratio suggests that the critical volume for the elements may be predicted with the expression

$$v_c = \frac{7}{3}b \qquad (10)$$

Values calculated with Equation (10) have been compared with the available experimental values presented in Table 1 and produce an average deviation of 1.75%.

Figures 5 and 6 can be used to predict the critical constants of the elements. Volume van der Waals' constants, obtained from Figure 6, when substituted in Equation (10) enable the calculation of the critical volumes of the elements. It is noteworthy that for this development the state of association of the elements in the critical region has not been utilized. A review points to some interesting speculations about the state of aggregation for elements such as sodium and copper. For these elements critical volumes are calculated to be 438 and 263 cc./g.-mole respectively, as compared with 75.3 and 90.2 cc./g.-mole for argon and nitrogen.

As a result of these studies Equations (3) and (10) are presented for the prediction of the critical temperature and volume of the elements. In addition to the experimental critical temperatures and pressures for seventeen elements, the critical temperatures and pressures for thirty-six other elements have been estimated through the use of vapor-pressure data and Equation (3).

Attention should be directed to the fact that the proposed critical constants for elements for which no experimental data exist must be considered tentative until these values are verified experimentally.

NOTATION

- a = pressure van der Waals' constant, (cc./g.-mole)^2 atm.
- b = volume van der Waals' constant, cc./g.-mole
- p = vapor pressure, mm. of mercury
- P_c = critical pressure, atm.
- R = gas constant, 82.055 (cc.) (atm.)/(g.-mole) (°K.)
- T = absolute temperature, °K.
- T_b = normal boiling point, °K.
- T_c = critical temperature, °K.
- v_c = critical volume, cc./g.-mole

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