On the Tait and Related Empirical Equations of State

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The nature of the empirical parameters in the Tait equation and related empirical equations of state are examined and the dependence of these parameters upon the intermolecular-pair potential is investigated. The empirical parameters of the various equations of state considered are shown to be rather simply related. Explicit theoretical relationships for the parameters of a slightly modified form of the Tait equation, $(-1/v)(\partial v/\partial p)_T = C/[p + B(T)]$, are derived. The semiquantitative dependence of the Tait parameters on repulsive and attractive forces is obtained from the investigation of a hard-sphere model and a hard-sphere model with attractive forces. Quantitative dependence of the parameters in the various equations considered is found from the consideration of a classical equation of state valid at high number densities, which is derived from the cell model of Lennard-Jones and Devonshire. This equation of state gives the explicit dependence of the pressure upon all the parameters of the Mie potential. Values for the compressibility factors at high densities calculated using this equation of state are found to be in excellent agreement with those values calculated by the numerical integration of the free volume integral and associated integrals. The C and B parameters calculated from this theoretical equation of state are shown to depend upon both the attractive and repulsive forces. It is found in agreement with experimental observations that the C parameter is only slightly temperature dependent, and that the B parameter is a decreasing function of the temperature. The theoretically calculated C and B parameters for solid argon are found to be in good agreement with the experimentally determined values.

I. Introduction

Toward the end of the nineteenth century, Tait,[2] a noted Scottish mathematician and physicist, studied the compressibilities of glass, mercury, and water, and in the course of these studies he introduced an empirical equation which historically is usually written in the following form

$$-\frac{1}{v_0}\left(\frac{\partial v}{\partial p}\right)_T = \frac{C^*}{p + B^*(T)} \tag{1}$$

where p is the pressure, v_0 is a reference volume, and C^* and B^* are constants characteristic of the material being studied. During the intervening years, this empirical equation has proved to be very successful for both liquids and solids. Experimental data have been obtained and the two Tait parameters, C^* and B^*, have been experimentally determined and qualitatively discussed for a variety of liquid systems.[3-7] The C^* parameter has been found to be nearly independent of temperature and density for a given liquid; the values for C^* have been found to range from 0.089 for liquid hydrocarbons to 0.149 for liquid water. The B^* parameter has been found to be a decreasing function of the temperature and is usually several hundred atmospheres in magnitude.

Often the Tait equation is modified so that the left-hand side of the equation may be identified with the isothermal compressibility, K

$$-\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T = \frac{C}{p + B(T)} \tag{2}$$

Frequently, this modified form is identified as the Tait equation.[8] For dense systems the values of the parameters for the above equations will differ only slightly as may be seen from the following relationships between the parameters of eq 1 and 2

$$C^* = \frac{v}{v_0}\frac{C}{1 + C} \tag{3}$$

$$B^* + p = \frac{B + p}{1 + C}$$

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[2] P. G. Tait, "Physics and Chemistry of the Voyage of H.M.S. Challenger," Vol. II, Part IV, 1888 S.P. LXI.

[3] A. Carl, *Z. Physik. Chem.*, **101**, 238 (1922).

[4] R. E. Gibson, *J. Am. Chem. Soc.*, **56**, 4 (1934).

[5] R. E. Gibson and O. H. Loeffler, *J. Phys. Chem.*, **43**, 207 (1939).

[6] R. E. Gibson and O. H. Loeffler, *Ann. N. Y. Acad. Sci.*, **51**, 727 (1949); contains a rather complete bibliography.

[7] W. G. Cutler, R. H. McMickle, W. Webb, and R. W. Sciessler, *J. Chem. Phys.*, **29**, 727 (1958).

[8] "Handbook of Chemistry and Physics," 47th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1966, p F9.

Thus, it can be seen that it matters little which empirical form one chooses to describe the isothermal behavior of dense systems.

The Murnaghan equation[9] for solids at high pressures is given by the expression

$$p = b^{-1}K_0\left[\left(\frac{v_0}{v}\right)^b - 1\right] \tag{4}$$

where K_0 is the bulk modulus corresponding to the reference volume v_0 and b is a constant. The integrated form of eq 2 is equivalent to eq 4 with the following relationships holding between the parameters of the two equations

$$b = \frac{1}{C} \tag{5}$$

$$K_0 = \frac{B}{C}$$

Experimental work has shown that eq 1 and 2 closely fit observed compressibilities over several thousand atmospheres for numerous liquids and solutions. MacDonald[10] has pointed out the applicability of eq 1 and 2 in considerable detail.

In addition, eq 2 seems to describe the compressibilities of highly compressed gases quite well as is indicated in Figure 1 where $-v(\partial p/\partial v)_T$ *vs.* p is plotted for highly compressed argon gas[11] at 328°K and solid argon[12] at 77°K; according to eq 2, the slopes of these lines should be C^{-1} and the intercepts BC^{-1}. The insensitivity of the C parameter for argon to temperature can also be noted from Figure 1. Unfortunately, the data available on liquid argon are over such a short pressure range (pressures not exceeding 200 atm) that they were not plotted on the figure.

Although the Tait equation has been used for many years and is thought to be one of the most successful empirical equations for describing the isothermal equilibrium properties of liquids and solids,[8,13] little theoretical work has been done on the equation. Kirkwood and Bethe[14] have derived a modified form of the equation for extremely high pressures. Ginnell[15] has interpreted the Tait equation in terms of his theory of molecular association. Recently Nanda and Simha,[16] utilizing the principle of corresponding states, have examined the relationship between the Tait parameters and a theoretical equation of state, derived from a cell theory for oligomer and polymer liquids. However, in none of these investigations are the Tait parameters related to the parameters of the potential of intermolecular interaction. It has been suggested[5] from qualitative arguments that C^* is a constant independent of the temperature, because it depends only on the repulsive forces between molecules, and that B^* represents the net internal pressure of the liquid; *i.e.*, an increase in the attractive potential between molecules, a decrease in temperature, and an increase in free volume all cause B^* to increase. It has been found experimentally that C^* is nearly independent of temperature and volume, and that B^* is a decreasing function of the temperature. The C and B parameters of the modified equation behave similarly. The empirical b parameter of the Murnaghan equation, which was derived from the theory of finite strain, is not theoretically well understood. It has been generally observed that the b parameter is nearly independent of volume and temperature.[17]

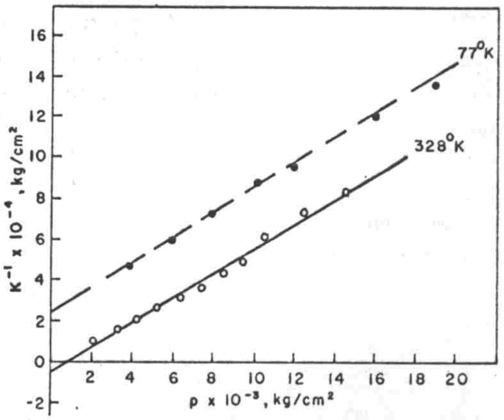

Figure 1. The inverse of the isothermal compressibility plotted *vs.* the pressure for solid argon at 77°K from Stewart,[12] - - - —, and for gaseous argon at 328°K from Bridgman,[11] ———.

In this paper we have attempted to relate the parameters of eq 1 and 2 to the parameters of an intermolecular-pair potential and to analyze the temperature dependence and other properties of these empirical parameters. In the following section, expressions are derived for the parameters of the Tait equation for a model in which there are only repulsive forces and compared with those derived from a model to which attractive forces have been added. In the third section, we derive from cell theory an equation of state which is accurate at high densities and which contains, explicitly, the dependence of the pressure upon the parameters of a general Mie potential. From this equation of state, the C and B of eq 2 are derived and their behaviors described.

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(9) F. D. Murnaghan, "Finite Deformation of an Elastic Solid," John Wiley and Sons, Inc., New York, N. Y., 1951, Chapter 4.

(10) J. R. MacDonald, *Rev. Mod. Phys.*, **38**, 669 (1966).

(11) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **70**, 1 (1935).

(12) J. W. Stewart, *J. Phys. Chem. Solids*, **1**, 146 (1956).

(13) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954, p 261.

(14) J. G. Kirkwood and H. Bethe, "The Pressure Wave Produced by an Underwater Explosion," OSRD Report No. 588, Part 1, Department of Commerce Bibliography No. PB 32182.

(15) R. Ginnell, *J. Chem. Phys.*, **34**, 1249 (1961).

(16) V. S. Nanda and R. Simha, *J. Phys. Chem.*, **68**, 3158 (1964).

(17) J. J. Gilvarry, *J. Appl. Phys.*, **28**, 1253 (1957).

II. Tait Parameters from a Rigid-Sphere Model

In order to show in a semiquantitative way the dependence of the Tait parameters on repulsive and attractive forces, we consider first a system of rigid spheres and then a rigid-sphere system with attractive forces. An equation of state for a system of rigid spheres has been theoretically derived both from the scaled-particle theory[18] and from solutions of the Percus–Yevick integral equation.[19,20] This equation of state is given by

$$p_0 = \frac{kT}{v}\,\frac{(1 + y + y^2)}{(1 - y)^3} \qquad (6)$$

where

$$y = \frac{\pi\sigma^3}{6v}$$

and v is the volume per molecule and σ is the diameter of a rigid sphere in the system. This equation of state should best be applicable at very high temperatures where attractive forces can be neglected. At lower temperatures, it is necessary to include the effects of attractive forces on the equation of state. Widom[21] has shown that if the attractive forces in a system of rigid spheres provide a uniform negative potential, then thermodynamic consistency demands that the equation of state be given by

$$p = p_0 - \frac{a'}{v^2} \qquad (7)$$

Guggenheim[22] has shown that eq 7 works quite well for liquid argon at densities and temperatures between those at the triple and critical points.

From eq 1 the following general relationships can be obtained for calculating the C^* and B^* parameters

$$C^* = \frac{-\left(\frac{\partial p}{\partial v}\right)_T}{v_0\left(\frac{\partial^2 p}{\partial v^2}\right)_T} \qquad (8)$$

$$B^* = -\left[C^* v_0\left(\frac{\partial p}{\partial v}\right)_T + p\right] \qquad (9)$$

By taking the appropriate derivatives of eq 6 and 7, one can find the Tait C^* parameters to be

$$C^* = \frac{(1 + 2y)(1 - y)}{2(1 + 5y)} \qquad (10)$$

for rigid spheres and

$$C^* = \frac{(1 + 2y)^2(1 - y) - \dfrac{2a'(1 - y)^5}{kTv}}{2(1 + 5y)(1 + 2y) - \dfrac{6a'}{kTv}(1 - y)^5} \qquad (11)$$

for eq 7 where we have used the approximation

$$v\left(\frac{\partial^2 p}{\partial v^2}\right)_T \cong v_0\left(\frac{\partial^2 p}{\partial v^2}\right)_T$$

At high temperatures, the temperature-dependent terms in the numerator and denominator in eq 11 become small and eq 11 reduces to eq 10. The C^* parameter of eq 10 is temperature independent, but it is density dependent through the y parameter, which in turn is directly proportional to the density.

The value of the y parameter is less than or equal to 0.740, and for $0.5 \leq v^*/v \leq 1.0$, C^* is of the order of 10^{-1}. For small variations of the density, which at high densities correspond to very large pressure changes, C^* does not change rapidly. The effect of adding an attractive term to the hard-sphere equation of state is to reduce the value of C^* by several per cent and to introduce into the C^* expression temperature-dependent terms. The variation with temperature of the C^* parameter in eq 11 is not very great, principally because the temperature-dependent terms occur as corrective terms in a ratio of two temperature-dependent expressions so that C^* varies only as the numerator changes relative to changes in the denominator of eq 11. At the triple point of argon, the empirically fitted values[22] of y and a'/kTv are 0.427 and 8.56, respectively, so that $C^* = 0.108$. If the temperature-dependent terms are omitted, then $C^* = 0.169$. (From least-squares fits of plots of K^{-1} *vs.* p,[23] the average value of C^* is 0.112 ± 0.02 for liquid argon.)

From this example, it seems that by considering only repulsive forces in the system, one can find the correct order of magnitude of C^*, but the attractive terms are very important at liquid temperatures and densities.

The B^* parameter can be found from eq 6–8 to be

$$B^* = -\frac{kT}{v}\,\frac{(1 + 6y + 2y^3)}{2(1 - y)^3(1 + 5y)} \qquad (12)$$

for rigid spheres and

$$B^* = -\frac{kT}{v}\,\frac{1 - y^3 - C^*(1 + 2y)^2}{(1 - y)^4} + \frac{a'}{v^2}(1 - 2C^*) \qquad (13)$$

for eq 7. The B^* parameter for rigid spheres is always negative; the B^* parameter for hard spheres with attractive forces contains a negative term, which is linearly dependent upon the temperature, and a positive temperature-independent term. (Here we are considering the temperature dependence of C^* param-

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(18) H. Reiss, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.*, **31**, 369 (1959).

(19) M. S. Wertheim, *Phys. Rev. Letters*, **8**, 321 (1963).

(20) E. Thiele, *J. Chem. Phys.*, **38**, 1959 (1963).

(21) B. Widom, *ibid.*, **39**, 2808 (1963).

(22) E. A. Guggenheim, *Mol. Phys.*, **9**, 43 (1965).

(23) A. Van Itterbeck and O. Verbeke, *Physica*, **26**, 931 (1960).

eter to be negligible.) The positive term arises from the presence of attractive forces in the system. We thus conclude that the B^* parameter is a decreasing function of the temperature which depends strongly on both attractive and repulsive forces in the system.

III. Relationship of the Tait Parameters to the Mie Potential

In the preceding section it was demonstrated that the dependence of the Tait parameters on the intermolecular pair potential can be ascertained from the consideration of theoretical equations of state. By the nature of the equations considered, the nature of the dependence of the Tait parameters upon the intermolecular potential is necessarily limited to being only semiquantitative in character. However, the explicit dependence of the parameters of the Tait and related empirical equations of state upon the parameters of an intermolecular-pair potential such as a Mie potential can be successfully obtained from the consideration of a suitable model applicable to condensed systems.

In this section a classical equation of state valid at high number densities is derived from the cell model of Lennard-Jones and Devonshire. The equation is in excellent agreement with the numerically calculated results, under the conditions mentioned, and gives the explicit dependence of the pressure upon all the parameters of the pair potential used. The parameters of eq 2 are then calculated from this equation of state and their dependence upon the parameters of the intermolecular-pair potential and the temperature are analyzed.

In recent years several authors[24,25] have pointed out that the cell model is indeed an excellent model for solids and high-density systems. Equation of state calculations based upon this model have been carried out for solid argon[26] and the results are in excellent agreement with experiment.

We proceed following the well-established approach beginning with the free-volume theory of liquids and solids for which the Helmholtz free energy is given by the relation

$$A = NkT \ln \frac{v_f \alpha}{\Lambda^3} + \frac{N\phi^*(0)}{2} \qquad (14)$$

and

$$\Lambda = \frac{h}{(2\pi wkT)^{1/2}}$$

where v_f is the free volume per molecule, $N\phi^*(0)/2$ is the energy of the system when all the molecules are located at the centers of their cells, and α is the communal entropy term which is usually considered to be a constant and for crystalline solids is set equal to unity. In the one-shell LJD theory,[27] it is assumed that the nearest neighbors are smeared over a sphere of radius equal to the nearest neighbor distance a, and v_f is given by

$$v_f = \int 4\pi r^2 \exp\left[-\frac{\Psi(r)}{kT}\right] \mathrm{d}r \qquad (15)$$

where

$$\Psi(r) = \phi(r) - \phi(0) \qquad (16)$$

and

$$\phi(r) = \frac{c}{2}\int_0^{\pi} U(R) \sin\theta \, \mathrm{d}\theta \qquad (17)$$

where

$$R^2 = r^2 + a^2 - 2ar\cos\theta$$

$$a^3 = \gamma v$$

Here, v is the volume per molecule, and $U(R)$ is the potential of interaction.

Lennard-Jones and Ingham,[28] who included the effects of all shells, obtained the following general result for $\phi^*_\gamma(0)$

$$\phi^*_\gamma(0) = \frac{\epsilon}{n - m}\left[mc_\gamma f_{n,\gamma}\left(\frac{r^*}{a}\right)^n - nc_\gamma f_{m,\gamma}\left(\frac{r^*}{a}\right)^m\right] \qquad (18)$$

where c_γ is the number of nearest neighboring molecules for the geometry indicated by γ, and $f_{n,\gamma}$ is a coefficient derived by adding the contributions to $\phi^*_\gamma(0)$ by all shells in which the molecules interact with a central molecule with a potential inversely proportional to r^n. The values of these coefficients are given in Table I for the Lennard-Jones 6:12 potential for the cubic lattices.

Table I: Values of $c_\gamma f_{12,\gamma}$ and $c_\gamma f_{6,\gamma}$

Lattice geometry	c_γ	γ	$cf_{12,\gamma}$	$cf_{6,\gamma}$
Simple cubic	6	1	6.2021	8.40192
Body-centered cubic	8	$3\sqrt{3}/4$	9.1142	12.2533
Face-centered cubic	12	$\sqrt{2}$	12.1318	14.4539

It is to be noted that $\phi^*_\gamma(0)$ is different from the lattice energy found by considering eq 17, since the lattice energy, $\phi(0)$, derived from eq 17 is based upon a one-shell calculation. Equation 17 can be applied to each shell surrounding a central molecule with appropriate changes of c and a. When three shells are considered

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(24) W. L. Hoover and B. J. Alder, *J. Chem. Phys.*, **45**, 2361 (1966).

(25) J. A. Barker, "Lattice Theories of the Liquid State," Macmillan and Co., Ltd., New York, N. Y., 1963, Chapter 3.

(26) H. G. David and S. D. Harmann, *J. Chem. Phys.*, **38**, 3037 (1963).

(27) J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc.* (London), **A163**, 53 (1937).

(28) J. E. Lennard-Jones and A. E. Ingham, *ibid.*, **A107**, 636 (1925).

Table II: A Comparison of One-Shell and Three-Shell Integrals for $c\epsilon/kT$ = 18.701[a]

v/v^*	g	g_l	g_m	G	g_L	g_M
1.00	2.172(−4)	2.732(−5)	5.886(−6)	2.273(−4)	2.952(−5)	6.671(−6)
0.95	1.491(−4)	1.471(−5)	3.202(−6)	1.551(−4)	1.573(−5)	3.595(−6)
0.90	1.009(−4)	7.716(−6)	1.695(−6)	1.043(−4)	8.179(−6)	1.887(−6)
0.85	6.722(−5)	3.938(−6)	8.716(−7)	6.910(−5)	4.138(−6)	9.620(−7)
0.80	4.399(−5)	1.949(−6)	4.341(−7)	4.499(−5)	2.032(−6)	4.754(−7)
0.75	2.821(−5)	9.321(−7)	2.086(−7)	2.873(−5)	9.650(−7)	2.269(−7)
0.70	1.768(−5)	4.287(−7)	9.634(−8)	1.794(−5)	4.410(−7)	1.041(−7)
0.65	1.079(−5)	1.884(−7)	4.248(−8)	1.090(−5)	1.927(−7)	4.565(−8)
0.60	6.371(−6)	7.853(−8)	1.774(−8)	6.420(−6)	7.991(−8)	1.897(−8)

[a] The symbols g, g_l, g_m, G, g_L, and g_M are the same as those used in ref 29. The number in parentheses is the power of 10 by which the entry is to be multiplied.

and $\phi(0)$ is found in this manner, the coefficient of the repulsive terms in $\phi(0)$ and $\phi^*_\gamma(0)$ are almost the same, but those for the attractive terms are quite different. Often it has been the custom to use for one-shell calculations $\phi_\gamma(0)$ derived from eq 17. On the other hand, for three-shell calculations, a $\phi^*_\gamma(0)$, derived from eq 18 and Table I, is used. We choose as the lattice energy for solids $\phi^*_\gamma(0)$ of eq 18. (In an ideal cell model for a perfectly ordered solid, one would choose to calculate both the lattice energy and the free volume by a consideration of the interaction of a molecule with all of its surrounding shells. Fortunately, the equation of state in the temperature and density regions where the model is most applicable is quite insensitive to the number of shells used in a calculation of the free volume term, as we shall show shortly.)

Table III: A Comparison of Contributions to the Compressibility Factor for $c\epsilon/kT$ = 18.701

v/v^*	Free-volume contribution to pv/kT 1 shell	3 shells	Approx	$\phi^*(0)$ contribution to pv/kT
1.00	8.38	8.52	9.50	−7.24
0.95	8.28	8.39	9.09	−3.49
0.90	8.17	8.27	8.75	+2.02
0.85	8.06	8.14	8.47	10.09
0.80	7.94	8.01	8.23	21.93
0.75	7.83	7.89	8.03	39.43
0.70	7.72	7.77	7.87	65.55
0.65	7.62	7.67	7.71	105.21
0.60	7.54	7.57	7.59	166.64

Table IV: A Comparison of Compressibility Factors for $c\epsilon/kT$ = 18.701

v/v^*	pv/kT 1 shell	3 shells	Approx
1.00	1.14	1.28	2.26
0.95	4.79	4.90	5.60
0.90	10.19	10.29	10.77
0.85	18.15	18.23	18.56
0.80	29.87	29.94	30.16
0.75	47.26	47.32	47.46
0.70	73.27	73.32	73.42
0.65	112.83	112.88	112.92
0.60	174.18	174.21	174.23

Calculations of the three-shell integrals at high densities with T = 77°K and ϵ/k = 120°K (corresponding to argon) were made and are compared to the single-shell integrals in Table II. All of our calculations of the various LJD integrals were done on an IBM 7072 computer using Simpson's rule. Accuracy to four significant figures was obtained by successively doubling the number of intervals until there was four place agreement. A direct comparison was made of our computed values for the three-shell integrals with the corresponding calculations of Wentorf, *et al.*,[29] and nearly exact agreement was found except at very low temperatures and high densities. Even under these conditions, the differences were found to be only a few per cent in most cases. It is evident from a consideration of these data that as the density increases, the differences in the one- and three-shell integrals correspondingly diminish. In Table III, it is noted that the free-volume contributions to the compressibility factors for the one-shell integrals become nearly equal at high densities, and from Table IV it can be seen that the compressibility factors for one-shell and three-shell calculations are virtually indistinguishable at high densities. The reasons for this can be seen by considering the relative contributions of the lattice energy and the free volume to the compressibility factors; the relative change of these contributions with increasing densities can be found in Table III where it may be observed that the lattice energy term changes rapidly and at high densities is by far the dominant term. Thus, at high ρ it hardly matters whether the free-volume contribution is calculated using one shell or three shells.

In the derivation of the high-density equation of state which follows, we limit ourselves to one-shell consider-

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(29) R. H. Wentorf, Jr., R. J. Buehler, J. O. Hirschfelder, and C. F. Curtiss, *J. Chem. Phys.*, **18**, 1484 (1950).

ations in determining the free volume and use for the pair-potential function the Mie potential

$$U(R) = \frac{\epsilon}{n-m}\left[m\left(\frac{r^*}{R}\right)^n - n\left(\frac{r^*}{R}\right)^m\right] \quad n > m \qquad (19)$$

Using eq 16–18 we find that the potential field is given by the relation

$$\Psi[r(x)] = \phi_{n,m}(x) - \phi_{m,n}(x) \qquad (20)$$

where

$$\phi_{n,m} = \frac{c\epsilon m}{2|m-n|}\left(\frac{r^*}{a}\right)^n \times \left[\frac{(1+x)^{n-2} - (1-x)^{n-2}}{(n-2)\,(1-x^2)^{n-2}} - 2\right] \qquad (21)$$

and

$$x = \frac{r}{a}$$

The usual procedure at this point has been to evaluate the free-volume integral numerically using eq 15, 20, and 21, and then to tabulate v_f and the associated integrals for different values of potential function parameters. Instead, we proceed by first expanding $\Psi(x)$ as given by eq 20 and retaining only the quadratic term, so that

$$\frac{\Psi(x)}{kT} \approx \lambda x^2 \qquad (22)$$

where

$$\lambda = \frac{c\epsilon mn}{6kT(n-m)}\left[(n-1)\left(\frac{r^*}{a}\right)^n - (m-1)\left(\frac{r^*}{a}\right)^m\right] \qquad (23)$$

Thus, in this approximation the free volume is

$$v_f = 4\pi a^3 \int_0^{0.55267} \exp(-\lambda x^2)x^2\,dx \qquad (24)$$

where the upper limit on the integral is that for a face-centered cubic lattice. At high number density, ρ, the value of the integral is insensitive to this limit and the results derived below are also valid for other cubic lattices. The free-volume contribution to the equation of state in this approximation is given by

$$kT\left(\frac{\partial \ln v_f}{\partial v}\right)_T = \frac{kT}{v} - \frac{kT\dfrac{\partial\lambda}{\partial v}\displaystyle\int_0^{0.55267}\exp(-\lambda x^2)x^4\,dx}{\displaystyle\int_0^{0.55267}\exp(-\lambda x^2)x^2\,dx} \qquad (25)$$

At high ρ and low T, λ is very large, and the ratio of the two integrals in eq 25 is $3/(2\lambda)$. Consequently

$$\left(\frac{\partial \ln v_f}{\partial v}\right)_T = \frac{1}{v} - \frac{3}{2}\frac{\partial \ln \lambda}{\partial v} \qquad (26)$$

and the compressibility factor is given by

$$\frac{pv}{kT} = 1 + \frac{1}{2}\,\frac{n(n-1)\left(\dfrac{v^*}{v}\right)^{(n-m)/3} - m(m-1)}{(n-1)\left(\dfrac{v^*}{v}\right)^{(n-m)/3} - (m-1)} + \frac{c_\gamma\, mn\epsilon}{6kT(n-m)}\left[f_{n,\gamma}\left(\frac{v^*}{v}\right)^{n/3} - f_{m,\gamma}\left(\frac{v^*}{v}\right)^{m/3}\right] \qquad (27)$$

where

$$v^* = \gamma^{-1}r^{*3}$$

For $n = 12$, $m = 6$, and $c_\gamma = 12$, the lattice energy contribution to the compressibility factor is given by

$$\left(\frac{pv}{kT}\right)_{\phi^*(0)} = \frac{24\epsilon}{kT}\left[1.0110\left(\frac{v^*}{v}\right)^4 - 1.2045\left(\frac{v^*}{v}\right)^2\right] \qquad (28)$$

and the free-volume contribution is

$$\left(\frac{pv}{kT}\right)_{v_f} = 1 + \frac{66\left(\dfrac{v^*}{v}\right)^2 - 15}{11\left(\dfrac{v^*}{v}\right)^2 - 5} \qquad (29)$$

In Table III, the free-volume contribution computed using eq 29 is compared with the numerically calculated one-shell and three-shell contributions; it is evident that the agreement is good and that it improves with increasing density. The compressibility factors computed using eq 28 and 29 are compared with the one shell and three shell numerically evaluated compressibility factors in Table IV. It is noted that the compressibility factors computed in this approximation at high densities are virtually indistinguishable from the numerically calculated values.

In the derivation of eq 27, we have used an expansion of $\Psi(x)/(kT)$ in which only the quadratic term was retained. To discuss this approximation briefly, we consider the expansion of eq 20, retaining the x^4 term

$$\frac{\Psi(x)}{kT} = \lambda(x^2 + \lambda^* x^4) \qquad (30)$$

It can be shown that λ^*, which is temperature independent, decreases slowly with increasing density and is equal to approximately 10 over the range $1.25 \leq v^*/v \leq 2$. On the other hand, λ is a rapidly increasing function of the density; for $c\epsilon/kT = 18.7$ corresponding to argon at 77°K and $m = 6$, $n = 12$, the coefficient λ increases from 712 to 5834 as v^*/v increases from 1.25 to 2.

We conclude from the fact that $\lambda^* x^4 \approx 10x^4$ that this term is less than 5% of x^2 for $x < 0.07$, but for a large value of λ, say 2000, if $x = 0.07$, then $\lambda x^2 = 10$, and the integrand in the free-volume expression given by eq 15 is very small, relative to its maximum value of approximately $(\lambda e)^{-1}$. Thus, for large values of λ corresponding to high ρ and low T, the x^4 term does not become important relative to the x^2 term until after the integrand in eq 15 is virtually zero. Similarly, one can show that higher order terms in the expansion of eq 16 can be neglected for high ρ and low T.

From eq 27, one can derive expressions for the C and B parameters of eq 2 and for the parameters of the Murnaghan equation and Tait equation for dense systems at low temperatures, which depend explicitly upon the parameters of a Mie potential and upon the density and temperature. The complete expressions for the B and C parameters as determined from eqs 2 and 27 are given by the equations

$$\frac{1}{C} + 1 = \frac{v^2\left(\frac{\partial^2 p}{\partial v^2}\right)_T}{-v\left(\frac{\partial p}{\partial v}\right)_T} \tag{31}$$

$$B = -C^* v\left(\frac{\partial p}{\partial v}\right)_T - p$$

where

$$p = Tj_1 + j_2$$

$$-v\left(\frac{\partial p}{\partial v}\right)_T = -Tj_3 + j_4 + p \tag{32}$$

$$v^2\left(\frac{\partial^2 p}{\partial v^2}\right)_T = p - v\left(\frac{\partial p}{\partial T}\right)_v - \frac{(n - m + 6)}{3}Tj_1 + Tj_5 + 2j_4 + j_6$$

with the j_i's defined by the relations

$$j_1 = \frac{k}{v}\left[1 + \frac{1}{2}\,\frac{n(n-1)t^{n-m} - m(m-1)}{(n-1)t^{n-m} - (n-1)}\right]$$

$$j_2 = \frac{c\gamma mn\epsilon}{6(n-m)v}\left[f_{n,\gamma}t^n - f_{m,\gamma}t^m\right]$$

$$j_3 = \frac{k}{6v}\,\frac{(n-m)^2(n-1)(m-1)t^{n-m}}{[(n-1)t^{n-m} - (m-1)]^2} \tag{33}$$

$$j_4 = \frac{c\gamma\epsilon mn}{18(n-m)v}\left[nf_{n,\gamma}t^n - mf_{m,\gamma}t^m\right]$$

$$j_5 = \frac{k}{9v}\,\frac{(n-m)^3(m-1)(n-1)^2t^{2(n-m)}}{[(n-1)t^{n-m} - (m-1)]^3}$$

$$j_6 = \frac{c_\gamma\epsilon mn}{54(n-m)v}\left[n^2f_{n,\gamma}t^n - m^2f_{m,\gamma}t^m\right]$$

with

$$t = \left(\frac{v^*}{v}\right)^{1/3}$$

A relatively simple expression for the C parameter can be derived from the preceding equations if some of the unimportant terms are dropped. Equation 31 shows the C parameter depends upon changes in the pressure with specific volume. A consideration of Table III shows that at high densities the change with density of the $\phi^*_\gamma(0)$ contribution to the pressure is over two orders of magnitude larger than the change in the free-volume contribution. Neglecting the contributions to the C parameter from free-volume contributions to pressure, one can show that

$$C = \frac{\left(\frac{v^*}{v}\right)^{(n-m)/3} f_{n,\gamma}(9 + 3n) - f_{m,\gamma}(9 + 3m)}{\left(\frac{v^*}{v}\right)^{(n-m)/3} f_{n,\gamma}(3 + n)^2 - f_{m,\gamma}(3 + m)^2} \tag{34}$$

One will note immediately that the expression above is independent of temperature. The temperature-dependent terms in C were lost when the free-volume contributions were dropped. In the complete expression, the temperature-dependent terms occur as small subtractive terms in the numerator and denominator of eq 31, and at high densities, these terms have a small effect on the value of C. The dependence of the C parameter upon the density is not small over all ranges of the density as Figure 2 shows. There C is plotted *vs.* v^*/v for $n = 12$, $m = 6$, $f_{n,\gamma} = 1.011$, and $f_{m,\gamma} = 1.2045$. However, for compressibility experiments carried out at high pressures and high densities, C can be considered to be nearly a constant, as the following illustration will show. In compressibility experiments on solid argon at 77°K, v^*/v ranges from about 1.15 to 1.34 as the pressure is changed from 4000 to 16,000 kg/cm². Over this range of pressure the theoretical value of C is 0.146 ± 0.015 including all the temperature-dependent terms (excluding the temperature-dependent terms C has a value of 0.129 ± 0.010 over this pressure range). Hence, within experimental accuracy, C is indeed nearly a constant over this pressure range.

From eq 31 and 32, one can express the B parameter by the relation

$$B = [C(j_2 + j_4) - j_2] - [j_1 + C(j_3 - j_1)]T \tag{35}$$

The algebraic expressions in square brackets in eq 35 are positive at high densities. The most important facts to notice about this expression are that B is a linearly decreasing function of the temperature, if the dependence of the C parameter upon the temperature is neglected, and that B depends not only upon n, m, and v^*, but also upon ϵ. (The C parameter given by eq 34 does not depend upon the well depth parameter ϵ.) The temperature-dependent and the temperature-independent terms in B at low temperatures are the same order in magnitude. Since B depends upon the difference between these two large positive terms in brackets, it is quite sensitive to small changes in the

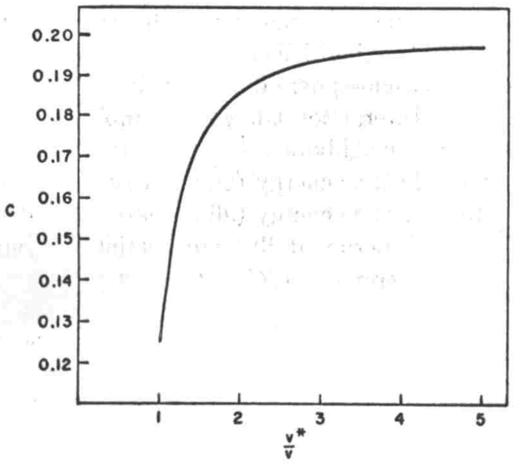

Figure 2. The C parameter plotted *vs.* the inverse of the reduced specific volume for a Mie potential with $n = 12$, $m = 6$, $f_{n,\gamma} = 1.011$, and $f_{m,\gamma} = 1.2045$.

parameters in each term, and it is particularly sensitive to the $v^* = \gamma^{-1}r^{*3}$ parameter. The C parameter is not as sensitive as B to the v^* parameter, and hence B would be expected to change more than C as one considers molecules of different sizes. For solid argon at 77°K the experimentally determined values from a least-squares analysis of Stewart's data[11] for C and B are 0.168 ± 0.002 and 3940 ± 140 kg/cm², respectively, while over the same range of densities eq 32 predicts C to be 0.146 ± 0.015 and B to be 3680 ± 660 kg/cm². Both theoretical values are in good agreement with experiment.

IV. Discussion

Many empirical isotherms for liquids have been proposed over the years, and, as remarked by Moelwyn-Hughes,[30] they bear the marks of considerable similarity. In his book referenced above the following isotherm is introduced for liquids

$$v = v^0[1 + \omega K^0(p - p^0)]^{-1/\omega} \tag{36}$$

where v^0 is the volume and K^0 is the isothermal compressibility of the system at some reference pressure, p^0; ω is a constant which is experimentally determined by

$$\left(\frac{\partial \dfrac{1}{K}}{\partial p}\right)_T = \omega \tag{37}$$

Equation 36 can be shown to be identical with the Murnaghan equation and to the isotherm obtained from eq 2 where the B and C parameters are related in the following way to the parameters in the Moelwyn-Hughes equation

$$C = \frac{1}{\omega}$$

$$B = \frac{1}{K^0} - \omega p^0 \tag{38}$$

As discussed by Moelwyn-Hughes, eq 36 has some theoretical basis, since it has been shown that for molecules which obey Mie's potential, ω can be approximately derived from a harmonic oscillator model.[31] A simple expression for ω for this model is found to be equal to $(n + m + 6)/3$ at a single value of the density, which he discusses. It is to be noted that eq 34 leads to this same result when v^*/v and the summation coefficients are set equal to unity.

In summary, the theoretical expressions derived for the Tait parameters, from eq 1 and 27, yield results which are in agreement with experimental observations in that C^* is found to be nearly temperature independent and 0.1 in order of magnitude, and B^* is found to be a decreasing function of the absolute temperature and more dependent on the particular substance than the C^* parameter. Good agreement was found between the theoretically calculated values of the C and B parameters and the experimentally determined values for solid argon. Finally, eq 5 and 34 indicate that the b parameter is nearly independent of temperature and depends only slightly on the specific volume if the range of pressures is not too wide, as observed experimentally.

Glossary of Symbols

a	Nearest neighbor distance
a'	van der Waals cohesive energy
A	Helmholtz free energy
b	Dimensionless parameter in the Murnaghan equation
B	Temperature-dependent parameter in the modified Tait equation
B^*	Temperature-dependent parameter in the Tait equation
c	Number of nearest neighbors
C	Dimensionless parameter in the modified Tait equation
C^*	Dimensionless parameter in the Tait equation
h	Planck's constant
k	The Boltzmann constant
K_0	Bulk modulus corresponding to reference volume, v_0
K	Isothermal compressibility
m	Integer exponent in the attractive energy term in the Mie potential
n	Integer exponent in the repulsive energy term in the Mie potential
N	Avogadro's number
p	Pressure

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(30) E. A. Moelwyn-Hughes, "States of Matter," Interscience Publishers, Inc., New York, N. Y., 1961, Chapter V.

(31) E. A. Moelwyn-Hughes, *J. Phys. Chem.*, 55, 1246 (1951).

r^*	Length parameter in the Mie potential
T	Absolute temperature
U	Mie potential function
v	Volume per molecule
v_f	Free volume per molecule
w	Molecular mass
α	Communal entropy
γ	Numerical constant that depends on the geometry of the lattice
ϵ	Energy parameter in the Mie potential
ρ	Number density
σ	Rigid-sphere diameter
$\phi(r)$	Interaction energy of a molecule with its neighbors
$\phi(0)N/2$	Lattice energy (one shell)
$\phi^*(0)N/2$	Lattice energy (all shells)
ω	Experimentally determined constant equal to $1/C$

Application of the Electron-Donation Model for Hydrogen Absorption to Palladium-Rich Alloys. Hydrogen–Gold–Palladium

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(Received May 31, 1967)

Detailed data for absorption of hydrogen by a series of gold–palladium alloys have been obtained in the low-content α phase. Heats of absorption at infinite dilution determined from the extrapolation of the isosteric heats are: 5980 (cal/mole of H_2) (5.7), 7000 (15.3), 7540 (18.8), 9040 (26.5), and 9340 (44.7), where the number in parentheses refers to the atom per cent of gold in the alloy. Entropies of absorption have been obtained and are compared to values calculated from a model of localized protons treated as three-dimensional oscillators. Results are interpreted in terms of a model where both gold and hydrogen are assumed to donate electrons to the empty combined s and d bands of the palladium.

Introduction

The absorption of hydrogen by palladium-rich alloys is of interest from several points of view. Such investigations serve as useful tests of the electron-donation model for proton absorption proposed by Mott[1] for pure palladium–hydrogen and extended to a statistical mechanical model by Lacher.[2] It may also prove to be feasible to probe the band shape of palladium and its alloys by utilizing the data on hydrogen absorption. Finally, it may be pointed out that palladium alloys have frequently been utilized to show the influence of the electronic band of metals upon heterogeneous reactions.[3] It appears to the present authors that the role of the electronic band structure of metals in influencing reactions of chemical interest should be probed with absorption systems such as those described here *before* the more complex problem of the correlation of electronic structure with surface catalysis is attempted. The main reasons for this suggested sequence is that absorption data can be treated using bulk metallic properties, whereas heterogeneous catalytic data must be interpreted using more poorly characterized surface properties. In addition, these absorption systems are not as subject to the experimental problems associated with surfaces, *e.g.*, irreproducibility arising from contamination.

Although there have been data available on hydrogen absorption by palladium alloys, aside from the early work of Sieverts at elevated temperatures,[4] the majority of the data at temperatures below approximately 120°

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[1] N. F. Mott and H. Jones, "Theory of Metals and Alloys," Clarendon Press, Oxford, 1936; N. F. Mott, *Advan. Phys.*, 13, 325 (1964).

[2] J. R. Lacher, *Proc. Roy. Soc.* (London), A161, 525 (1937).

[3] *E.g.*, G. Bond, "Catalysis by Metals," Academic Press, London, 1962.

[4] Sieverts' extensive contributions are reviewed by F. A. Lewis, "The Palladium Hydrogen System," Academic Press, London, 1967.