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Critical Point of Metals from the van der Waals Model*

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The classical van der Waals model of fluids is modified by a more accurate equation of state for hard spheres. The hard-sphere diameter and the van der Waals constant a are obtained from experimental data. The model is used to predict the critical constants of metals, as well as the equation of state, cohesive energy, and coexistence curves near the critical point. The model is also applied to rare gases and ionic salts. The semiquantitative predictions of the model are at least as accurate as those of other theories. Of the three critical constants, the critical temperature is most accurately predicted, being within 11% of experiment. More information about the interatomic potential in metals is needed before the theory can be substantially improved.

I. INTRODUCTION

Recent high-temperature research has determined the critical constants of mercury and the alkali metals.[1–3] Because of the large cohesive energies of metals, the temperatures and pressures at the critical point are high, and experimental work is correspondingly difficult. Thus, mercury and cesium are the only metals whose critical constants have been directly measured. For other metals, the critical constants have been obtained by extrapolation.

At present a theoretical foundation for this experimental work on metals is lacking. One of the main difficulties in the theoretical treatment of metals is the absence of an adequate interatomic-potential function. The inert gases may be accurately treated as molecules interacting according to a pairwise additive potential, and the statistical-mechanical theory may be developed accordingly. Unfortunately, for liquid metals this state of affairs does not yet prevail. Hence, we must at present resort to a mean-field type of theory for the equation of state of metals. One of the simplest such theories is the van der Waals model, which assumes that the liquid consists of hard-sphere particles moving in a uniform potential field.

Several experimental facts may be called upon to support the plausibility of a van der Waals model for metals. First, the diffusion coefficient[4] and the first peak of the structure factor[5] in liquid metals may be accurately described by the hard-sphere fluid model, as predicted by the van der Waals model. Second, the vapor-liquid coexistence curve for metals appears to be more nearly quadratic in form near the critical point, as predicted by van der Waals, than for the rare-gas fluids. Third, experimental values of the critical compressibility ratio $Z_c = P_c V_c / R T_c$ vary between 0.2 and 0.4 for metals, and this is sufficiently close to the classical van der Waals prediction of 0.375 to suggest that the theory might apply. Finally, the cohesive energy of mercury is predicted at least as well by the van der Waals model as by other theories.

II. REVIEW

There has been little pure theoretical work on the critical points of metals. Attempts have been made to use the classical van der Waals model[6–8] to obtain critical constants by estimating the parameters a and b in the model. Also, there have been attempts to correlate empirically critical temperatures with some other physical property, such as the boiling temperature,[9] heat of vaporization,[10,11] or surface tension.[12] Many of these calculations implicitly use a corresponding states argument, as, for example, among the alkali metals or with mercury as a reference metal. All of these theories suffer either from incompleteness because not all of the critical constants can be predicted, or from lack of theoretical justification for the assumptions made.

Experimental work has been done on the determination of the critical constants of mercury and the alkali metals. Extensive work on mercury has been done during the past few years.[1,13-15] There is good agreement among the experiments on the critical pressure and temperature, but the critical volume has been poorly determined. We shall use the critical constants of Kikoin and Senchenkov[1] because their data is the most extensive. Alkali metals have been less thoroughly studied than mercury. Cesium is the only alkali metal whose critical constants have all been determined.[3] Estimates of the critical constants of sodium, potassium, and rubidium have been made from measurements close to their critical points, and this data has been used, with the principle of corresponding states, to estimate the critical constants for lithium.[2]

Grosse[16] has estimated critical constants from experimental data in several ways. One way is to get T_c by matching the entropy of vaporization at some T_0 to a curve of ΔS_{vap} versus T/T_c obtained from mercury data. Then one reads off the corresponding value of T_0/T_c and calculates T_c. Grosse has also measured the densities of liquid metals from their melting points to their boiling points. These data, combined with the law of rectilinear diameter of Cailletet and Mathias, and T_c obtained above, give the critical density ρ_c. Extrapolation of vapor-pressure curves then yields p_c. Alternatively, T_c can be calculated by requiring $\rho_{\text{b.p.}}/\rho_c = 4.35$ and using the law of rectilinear diameter. Grosse's estimates of the alkali-metal critical constants compare favorably with later experimental data.[17]

III. METHOD

The classical van der Waals equation of state for one mole of fluid is

$$(p + a/V^2)(V - b) = RT \ . \tag{1}$$

This equation of state is of little value in predicting critical constants because the two parameters a and b are usually obtained by fitting the equation to the critical constants themselves or to low-density PVT data, which are not generally available for metals. Instead, we make use of the rigorous expansion of the free energy as a perturbation series about the hard-sphere free energy.[18,19] The first correction to the hard-sphere free energy is the cohesive energy of the fluid taken as an average of the interatomic pair potential over the hard-sphere radial distribution function. The ion-ion pair potentials which have been calculated from theory and experimental data[20] for liquid metals near the melting point have the difficulty that the attractive well is not nearly deep enough to predict the correct critical temperatures. This is based on the argument, which holds for rare gases, that the well depth is roughly kT_c. This presumably means that the depth of the potential well is strongly dependent upon temperature and density. Until these potentials are better understood over the whole liquid range of the metal, we cannot use them to calculate the first-order perturbation term in the free energy.

Instead of attempting to make an exact calculation of the cohesive energy, we make use of the mean-field approximation used in the classical van der Waals model:

$$E = -a/V \ , \tag{2}$$

where a is a positive constant. This has the simplest form consistent with the condition $E = 0$ at $\rho = 0$.

We have used PVT data[1] for mercury to calculate E as a function of ρ for a given supercritical temperature (1823 °K). A plot of E versus ρ for mercury is shown in Fig. 1. The predicted energy from the van der Waals theory is a straight line which falls reasonably close to the mercury data.

The form of the energy generally assumed for a dense metallic phase is

$$E = A/V^{1/3} + B/V^{2/3} + C/V + D \ , \tag{3}$$

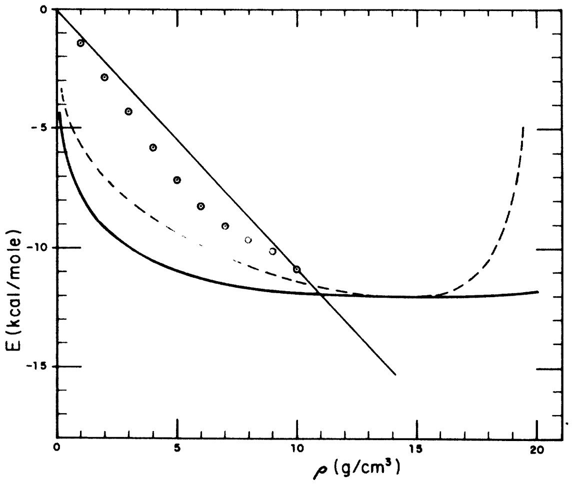

FIG. 1. Comparison of the cohesive energy of mercury at 1823 °K calculated from experimental data (circles) (Ref. 1) with the van der Waals model (straight line), a free-electron theory of the form $A/V^{1/3} + B/V^{2/3}$ (solid curve), and a modified free-electron theory of the form $A/V^{1/3} + B/(V - V_i)^{2/3}$ (dashed curve).

where the first term includes electron exchange energy and the ion-ion potential; the second term is the electron kinetic energy; the third term is the dominant term of the electron-ion potential; and D contains terms due to electron correlation and band effects. Recent calculations with this model[21] have produced good agreement with experimental binding energies (based on a reference state of separated ions and electrons) and compressibilities for nearly free-electron metals such as the alkalis. Thus the theory provides a fairly accurate description of the region near the minimum in the curve of energy versus density. At lower densities, deviations from the theory will occur because the electrons will attach themselves to the ions. There is evidence based on conductivity measurements[22] that this metal-nonmetal transition occurs near the critical density. At very low densities the metal vapor will behave like a normal imperfect gas and the energy will vary as V^{-1} rather than $V^{-1/3}$.

A curve of the form $A/V^{1/3}+B/V^{2/3}$ is given in Fig. 1 in order to show qualitatively how the free-electron theory compares with experiment and van der Waals. The curve is given a minimum value at normal solid density and $E=-12$ kcal/mole, the best estimate of the minimum point at 1823 °K. This curve is obviously unrealistic at low density and near the energy minimum. Use of this form of the cohesive energy in the van der Waals model yields very poor critical constants as a consequence. Also in Fig. 1 we show a curve of the form $A/V^{1/3}+B/(V-V_i)^{2/3}$. The quantity V_i represents the volume excluded from the electrons by the ion cores. We arbitrarily set $V_i=10.0\ \mathrm{cm}^3/$mole for mercury in order to illustrate the improvement which this form represents over the previous one. The theoretical curve now exhibits more realistic behavior near the energy minimum but still fails at low density. Given this uncertainty about the validity of the free-electron theory and the present lack of experimental data in the critical region, the use of the simple mean-field approximation to the cohesive energy appears to be justified.

The mean-field approximation yields a pressure of $-\partial E/\partial V=-a/V^2$, so that the first-order perturbation theory is

$$p=p_0-a/V^2 \quad . \tag{4}$$

Here p_0 is the hard-sphere pressure, and this is a significant improvement over the classical van der Waals theory. The hard-sphere pressure has been calculated by machine experiments[23] and several good algebraic approximations to it are available. The approximation to p_0 which we use is[24]

$$p_0=\frac{RT}{V}\,\frac{1+y+y^2-y^3}{(1-y)^3} \quad , \tag{5}$$

where $y=\pi N\sigma^3/6V$, σ is the hard-sphere diameter, and N is Avogadro's number. This pressure is accurate to a few tenths of 1% for the hard-sphere fluid up to the freezing point.

The constant a is equal to $-E_0V_0$, where E_0 is the molar cohesive energy and V_0 is the molar volume of the metal. The subscripts refer to some reference state. Theoretically, the reference state is at infinite temperature, where the hard spheres are uninfluenced by the attractive potential. This is, of course, experimentally absurd. The region in which E_0 should be measured for best results is the supercritical fluid near normal liquid density. Unfortunately, there is almost no experimental data avaliable for metals in this region. The most reliable values of E_0 and V_0 are available for metals in the solid state.[25] The use of solid-state data to calculate a is justified by noting that the value of a shows no significant difference between solid and liquid mercury.

Now we need to determine an effective hard-sphere diameter σ for each metal. The best way to do this appears to be that of Ashcroft and Lekner,[5] who determined σ by fitting the first peak of the Percus-Yevick hard-sphere structure factor $S(k)$ to the experimental curves for liquid metals. They determined that $y=0.45$ is a close approximation for a liquid metal near the melting point. Hence, all that is needed is the molar volume V_L of the liquid metal at the melting point and σ can be immediately computed:

$$y=\tfrac{1}{6}\pi N\sigma^3/V_L=0.45 \quad . \tag{6}$$

We can now calculate σ for metals for which the liquid density is known, and for the others we can use a simple scaling method to obtain approximate values.

Table I shows a list of computed values of σ compared with other estimates of the diameter.[26] It can be seen that the effective hard-sphere diameters are much larger than the ionic-crystal diameters

TABLE I. Diameters of metal atoms in angstroms calculated by different methods.

	σ^{a}	σ^{b}	σ^{c}	σ^{d}	σ^{e}
Na	3.28	1.90 (+1)	3.14	3.14	3.71
Cs	4.69	3.38 (+1)	4.70	4.66	5.30
Hg	2.75	2.20 (+2)	2.77	2.88	3.21
Pb	3.02	1.68 (+4)	3.00	3.08	3.50
Fe	2.25	1.28 (+3)	2.34	2.33	2.48

[a] Calculated from liquid-metal density by Ashcroft-Lekner rule.

[b] Calculated from ionic-crystal radii in Ref. 26, p. 514. The ionic charges are shown in parentheses.

[c] Calculated from metallic radii in Ref. 26, p. 403.

[d] Calculated from metallic radii of diatomic metal hydrides in Ref. 26, p. 257.

[e] Internuclear distance in the solid metal.

TABLE II. Comparison of experimental rare-gas critical constants with predictions of the van der Waals model.

	V_c (cm^3/mole)		T_c (°K)		p_c (bar)		Z_c	
	Theory	Expt	Theory	Expt	Theory	Expt	Theory	Expt
Ne	51.9	41.7	42.0	44.5	24.1	26.2	0.359	0.295
Ar	95.4	75.3	159	151	49.7	48.9	0.359	0.294
Kr	112.8	92.1	233	209	61.7	55.0	0.359	0.292
Xe	166.6	118.8	290	290	52.0	58.4	0.359	0.288

and about the same size as the metallic-bond diameters listed in the third column of Table I. This indicates that although the species in the metal are ionic, they are screened by electrons so that their repulsion envelopes are much larger than the bare ions. This is an important result because it means that as the metal passes from a condensed phase to a dilute atomic vapor, the effective size of the metal atoms changes very little. This is just what we have assumed in the hard-sphere theory.

The calculation of the critical constants V_c, T_c, and p_c proceeds in the usual way:

$$\frac{\partial p}{\partial V} = \frac{\partial^2 p}{\partial V^2} = 0 \ .$$

These two equations, along with Eq. (4), are solved simultaneously to yield

$$v_c = 0.13044$$

or

$$V_c = 2.417 \times 10^{24} \sigma^3, \quad T_c = 0.7232 a / R V_c \ , \tag{7}$$

$$p_c = 0.2596 a / V_c^2 \ , \quad Z_c = p_c V_c / R T_c = 0.3590 \ .$$

IV. CALCULATIONS

As a check on the van der Waals model, we have calculated the critical constants for rare gases. In this calculation we have used hard-sphere diameters computed from the second virial coefficents[27] rather than from the liquid densities because the empirical $v = 0.45$ rule is not accurate for nonmetals.[28] The constant a is computed from 0 °K solid data.[29] It can be seen from Table II that there is satisfactory agreement between theory and experiment for the four elements. Some discrepancies must appear between theory and experiment independently of the choice of a and σ, since the van der Waals prediction (0.36) of the dimensionless quantity Z_c does not conform to the experimental value, $Z_c = 0.29$, for the rare gases. Plots of the cohesive energy versus the density for supercritical isotherms of argon and xenon[30] show good agreement (within 15%) with van der Waals over the whole density range. The generally accurate predictions of the van der Waals model for the rare gases give us confidence in applying it to metals.

For the alkali metals (Table III), the theoretical critical volumes are uniformly too small. The theoretical temperatures are in good agreement with experiment except possibly for lithium, where the experimental uncertainties are large. The theoretical pressures are much too large. The critical compressibility factor for the alkali metals is $Z_c \cong 0.2$, whereas the van der Waals model predicts 0.36. Hence to an even greater degree than for rare gases, the algebraic form of the equation of state forces disagreement between theory and experiment for at least one critical constant, and the pressure is the worst of the three. The critical-pressure values are made still larger by the small values of the predicted critical volumes. It is interesting to compare these calculations on the alkali metals with the predictions of the classical van der Waals model. For this calculation we write $a = -E_0 V_0$ and $b = \frac{2}{3} \pi N \sigma^3$ (see Table III). The classical model predicts pressures in better agreement with experiment, but now the volumes and temperatures are worse.

For mercury (Table III) the errors in the predicted critical constants are more evenly distributed

TABLE III. Comparison of experimental metal critical points with predictions of the van der Waals model. Classical van der Waals model predictions are shown in parentheses.

	V_c (cm^3/mole)		T_c (°K)		p_c (bar)		Z_c	
	Theory	Expt	Theory	Expt	Theory	Expt	Theory	Expt
Li	47.2(73.9)	66 ± 19	3831(3008)	3223 ± 600	2422(1269)	689 ± 140	0.359	0.17 ± 0.12
Na	85.4(134)	116 ± 23	2635(2069)	2573 ± 350	921(482)	354 ± 70	0.359	0.20 ± 0.12
K	165 (258)	209 ± 40	2185(1716)	2223 ± 330	396(208)	162 ± 30	0.359	0.21 ± 0.13
Rb	200 (313)	247 ± 7	2061(1619)	2093 ± 35	308(161)	159 ± 30	0.359	0.22 ± 0.02
Cs	249 (390)	299	1942(1515)	2050	233(122)	117	0.359	0.205
Hg	50.5(79.1)	35 ± 1	1563(1227)	1753 ± 10	923(484)	1520 ± 10	0.359	0.367

TABLE IV. Comparison of critical constants of metallic elements computed from the van der Waals model with estimates by Grosse and his colleagues

Element	V_c (cm^3/mole) Theory	V_c (cm^3/mole) Grosse	T_c (°K) Theory	T_c (°K) Grosse	p_c(bar) Theory	p_c(bar) Grosse	Reference
Mg	52.7	59	3408	3850	1929	1750	a
Al	39.1		7151	8550	5458		b
Ca	101.4	134	3958	4590	1166		c
Sc	59.0		7431		3759		
V	32.8		11 325		10 314		
Fe	27.5	41.7	9340	6750	10 154		d
Ni	25.6	40.5	9576	6000	11 159		d
Cu	27.4	61	7625	8900	8300		e
Zn	32.6	30	3170	3430	2904		f
Ga	39.5	75	7043	7620	5329		g
Ge	45.0		9803	8400	6511		b
Mo	36.8		14 588	17 000	11 844		g
Pd	35.0		8301		7085		
Ag	39.8	58	6410	7500	4807	5060	h
Cd	48.4	41	2619	2970	1615		f
In	56.4	83	5823	6680	3083	2430	i
Sn	58.5	100	7297	8000	3724	2030	j
Sb	64.8		6370	5070	2936		b
Ba	142.7	193	4154	4720	869		c
Ce	81.1		9089		3347		
Sm	78.2		4661		1780		
Dy	74.4		6211		2492		
Yb	97.5		3741		1146		
Ta	42.3		17 329	22 000	12 223		g
W	37.4		18 538	23 000	14 787	> 10 000	g
Re	34.7		17 293	20 500	14 877		g
Pt	35.6		12 526	14 650	10 505		b
Au	39.4		8267	9460	6265		f
Tl	62.4	85.5	4353	4830	2080		f
Pb	66.9	94	4668	5400	2082	860	h
Bi	71.9	80	5395	4620	2239		k
Th	69.0		14 257		6166		
U	45.9		13 043	12 500	8487		g

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than for the alkali metals. In this case, the experimental value of Z_c is 0.367, coincidentally in close agreement with the theory. The predictions of the classical van der Waals model are uniformly poor.

The very different values of Z_c for mercury and the alkali metals present a theoretical problem. This difference must be due to some basic difference in the effective interaction between the ions in the metal. A qualitative explanation of the difference is provided by the calculation of the cohesive energy for certain model interatomic potentials in the hard-sphere limit. The potentials chosen have the Sutherland form $u(r) = -\epsilon(\sigma/r)^n$ for $r > \sigma$, and where the exponent n is allowed to vary between 3 and 10. The Percus-Yevick hard-sphere radial distribution function is used as a good approximation to the true function in this calculation. The values of $E(V)$ thus calculated are then used in the first-order perturbation theory to calculate Z_c. As n decreases from 10 toward the long-range limit of 3, Z_c steadily decreases from 0.608 to the van der Waals limit of 0.359. The same result may be obtained with a square-well potential whose well width increases indefinitely. More terms in the perturbation series are needed to bring the predicted values of Z_c into closer agreement with experiment, but the trend in Z_c suggests that the smaller value of Z_c in cesium compared to mercury corresponds to a longer-ranged interaction potential or a broader potential well in cesium.

An alternative approach to the problem of predicting different values of Z_c is simply to vary the functional form of the cohesive energy. Specifically we let $E = -a/V^n$ and

$$p = p_0 - a/V^{n+1} \ , \qquad (8)$$

where $n > 0$. Calculations with this equation of state show that, given the appropriate value of n, any desired value of Z_c may be obtained. For the case of cesium, $n = 0.525$. By defining $a = -E_0 V_0^n$ and using the previously determined values of σ, E_0, and V_0, the critical constants for cesium are calculated to be $V_c = 483$ cm^3/mole, $T_c = 3060$ °K, and $p_c = 108$ bars. Although Z_c has been adjusted to the correct value, only the critical pressure is accurately predicted by this theory. Of course, we can adjust a and σ to give the correct critical constants, but this leads to rather unrealistic values of E_0 and σ. The best check on this type of equation of state would be to compare it directly with experimental cesium data in the supercritical region, just as we do for mercury in Sec. V. For mercury, n is close to the van der Waals value of 1.0, as we have seen. Once again, the more slowly decaying cohesive energy, and hence the longer-ranged potential, correspond to lower values of Z_c. According to this discussion, cesium would have a broader potential well than mercury. In agreement with this picture is the correct prediction that $V_c/N\sigma^3$ will be greater for the metal with the wider well, namely, cesium.

As a result of the mean-field approximation to the cohesive energy, the van der Waals model given by Eq. (4) obeys the principle of corresponding states. However, the different values of Z_c imply that all metals do not obey this principle, and that a more accurate approach will involve the unique

TABLE V. Comparison of alkali-halide critical constants computed from the van der Waals model with estimates by Kirshenbaum *et al.* (Ref. 33).

		NaCl		
	V_c(cm^3/mole NaCl)	T_c (°K)	p_c(bar)	Z_c
Na$^+$Cl$^-$(ionic)	129.6	6808	3139	0.359
NaCl (diatomic)	129.6	4050	933	0.359
Kirshenbaum	266 ± 60	3400 ± 200	350 ± 120	0.332
		KCl		
	V_c(cm^3/mole KCl)	T_c (°K)	p_c(bar)	Z_c
K$^+$Cl$^-$ (ionic)	168.7	6717	2378	0.359
KCl (diatomic)	168.7	4870	862	0.359
Kirshenbaum	466 ± 150	3200 ± 200	220 ± 85	0.385

calculation of the cohesive energy as a function of density for each metal. Corresponding states may be valid within certain groups of metals such as the alkalis, but certainly not between groups. This principle will probably also fail for light metals such as lithium and beryllium within their respective groups because of quantum effects. Thus it is not possible to use the principle to predict accurately the Z_c values for other elements. Also it is not possible to predict the relative size of theoretical and experimental values of V_c and p_c for other metals, since the trends are opposed in mercury and the alkalis. Generally, however, we expect that the predicted critical temperatures will be accurate.

In Table IV we show values of V_c, T_c, and p_c for 33 metals from the van der Waals model and from previous estimates. There are possible large errors in the estimated quantities owing to the approximations and extrapolations used to obtain them. Because of this there is little point in a detailed comparison of the van der Waals predictions with the estimates, but the critical temperatures, at least, show satisfactory agreement.

The generally successful predictions of the van der Waals model for metals and the rare gases suggest that the model should be applied to another class of substances, namely, the ionic salts. This calculation is used to demonstrate the importance of properly identifying the molecular species which exist at low density near the critical point.

In Table V the critical constants of sodium and potassium chlorides have been calculated in two ways. First, these salts are assumed to dissociate completely into ions at infinite volume. For this process E_0(NaCl) = − 182.6 kcal/mole and E_0(KCl) = − 165.8 kcal/mole.[31] To make an estimate of σ we assume that cation and anion have the same size and that the rule $y = 0.45$ for the liquid near the melting point holds. The molar volume of the liquid here refers to 1 mole of hard spheres, or $\frac{1}{2}$ mole of alkali-halide molecules. In the second calculation it is assumed that the salts form diatomic molecules at infinite volume. For this process, E_0(NaCl) = − 54.3 kcal/mole and E_0(KCl) = − 60.1 kcal/mole, as determined from spectroscopic observations on the molecules.[32] Again we use the rule $y = 0.45$, this time with the volume of one mole of diatomic molecules, each considered to be a hard sphere.

Now we construct a rough argument which suggests that the diatomic molecules predominate near the critical volume. If an alkali-halide salt is isothermally expanded, the Coulombic energy will approach zero roughly as $-E_0/(V/V_0)^{1/3}$. Alternatively, the energy (relative to separated ions) of a solid composed of diatomic molecules is assumed to re-

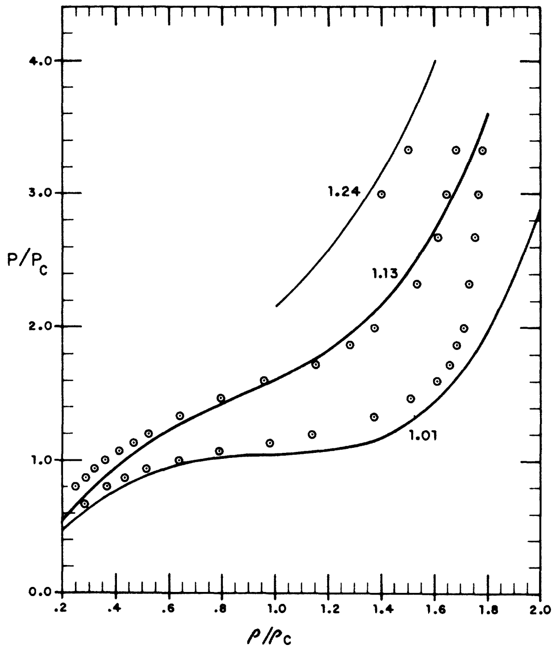

FIG. 2. Comparison of the reduced experimental equation of state (Ref. 1) for mercury (circles) with the van der Waals model (solid curve). Values of T/T_c are shown for each isotherm.

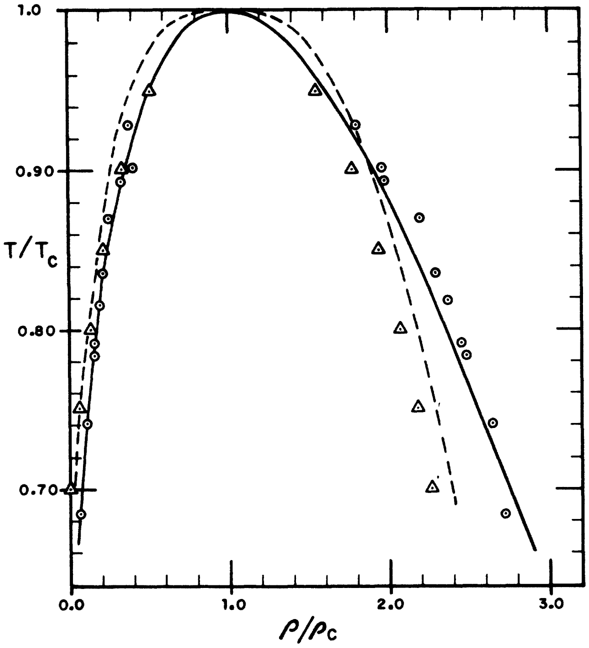

FIG. 3. Comparison of reduced coexistence curves computed from the van der Waals model (solid curve) with experimental cesium data (circles) (Ref. 2), mercury data (triangles) (Ref. 34), and with smoothed rare-gas data (dashed curve) (Ref. 35).

main roughly constant, because of the much weaker interaction between diatomic molecules than between ions. Where these two energy curves cross then determines the boundary of stability between the ionic and diatomic assembles. Thus for NaCl and KCl, the diatomic system will be more stable for $V/V_0 > 2.86$ and $V/V_0 > 3.86$, respectively. In fact $V_c/V_0 = 4.80$ for NaCl and $V_c/V_0 = 4.49$ for KCl as predicted from the theory.

These calculations favor the predominance of diatomic molecules near the critical point, both in satisfying the volume criterion just mentioned, and in predicting T_c and p_c closer to the values estimated by Kirshenbaum[33] in Table V. These estimates are based on extrapolation of the experimental vapor-liquid coexistence curve to the critical point, using the law of rectilinear diameter.

V. THERMODYNAMICS

As a further check on the validity of the van der Waals model as applied to metals, we compare theoretical and experimental equation-of-state data for mercury. The experimental data must be reduced in order to make the comparison. Thus in Fig. 2, p/p_c versus ρ/ρ_c is plotted for three values of T/T_c. There is moderately good quantitative agreement between theory and experiment except at the highest densities. This deviation at high density is undoubtedly due to the inadequacy of the hard-sphere model for mercury under extreme conditions.

It is worthwhile to compare the vapor-liquid coexistence curve predicted by the model and observed for metals. Figure 3 shows reduced T-versus-ρ curves for mercury,[34] cesium,[2] the rare gases,[35] and the van der Waals model. The cesium curve is well reproduced by the van der Waals result. The fact that the mercury coexistence curve does not match the cesium curve simply restates the previous observation that the corresponding states principle is not valid for these metals. Egelstaff[36] has plotted the experimental alkali-metal coexistence curves[2] logarithmically to show that they appear to be more nearly quadratic in form than the inert gases, which have a cubic form. This conclusion is based on metal data not very close to the critical point, so it remains tentative. The van der Waals model predicts a quadratic coexistence curve near the critical point, and the existence of an experimental curve of this form would suggest that long-range forces, which underlie the van der Waals model, really do exist in liquid metals. In contrast, molecular fluids have a cubic coexistence curve and a short range of interaction. More experimental work on metals close to the critical point is needed to clarify the situation.

The vapor-pressure curve is also of interest. For mercury[34] and cesium[37] this curve is closely logarithmic, so that $\ln p = A/T + B$. Van der Waals also produces a curve of this form. Figure 4 shows $\ln(p/p_c)$ versus T_c/T for inert gases,[35] van der

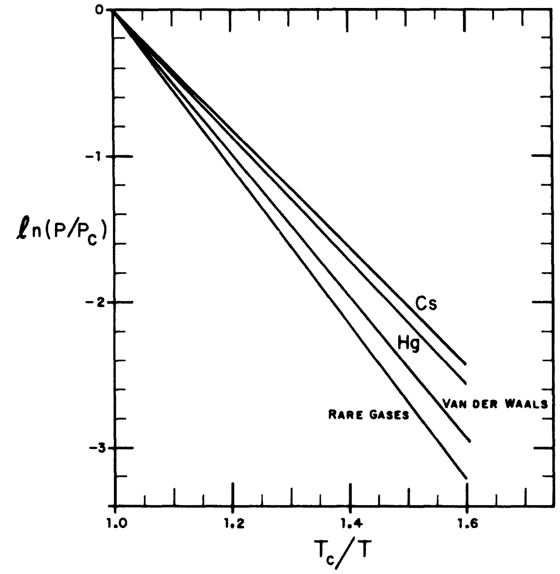

FIG. 4. Comparison of reduced vapor-pressure curves computed from the van der Waals model with smoothed experimental cesium (Ref. 37), mercury (Ref. 34), and rare-gas (Ref. 35) data.

Waals, mercury, and cesium. The van der Waals result lies between the inert gas and metal curves.

VI. CONCLUSION

We have shown that the van der Waals model provides semiquantitative agreement with experimental data on metals near the critical point. At present, this model is at least as accurate as other theories in predicting thermodynamic properties in the critical region. Of the three critical constants, the critical temperature is most accurately predicted by the model. Substantial improvement of the model will require more data on which to check the assumptions embodied in the constant hard-sphere diameter, the mean-field form of the cohesive energy, and the magnitude of the constant a. Also, more reliable determination of the interatomic potential in liquid metals as a function of density and temperature over the whole liquid range is needed.

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