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TOPICS IN STATISTICAL MECHANICS OF FLUIDS

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TOPICS IN STATISTICAL MECHANICS OF FLUIDS

Fortunato Danon

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INTRODUCTION

It may be said that one of the main objectives of scientific research is not only to describe how things in nature appear to us to happen, but also why they happen thus and not otherwise.

Our pursuit of understanding nature, and by understanding we mean answering why-questions, leads us to "explain" facts, that is, show how they can be derived from general principles.

Much of the work being done in experimental physics and chemistry at the present time is devoted to the study of the properties of microscopic systems - nuclei, atoms and molecules - and of matter in bulk.

The science of statistical mechanics provides a mean of making the interpretation, i.e. "explanation", of the properties of macroscopic systems in terms of their structure on the molecular and atomic levels.

The research topics studied in this thesis are mainly concerned with the equation of state of substances.

The statistical-mechanical derivation of the equation of state requires a knowledge of the law of force between the molecules constituting matter. Although in principle this law of force could be derived from quantum mechanical considerations, the complex mathematics involved makes this approach to solving the problem impractical. We are then forced to construct simplified models of molecules using experimental information as a guide. These models must give a description of the molecular behavior fairly close to reality, and furthermore, the necessary mathematical treatment must not become unduly complex.

If these difficulties are encountered in the formulation of a "good"

intermolecular potential for only two molecules - the pair potential - we can then imagine the formidable task involved in the treatment of a many-body interaction problem. It is necessary to introduce further assumptions, the most important one being that of the additivity of the pair potential.

In Section I of the present work a study is made of an extended treatment of the principle of the corresponding states. Pitzer has shown by simple statistical-mechanical considerations, how one can introduce a parameter related to the entropy of vaporization of a fluid into the formulation of the corresponding states principle in such a way as to make its domain of validity much larger. This parameter, called the acentric factor, is now correlated to molecular properties and to characteristics of the intermolecular potential by use of the Kihara molecular core model.

An interesting consequence of this study is that even the rare gas atoms show some "core effect" in the determination of their physical properties. An improved intermolecular potential is thus obtained and applied to the study of not only the gas phase but also solid state properties of argon. This constitutes Section II of this thesis.

Section III is a treatment of very recent volumetric measurements for argon in connection with the principle of corresponding states. It is shown that argon and xenon follow corresponding state behavior within the uncertainty of the experimental data provided the principle is applied correctly, thus refuting conclusions drawn by other investigators.

The last part, Section IV, is a short study on the condensation coefficient of liquids. We show how a very simple kinetic argument leads to a theoretical formulation for the condensation coefficient in satisfactory agreement with the experiment.

The four sections are presented in what follows.

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The research topics studied in this thesis are mainly concerned with the equation of state of substances.

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The last part, Section IV, is a short study on the condensation coefficient of liquids. We show how a very simple kinetic argument leads to a theoretical formulation for the condensation coefficient in satisfactory agreement with the experiment.

The four sections are presented in what follows.

SECTION I

THE VOLUMETRIC AND THERMODYNAMIC PROPERTIES OF FLUIDS

RELATIONSHIP OF MOLECULAR PROPERTIES TO THE ACENTRIC FACTOR

ABSTRACT

A method is developed for the derivation of improved intermolecular potentials from empirical second virial coefficient data together with the acentric factors of the fluids. The Kihara core model is considered first and relationships are derived between the acentric factor and the core size for several shapes. The resulting cores for CH_4, CF_4, $C(CH_3)_4$, C_6H_6 and N_2 are reasonable in view of semiquantitative theoretical expectations, but the core for CO_2 is somewhat larger than expected. An approximate treatment is given which combines the Kihara core model with an electric quadrupole interaction. The core calculated for CO_2 on this model including the quadrupole moment is of a reasonable size.

INTRODUCTION

The empirical success of the numerical equation of state based upon critical properties and the acentric factor led us to explore further the relationship of the intermolecular potential to these macroscopic properties. The previous work is presented in a series of five papers.[1] In the present work we will deal almost exclusively with the second virial coefficient and the corresponding interaction between pairs of molecules. The empirical second virial coefficient is presented in paper III while paper I gives a general discussion of the nature of intermolecular forces between the molecules of normal fluids.

Several mathematical models[2] have been proposed which may be expected to yield good approximations to the intermolecular forces in particular cases of normal fluids and for which the second virial coefficient has been calculated.

---

[1] Papers in the series will be cited by the roman numerals as follows: I. K.S. Pitzer, J. Am. Chem. Soc 77 3427(1955); II. K.S. Pitzer, D.Z. Lippmann, R.F. Curl, Jr., C.M. Huggins and D.E. Petersen, ibid 77 3433(1955); III. K.S. Pitzer and R. F. Curl, Jr., ibid 79 2369 (1957); IV. R.F. Curl, Jr., and K.S. Pitzer, Ind. Eng. Chem. 50 265 (1958); V. K.S. Pitzer and G.O. Hultgren, J. Am. Chem. Soc. 80 4793 (1958).

[2] J.O. Hirschfelder, F.T. McClure and I.F. Weeks, J. Chem. Phys. 10 201 (1942); J.S. Rowlinson, Trans. Faraday Soc. 45 974(1949).

Most of these proposals are limited in their application to a particular class of normal fluids, such as those with spherical molecules, but the core model of Kihara[3] is quite general in nature. Kihara assumes a core of any shape within each molecule and takes the intermolecular potential to be the Lennard-Jones potential for the shortest distance between the outer surfaces of molecular cores. Thus the potential is

$$U = U_0 \left[\left(\frac{\rho_0}{\rho} \right)^{12} - 2 \left(\frac{\rho_0}{\rho} \right)^{6} \right] \tag{1}$$

where ρ is the shortest distance between cores and ρ_0 is this distance for the potential minimum.

In paper I Kihara's functions for this model were reduced on the Boyle point basis to equations for the second virial coefficient. Consequently, a comparison of these equations based on the core model with the empirical second virial coefficients of paper III provides a convenient way of relating the acentric factor to this molecular model.

Our results indicate in most cases smaller cores than those assumed by Kihara from molecular structure information and this conclusion finds support in recent independent reports on benzene[4] and methane[5] as well as the general considerations of the intermolecular potential in paper I.

---

[3] T. Kihara, Rev. Mod. Phys. 25 839(1953) and references given therein.

[4] J.F. Connolly, G.A. Kandalic, Phys. of Fluids 3 463(1960).

[5] G. Thomaes, R. Van Steenwinkel, Nature, 187 229(1960).

VIRIAL COEFFICIENT EQUATIONS

The equation for the second virial coefficients given in III in dimensionless form is

$$\frac{BP_c}{RT_c} = \frac{B^{(0)}P_c}{RT_c} + \omega \frac{B^{(1)}P_c}{RT_c} \tag{2}$$

where
$$\frac{B^{(0)}P_c}{RT_c} = 0.1455 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^{\,2}} - \frac{0.0121}{T_r^{\,3}} \tag{2a}$$

$$\frac{B^{(1)}P_c}{RT_c} = 0.073 + \frac{0.46}{T_r} - \frac{0.50}{T_r^{\,2}} - \frac{0.097}{T_r^{\,3}} - \frac{0.0073}{T_r^{\,8}} \tag{2b}$$

and
$$\omega = \log P_r - 1.000 \tag{2c}$$

where T_r is the reduced temperature T/T_c and P_r in Eq. (2c) is the reduced vapor pressure P/P_c at $T_r = 0.71$ It is convenient to transform Eq. (2) from the critical point basis to the Boyle point basis whereupon the result may be compared with Eqs. (15), (15a) and (15b) of paper I. At the Boyle point, $B = 0$, $T = T_B$, and we define the Boyle volume

$$V_B = \left[T \frac{dB}{dT}\right]_{T = T_B} \tag{3}$$

In this special case of zero acentric factor Eq. (2a) readily yields the result $T_r = 2.656$ at the Boyle point and $V_B = 0.1651\ R\ T_c/P_c$ (with $\omega = 0$). Substitution of these results gives

$$\frac{B^{(0)}}{V_B} = 0.8736 - 0.7512\left(\frac{T_B}{T}\right) - 0.1185\left(\frac{T_B}{T}\right)^2 - 0.0039\left(\frac{T_B}{T}\right)^3 \tag{4}$$

The values for T_B and V_B for $\omega = 0$ may be substituted into Eq. (2b), but we find then that the general equation for non-zero values of the acentric factor indicates that T_B and V_B depend on ω as well as the critical constants.

Hence the criterion for the Boyle point must be reapplied to the general Eq. (2) and yields

$$T_B = \frac{2.656\ T_c}{(1+1.028\ \omega)} \qquad \text{and} \qquad V_B = \left(\frac{RT_c}{P_c}\right)(0.1651 + 0.1981\ \omega)$$

Now the second virial coefficient is

$$B = B^{(0)} + \omega\, B^{(1)} + \ldots \tag{5}$$

with

$$\frac{B^{(1)}}{V_B} = -0.6087 + 1.11760\left(\frac{T_B}{T}\right) - 0.5299\left(\frac{T_B}{T}\right)^2 - 0.0386\left(\frac{T_B}{T}\right)^3 - 1.79 \times 10^{-5}\left(\frac{T_B}{T}\right)^8 \tag{6}$$

The last term in Eq. (6) is negligible except at low temperature and can usually be omitted. In these transformations only linear terms in ω were retained.

We now wish to compare Eqs. (4), (5) and (6) with the corresponding equations for the core model. Kihara's general expression for the second virial coefficient is

$$B = \frac{2\pi}{3}\rho_0^3 F_3(Z) + M_0\rho_0^2 F_2(Z) + \left(S_0 + \frac{M_0^{\ 2}}{4\pi}\right)\rho_0 F_1(Z) + \left(V_0 + \frac{M_0 S_0}{4\pi}\right) \tag{7}$$

where $Z = \frac{U_0}{kT}$, M_0 is the surface integral of the mean curvature of the core, S_0 and V_0 are the surface area and the volume of the core respectively, F_1, F_2, F_3 are functions given in Kihara's paper[3] and have recently been extended by Connolly and Kandalic.[4] Considering only first order deviation we obtain for all shapes of cores

$$B = \frac{2\pi}{3}\rho_0^{\ 3}\left[F_3(Z) + xF_2(Z)\right] \tag{8}$$

with

$$x = \frac{3M_0}{2\pi\rho_0}. \tag{9}$$

Thus x is proportional to a linear dimension of the core.

In paper I Eq. (8) was converted to the Boyle point basis and expressed as

$$\frac{B}{V_B} = \left[\frac{B}{V_B}\right]_0 + x\left[\frac{\partial}{\partial x}\left(\frac{B}{V_B}\right)\right] x = 0 \tag{10}$$

Eqs. (15a) and (15b) of I give the expressions for the two terms as functions of $\left(T_B/T\right)$. The first term is just the usual Lennard-Jones function since $x = 0$ corresponds to zero core size. The empirical equation for zero acentric factor, i.e. for Ar, Kr, and Xe, is very similar to the Lennard-Jones function but a distinctly better fit is obtained with Eq. (10) if $x = 0.24$. The agreement is then within 0.5% over the range of validity of the empirical equation.

If the core model is in satisfactory agreement with the experimental data, the second term in Eq. (10) must equal $B^{(1)}/V_B$ given by Eq. (6) for some value of x. Table I gives this comparison for $x = 7.0\ \omega$ and shows good agreement over the range of interest. Thus the comparison of the empirical equations with those from Kihara's theory yields the relationship

$$x = \frac{3M_0}{2\pi\rho_0} = 7.0\ \omega + 0.24 \tag{11}$$

This result together with the fact that V_0 and S_0 are expressable in terms of M_0 for a particular shape of core enables us to write Eq. (7) depending parametrically on ω. By comparison between this function (7) and the experimental values of $B = B(T)$ a new set of parameters for the Lennard-Jones type potential function can be obtained.

For each particular substance with fixed ω, Eq. (7) depends on U_0/k and ρ_0 only. By plotting this theoretical expression for $B(T)$ versus $\log \frac{kT}{U_0}$ on transparent paper for different given values of ρ_0 a family of curves is

Table I Comparison of the equation based on the acentric factor and the core size parameter.

T_B/T	$-\frac{B^{(1)}}{V_B}$	$-7.0\left[\frac{\partial}{x}\left(\frac{B}{V_B}\right)\right]_{x=0}$
0.8	0.027	0.026
1.0	0.001	0.002
1.5	0.168	0.166
2.0	0.690	0.690
2.5	1.611	1.625
3.0	3.010	3.020

obtained which can be superimposed over a graph of the experimental curve B(T) versus log T. This gives ρ_0 and U_0/k. Thus for any given shape of core the intermolecular potential parameters are determined by the macroscopic properties.

The various transformations which led up to Eq. (11) were carried out only through the first order in ω. The adequacy of Eq. (11) for large ω values was tested by direct comparison of the calculated second virial coefficient curves for particular cores corresponding to large x values with the curves given by Eq. (12) with the corresponding ω. While this test was not extremely precise, it showed that the linear development was adequate in the rangeof ω values here considered and for the present accuracy of experimental data.

EXAMPLES

We consider first molecules with zero or negligible dipole of quadrupole electric moments.

i) Tetrahedral cores:

ℓ: Length of one edge of the tetrahedron

$M_0 = 5.733\ \ell$

$S_0 = 1.732\ \ell^2 \qquad \ell = \frac{1}{2.737}\rho_0 x \qquad x = 7.0\ \omega + 0.24$

$V_0 = 0.1178\ \ell^3$

$$B = \rho_0^3 \left[\frac{2\pi}{3} F_3(Z) + \frac{2\pi}{3} x F_2(Z) + 0.5802\ x^2 F_1(Z) + 0.3911 x^3 \right]$$

The distance d from the center to vertex of the tetrahedron is given by $d = \frac{\ell}{2 \sin\left(\frac{\alpha}{2}\right)}$ α is H-C-H bond angle in methane. Results of the calculations together with Kihara's values are given in Table II. For comparison the C-H distance in methane is 1.09 A and the C-F distance in CF_4 is 1.32 A.

TABLE II

Comparison of the constants for the core model with those derived from the acentric factor theory for tetrahedral molecules.-

Molecule		Kihara [a]	Kihara [b]	Present Work
CH_4	ρ_0 Å	1.92	3.15	3.75
	U_0/k °K	378	226	175
	d Å	1.09	0.596	0.28
CF_4	ρ_0 Å	2.48		3.08
	U_0/k °K	372		350
	d Å	1.32		1.01

a - Reference (3)

b - T. Kihara and S. Koba, J. Phys. Soc. Japan 14 247, (1959)

Figure 1 shows the curves for methane corresponding to our parameters of Table 11 and to those of Kihara. Although both curves fit the data above 273°K, the curve based upon the acentric factor agrees much better with the recent experimental data of Thomaes [5] at lower temperatures.

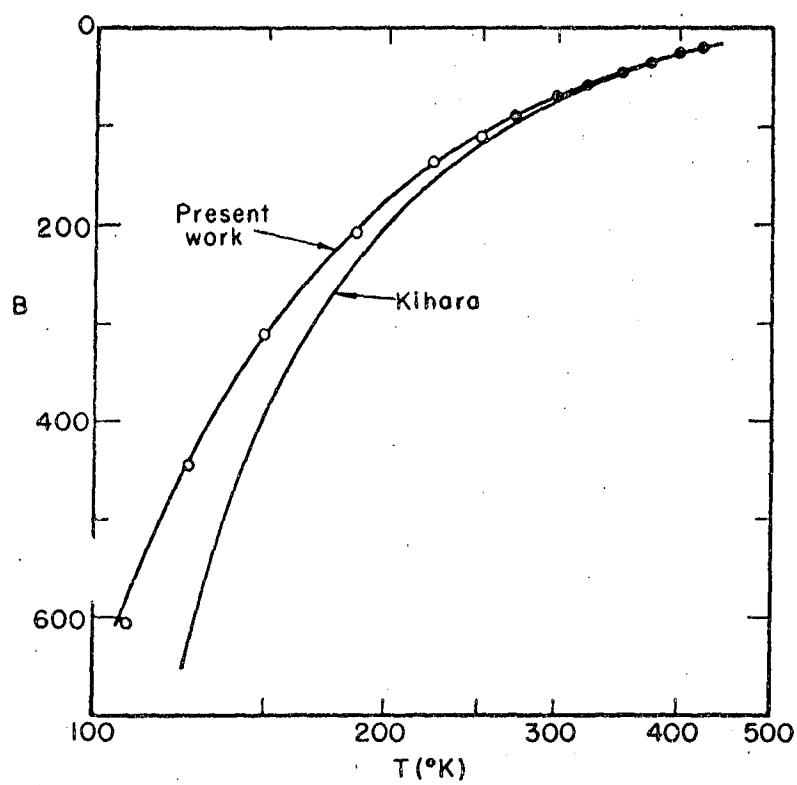

Fig. 1. The second virial coefficient ($Å^3$/molecule) for methane. The curves are theoretical; the points experimental. Solid circles show the experimental values (Michels and Nederbragt[a]) available to Kihara. Recent measurements of Thomaes[b] are shown as open circles.

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[a] A. Michels and G.W. Nederbragt, Physics 3, 569 (1936).

[b] G. Thomaes and R. Van Steenwinkel, Nature 187, 229 (1960).

ii) Hexagonal Cores

ℓ: length of one side of the hexagon

$M_0 = 3\pi\ell$

$S_0 = 5.2\ \ell^2$

$\ell = \frac{2}{9}\ x$

$$B = \rho_0^3\left[\ \frac{2\pi}{3} F_3\ (Z) + \frac{2}{3}\ \pi\ xF_2(Z) + 0.6057\ x^2F_1(Z) + 0.0428x^3\ \right]$$

At the time Kihara's work was published (1953) there were not sufficient observed values of the second virial coefficient for benzene to determine both U_0 and ρ_0. His value of ρ_0 is taken from the lattice constant of graphite. Recently, however, Andon et al[6] reported measurements on the second virial coefficient for benzene between 67.1 and 164.6°C. By use of their results together with the older values of Francis and McGlashan[7] we have calculated both ρ_0 and U_0 from second virial coefficient data only.

Results are given in Table III. For comparison the C-C distance in benzene is 1.397 Å.

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6 R.J.L. Andon, J.D. Cox, E.F. Herington and J.F. Martin, Trans-Faraday Soc. 53, 1074 (1957); J.D. Cox and R.L. Andon, ibid. 54, 1622 (1958).

7 P.G. Francis, M.L. McGlashan, S.D. Hamann and W.J. McManamey, J. Chem. Phys. 20, 1341 (1952).

TABLE III

Comparison of constants for the core model with those derived from the acentric factor theory for benzene.

Molecule		Kihara	Present Work
C_6H_6	ρ_0	3.4 Å (a)	3.0 Å (b)
	U_0/k	830 °K	990 °K
	ℓ	1.93 Å	1.16 Å

(a) From the lattice constant of graphite

(b) From second virial coefficient data

iii) Spherical core

If we assign spherical core for CH_4, which is a permissible approximation considering its rapid and relatively free rotation, we obtain for the radius of the spherical core a = 0.21 Å.

We also consider the globular-type molecule, neopentane, and assume a shperical core.

a: radius of the sphere $a = \frac{1}{6}\rho_0 x$

$$B = \frac{2}{3}\pi\rho_0^3 \left[F_3(Z) + xF_2(Z) + \frac{1}{3}x^2 F_1(Z) + \frac{x^3}{27} \right]$$

There results:

$\rho_0 = 3.96$

$\frac{U_0}{k} = 590\ ^oK$

a = 1.06 Å C-C bond length = 1.536 Å

iv) Thin rod shaped cores

We consider in this case N_2 and CO_2.

$M_0 = \pi\ell$, $\ell = \frac{2}{3}\rho_0 (7.0\,\omega + 0.24)$ where ℓ is the length of the rod.

$$B = \frac{2\pi}{3}\rho_0^3 \left[F_3(Z) + xF_2(Z) + \frac{1}{6}x^2 F_1(Z) \right] \qquad (12)$$

The results obtained are listed in Table IV. For comparison the N-N distance is 1.095 Å in N_2 and the O-O distance in CO_2 is 2.32 Å. The cores for N_2 and CO_2 seem peculiarly large, particularly so for CO_2. The fact that equation (11) gives non-zero core constants for $\omega = 0$ indicates that there is some small core effect even in the simple fluids (Ar, Xe, etc.). It is then reasonable to consider cylindrical cores in N_2 and CO_2 with the radius of the cylinder a obtained from the relationship between a and ρ_0 for simple fluids. underline a

From (10) and (11) for $\omega = 0$ one gets a spherical core radius $a = 0.04\ \rho_0$. This relationship for a enters the expressions for a cylindrical core which are

$$M_0 = \pi\ (\pi a + \ell) = \frac{2\pi}{3}\ x\rho_0,\ S_0 = 2\pi\ a(a + \ell)$$

$$V_0 = \pi a^2 \ell,\ \ell = \frac{2}{3}\ x\rho_0 - \pi a$$

One then obtains

$$B = \frac{2\pi}{3}\ \rho_0^3 \left[F_3(Z) - 0.010F_1(Z) - 0.0003 + [F_2(Z) + 0.080\ F_1(Z)]x + [\ \frac{1}{6}\ F_1(Z) + 0.0133\ ]\ x^2 \right]$$

The results considering cylindrical core are also given in Table IV.

TABLE IV

Comparison of constants for the core model with those derived from the acentric factor theory for linear molecules.

Molecule			Kihara [a]	Kihara [b]	Present Work: Thin rod core	Present Work: Cylindrical core
N_2	ρ_0	Å	3.47		3.40	3.30
	U_0/K	°K	124		132	125
	ℓ	Å	1.09		1.19	0.73
	a	Å	0.00		0.00	0.13
CO_2	ρ_0	Å	3.36	3.7	2.72	2.6
	U_0/K	°K	279	2.79	400	405
	ℓ	Å	2.20	2.30	3.29	2.82
	a	Å	0.00	0.00	0.00	0.10

a. Reference (3)

b. T. Kihara. J. Phys. Soc. Japan 6 289 (1951).

ELECTRIC QUADRUPOLE EFFECTS

The two linear molecules have electric quadrupole moments. The order of magnitude of quadrupole-quadrupole interaction energy is by no means negligible compound to pure London dispersion energy. The contribution to the second virial coefficient coming from quadrupole-quadrupole interactions should also be considered.

An attempt was made to extend the core model for angularly dependent potentials rigorously to include the quadrupole effect, but the mathematical complexity of the problem involving non-spherical cores makes an exact and rigorous treatment unduly complex.

An approximate treatment including quadrupole as well as core effects may be obtained by combining the first order correction term for each effect with the equation for a spherical Lennard-Jones potential.

The results obtained by Pople[8] allow one to write the virial coefficient for molecules interacting by a Lennard-Jones potential together with permanent quadrupole moments as

$$B(T) = \frac{2}{3}\ \pi N\ r_0^{\,3}\left[\ F(y) - \frac{7}{320}\left(\frac{\theta^2}{U_0 r_0^{\,5}}\right)^2 H_{10}(y)\right] \qquad (14)$$

where r_0 is the intermolecular distance at which the non-angular (Lennard-Jones) part of the potential energy function vanishes, and $F(y)$ is the usual Lennard-Jones function. U_0 is the most negative value of the same part of the potential, and y is defined as

$$y = 2\left(\frac{U_0}{kT}\right)^{1/2}$$

---

[8] J.A. Pople, Proc. Roy. Soc.(London) A221 498(1954) and ibid. A221 508(1954).

θ is the quadrupole moment[9] and $H_{10}(y)$ is the function expressing the quadrupole interaction which has been given as a series and is known in tabular form.[10]

We fitted a third degree polynomial to the tabulated values of $H_{10}(y)$ and by transformation to our set of variables obtained

$$H(Z) = 0.07089 - 0.78915Z = 0.05201\ Z^2 - 2.40478\ Z^3 \tag{15}$$

If we define the dimensionless parameter

$$s = \left(\frac{\theta^2}{U_0 \sigma_0^5}\right)$$

depending on the quadrupole moment, we can write for the second virial coefficient including first order core and quadrupole effects

$$B = \frac{2\pi}{3}\ \rho_0^3 \left[F_3(Z) + xF_2(Z) + sH(Z) \right] \tag{16a}$$

or in reduced form

$$\frac{B}{V_B} = \left[\frac{B}{V_B} \right]_0 + x \left[\frac{\partial}{\partial x}\left(\frac{B}{V_B}\right) \right]_0 + s \left[\frac{\partial}{\partial s}\left(\frac{B}{V_B}\right) \right]_0 \tag{16b}$$

As we want to compare equation (16b) with the empirical equations (4) and (6), we reduced the function H(Z) to Boyle point basis using the definition of Boyle volume given by (3). The result is

$$\left[\frac{\partial}{\partial s}\left(\frac{B}{V_B}\right) \right]_0 = -\ 0.1020 + 0.1105 \left(\frac{T_B}{T}\right) + 0.0842 \left(\frac{T_B}{T}\right)^2 - 0.0932 \left(\frac{T_B}{T}\right)^3 \tag{17}$$

Comparing equation (17) with the corresponding equation for x, equation 15b in paper I, one finds that in the low temperature range, where the quadrupole effect is most marked the relationship

$$\left[\frac{\partial}{\partial s}\left(\frac{B}{V_B}\right) \right] \Big/ \left[\frac{\partial}{\partial x}\left(\frac{B}{V_B}\right) \right] = 3.2 \tag{18}$$

is a fair approximation.

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[9] The quadrupole moment definition used in this paper is

$\theta = \Sigma_i z_i\ (z^2 - x^2)$ where z_i is measured along the molecular axis.

[10] Tables for $H_{10}(y)$ are given by A.D. Buckingham and J.A. Pople, Trans. Faraday Soc. 51 1173 (1955).

Substitution of Eq. (18) in (16b) and use of Eq. (11) yields

$$x + 3.2s = 7.0\ \omega + 0.24 \tag{19}$$

This relationship between core size, quadrupole moment and acentric factor enables us to write Eq. (16a) in terms of ω. As the parameter s depends on ρ_0 and U_0 by definition, a successive approximation method is necessary for the evaluation of ρ_0 and U_0. The results obtained[11] for CO_2 and N_2 are listed in Table V. These results show that, when the quadrupole effect is considered, the sizes of the cores are again smaller than the ones assumed by Kihara from molecular structure information. A few years after Kihara's work was published a measurement of the second virial coefficient for CO_2 at low temperatures was reported.[12] These values, together with the older results reported by Schafer[13] and MacCormack and Scheneider[14] are shown in Fig. 2. A distinctly better fit to this experimental data is obtained from the parameters of Table V of this paper than from the expression given by Kihara.

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[11] The numerical value for the quadrupole moment of N_2 is taken from W. Gordy, W.V. Smith and R. Trambarulo, "Microwave Spectroscopy", John Wiley and Sons, Inc., New York 1953 p.345; that for CO_2 from W.V. Smith and R. Howard, Phys. Rev., 79 132(1950).

[12] D. Cook, Can. Jour. of Chem. 35 369(1957).

[13] K. Schafer, Z. Phys. Chem. B36 85 (1937).

[14] K.E. MacCormack and W.G. Scheneider, J. Chem. Phys. 18 1269(1950).

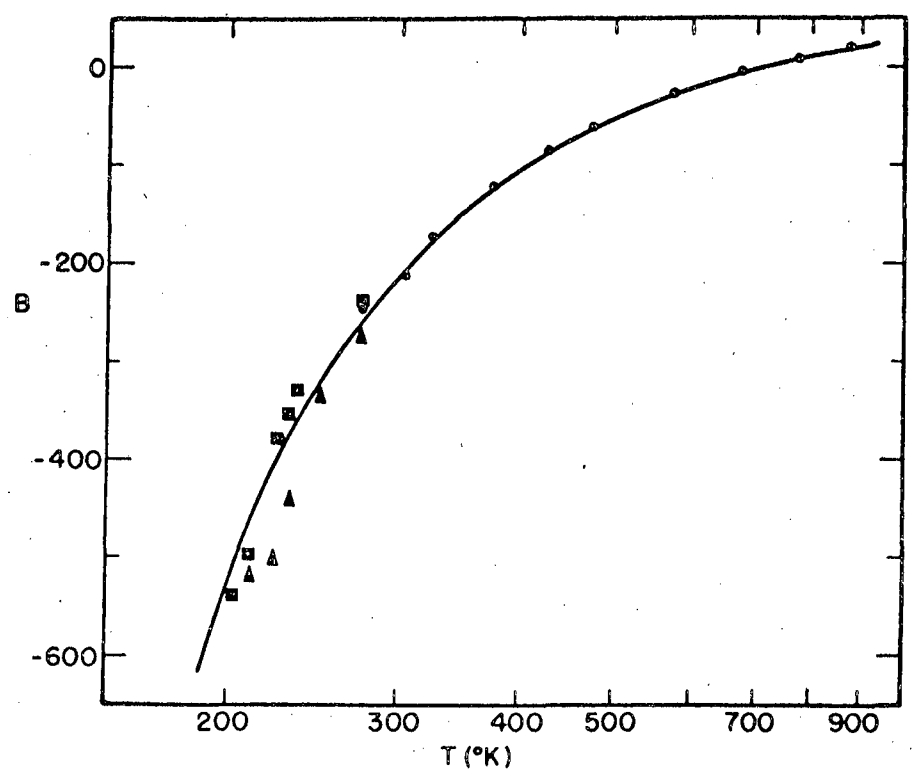

Fig. 2. The second virial coefficient (Å ^{3}/molecule) for CO_2. The curve is calculated using the results of this paper. Solid circles correspond to MacCormack and Scheneider measurements[14], triangles to Cook[12] and squares to Schafer.[13]

TABLE V

The constants derived from the acentric factor theory for linear molecules including quodrupole effect.

	θ e.s.u.	S	ρ_0 Å	U_0/K °K	ℓ Å
N_2	$1.488.10^{-26}$	0.05	3.60	115	0.86
CO_2	$3.12.10^{-26}$	0.33	3.42	270	1.73

Exp. Dist. N-N = 1.095 Å, O-C-O = 2.32 Å

DISCUSSION

Our aim has been to develop a system for the calculation of as accurate and realistic intermolecular potentials as possible from the microscopic data provided by the second virial coefficient and the acentric factor which is readily available from the vapor pressure curve. The resulting microscopic potential functions should be useful for other theoretical applications. It is also of interest to consider the results in comparison with the sizes of the polarizable electron clouds of the molecules. In paper I this problem was considered and it was concluded that the Kihara model core should be considerably smaller than the polarizable electron cloud of the molecule. Indeed the radius of a Kihara model core was found to be only one half of the radius of an equivalent sphere of uniformly polarizable electron cloud. In view of these results the cores found above seem quite reasonable. Thus in CF_4 and $C(CH_3)_4$ the cores extend about 2/3 of the way to the F or C (methyl) nuclei, respectively. Methene has a very small core since all of the polarizable electrons are partially centered on the single carbon atom. The hexagonal core for benzene extends almost to the ring carbon atoms. The cores chosen by Kihara in 1953 seem to have been selected rather arbitrarily; for example his core for methane extended to the hydrogen nuclei whereas in benzene the core extended only to the midpoints of the C-H bonds. Consequently it is not surprising that our results differ rather substantially. In the case of methane the results in Fig. I show clearly that the core selected from the acentric factor is the correct one to fit the wide range of data now available.

The tetrahedral molecules have zero electric quadrupole moment by symmetry but the linear molecules N_2 and CO_2 have significant moments. While our treatment including the quadrupole effect is only an approximate one for the model, it does show that the linear cores are thereby reduced to reasonable

sizes.

Also of considerable interest is the result that a Kihara core of radius $a = 0.04\ \rho_0$ yields considerably better results for the rare gases, Ar, Kr, Xe, than the simple Lennard-Jones potential. This is in agreement with the conclusions of Brown and Rowlinson[15] based upon totally different arguments.

With these results as a guide one should be able to estimate reasonable core sizes for other molecules if the acentric factor or equivalent data are unavailable. Conversely, the acentric factor and other data may be used, as has been illustrated in this paper, to derive an intermolecular potential for use in other calculations.

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[15] W.B. Brown and J.S. Rowlinson, Molec. Phys. 3 35(1960).

SECTION II

MOLECULAR INTERACTION IN ARGON

ABSTRACT

A core model intermolecular potential for argon is presented. The presently available experimental data on the second virial coefficient of the gas permit a check of the potential for the pair interaction. The calculated values for this model yield considerably better agreement with the observed values than those for the Lennard-Jones potential.

The cohesive energy and the nearest neighbor distance in the crystal are also calculated. The effect of the zero point vibrational energy is considered following the method given by Corner. Deviation from the observed values for the crystal properties are discussed in connection with the assumption of the pairwise additivity of the potential, as used in our calculations.

The relative stabilities of the crystal structures is investigated and the hexagonal close-packed is calculated to be the most stable one.

INTRODUCTION

Many studies of intermolecular interactions in rare gases have been made.[1] These substances present several advantages over any other group of substances. They have closed shell monatomic molecules and no dipole moment so that no complications due to strong electrostatic fields arise. They have spherical symmetry, crystalize in the simple closed-packed structure and their molecular field is mainly due to dispersion forces.

In this paper we limit our study to the second virial coefficient of the gas and the cohesive energy and lattice constant for the solid argon. The assumption of the additivity of the pair potential is used in the calculations of the properties of the crystal.

The potential energy functions applied to the study of molecular systems should satisfy the requirements of both accuracy and simplicity. The Lennard-Jones function

$$U(r) = U_0 \left[\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^{6} \right] \tag{1}$$

is the most widely used form of the potential. U_0 in Eq. (1) is the most negative value of $U(r)$ and r_0 is the intermolecular distance at which $U(r) = -U_0$. Attempts to apply the Lennard-Jones potential to the calculation of the second virial coefficient of more complex molecules and over a wide temperature range have shown the inadequacy of this potential. Considerable improvement was made by Kihara with the introduction of his molecular core model.[2]

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[1] Among the latest publication see E.A. Guggenheim and M.L. McGlashan, Proc. Roy. Soc. (London) A255, 456 (1960). A very complete review is given in G.A. Cook, Ed. "Argon, Helium and the Rare Gases." (Interscience Publ. New York, 1961), Vol. 1.

[2] T. Kihara, Revs. Modern Phys. 25, 831 (1953) and ibid 27, 412 (1955).

He assumes a hard core of a given shape within the molecule and defines the intermolecular distance ρ as the shortest distance between two cores.

The intermolecular potential is then taken to be a Lennard-Jones function of ρ

$$U(\rho) = U_0 \left[\left(\frac{\rho_0}{\rho}\right)^{12} - 2\left(\frac{\rho_0}{\rho}\right)^{6} \right] \tag{2}$$

The parameters U_0 and ρ_0 have a similar meaning to the corresponding ones in Eq. (1).

Core Model for Rare Gases

Kihara core model has successfully been applied to the evaluation of the second virial coefficient of several types of molecules.[2,3]

Molecules structure information (bond lengths, angles, etc.) was used in the assignment of a given core but this criterion cannot clearly be applied to the monatomic rare gases.

In a recent study of the relationship between an extended theory of corresponding states and molecular properties we have shown[4] how to give a reasonable estimate of the core size for the rare gases. If one defines a core parameter χ related to the mean curvature of the core we found

$$\chi = 7.0\,\omega + 0.24 \tag{3}$$

where ω is the acentric factor[5] of the fluid defined by $\omega = -\log P_r - 1.000$, P_r is the reduced vapor pressure P/P_c, at $T_r = 0.7$.

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3 D.R. Douslin, R.T. Moore and G. Waddington, J. Phys. Chem. 63, 1959 (1959); D.R. Douslin, R.H. Harrison, R.T. Moore and J.P. McCullough, J. Chem. Phys. 35, 1357 (1961); F.J. Connolly, G.A. Kandalic, Phys. Fluids 3 463 (1960).

4 This thesis, Section I.

5 G.N. Lewis and M. Randall, "Thermodynamics" revised by K.S. Pitzer and L. Brewer, (McGraw-Hill Book Co., New York, 1960) 2nd. Ed. App. 1, p. 605.

That the core effect should somehow be incorporated into the intermolecular potential has already been pointed out,[6,7] but no actual estimation was made.

Equation (3) above, although only approximate, provides a means of obtaining this estimation.

Second Virial Coefficient of Argon

The expression for the second virial coefficient for the core model is

$$^2B = \frac{2\pi}{3}\rho_0^3 F_3(z) + M_0\rho_0\,{}^2F_2(z) + \left(S_0 + \frac{M_0^2}{4\pi}\right)\rho_0 F_1(z) + \left(V_0 + \frac{M_0 S_0}{4\pi}\right) \qquad (4)$$

where $z = \frac{U_0}{kT}$, M_0 is the surface integral of the mean curvature of the core, S_0 and V_0 are the surface area and the volume of the core respectively, F_1, F_2 and F_3 are functions in Kihara's paper[2] and have recently been extended by Connolly and Kandalic.[8]

The core size parameter χ is defined by

$$\chi = \frac{3M_0}{2\pi\rho_0} \qquad (5)$$

By use of Eqs. (3) and (5) and assuming a spherical core for argon with $\omega = 0$, Eq. (4) transforms to

$$B = \frac{2\pi}{3}\rho_0^3\left[F_3(z) + \chi F_2(z) + \frac{1}{3}\chi^2 F_3(z) + \frac{1}{27}\chi^3\right] \qquad (6)$$

and d, the radius of the spherical core is given by

$$d = \frac{1}{6}\rho_0\chi.$$

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6 W.B. Brown and J.S. Rowlinson, Molec. Phys. 3, 35 (1960).

7 G. Boato and G. Casanova, Physics 27, 571 (1961).

8 J.F. Connolly, G.A. Kandalic, Documentation Institute, Library of Congress, Document No. 6307.

By using the method as described in Section I we obtained the parameters listed in Table I where the parameters for the Lennard-Jones potential are also included for comparison.

Table I

Potential parameters as derived from second virial coefficient data.

Lennard-Jones (a)	$r_0 = 3.86$ A ($\sigma = 3.44$ A)
Core Model	$\rho_0 = 3.452$ A $U_0/k = 139.0$ ^oK $d = 0.276$ A

(a) J.M.H. Levelt, Thesis, Amsterdam (1958) p. 94

Although the Lennard-Jones parameters can be adjusted to fit either high or low temperature data[9] there is no single set of values giving agreement over the entire temperature range on which measurements are now available. The values in Table I are those for the "best set" as given in Levelt's thesis. The Kihara potential, with a core size as given by Eq. (3) gives a good agreement over the entire range. Results are shown in Fig. 1 where the differences between experimental and theoretical reduced virial coefficients are plotted against reduced temperature.

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9 E. Whalley, Y. Lupien and W.G. Schneider, Can. J. Chem. 31, 722 (1953); A. Michels, H. Wijker and Herb. Wijker, Physica 15, 627 (1949); A. Michels, J.M. Levelt and W. Graaf, Physica 24, 659 (1958); J.M.H. Levelt, Physica 26, 361 (1960); J.M.H. Levelt, Thesis, Amsterdam, (1958).

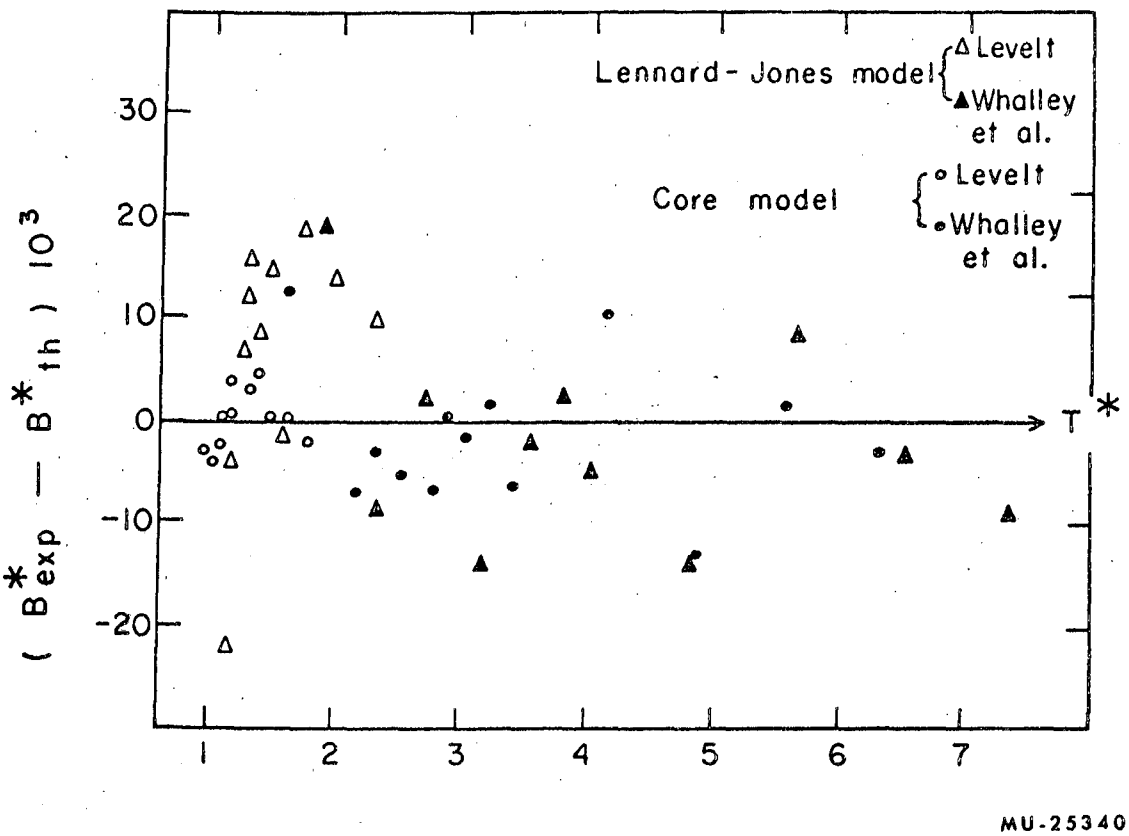

Fig. 1. Comparison of reduced second virial coefficient of argon for the Lennard-Jones and the core model potentials.

We defined the reduced virial coefficient $B^* = \frac{B}{\frac{2\pi}{3}\sigma^3}$ for the Lennard-Jones potential with $\sigma = 2^{-1/6} r_0$ and $B^* = \frac{B}{\frac{2\pi}{3}\rho_0^3}$ for the Kihara potential, experimental data being reduced correspondingly for each case.

In his critical study Kihara[2] concludes that "the real intermolecular potential for rare gases has a wider bowl and a harder repulsive wall than the Lennard-Jones (6,12) potential." Boato and Casanova[7], also noted the inadequacy of the potential in neglecting higher inverse power attractive terms, r^{-8} and r^{-10}, due to dipole-quadrupole and quadrupole-quadrupole interactions as required by the theory of intermolecular forces. They also suggest that the core effect should change as the atomic number is varied.

It is simple to show that these criticisms are no longer valid in discussing the Kihara potential. The distance between molecular centers, r, and the one between surfaces of the cores, ρ, are simply related by a general expression of the form $\rho = r-b$ where b is a parameter related to the core size and shape and small with respect to r. In the case of spherical cores b is simply twice the radius of the sphere. The inverse power terms can be expanded in a binomial series

$$\left(\frac{\rho_0}{\rho}\right)^s = \left(\frac{\rho_0}{r-b}\right)^s = \left(\frac{\rho_0}{r}\right)^s \left[1 + s\left(\frac{b}{r}\right) + \frac{s(s+1)}{2!}\left(\frac{b}{r}\right)^2 + \ldots \right]$$

so that the potential in Eq. (2) can be written as

$$U(r) = \left(\frac{\rho_0}{r}\right)^{12} \left[1 + 12\left(\frac{b}{r}\right) + 78\left(\frac{b}{r}\right)^2 + \ldots \right] - 2\left(\frac{\rho_0}{r}\right)^6 \left[1 + 6\left(\frac{b}{r}\right) + 21\left(\frac{b}{r}\right)^2 + \ldots \right] \quad (7)$$

Equation (7) involves both attractive and repulsive terms in higher inverse powers of r. The dependence on the atomic number is naturally introduced through

b and its relationship to the core size of the particular molecule considered. Figure 2 shows the two intermolecular potentials under discussion as a function of the separation of the molecular centers. The potential parameters have been evaluated from second virial coefficient data.

Solid State Properties

Although the core model of molecules has been applied by the Japanese group[10] to the study of several molecular crystals (methane, carbon dioxide, nitrogen, ethylene and benzene) its application to the solid rare gases has been limited by the undertainty with respect to the core size of these molecules.

By use of Eqs. (2) and (3) we are able to derive an intermolecular potential applicable to the rare gases in crystalline state. Calculations were made for argon, although extension to the other heavier inert gases can easily be made.

Cohesive energy and lattice constant. Assuming the pairwise additivity of the intermolecular potential and neglecting the zero point vibrational energy, the cohesive energy per molecule is given by the minimum of

$$\Phi(\rho_i) = \frac{1}{2} U_0 \sum_{i=1}^{\infty} n_i \left[\left(\frac{\rho_0}{\rho_i}\right)^{12} - 2\left(\frac{\rho_0}{\rho_i}\right)^{6} \right] \tag{8}$$

as a function of the nearest neighbor distance a. In Eq. (8) U_0 and ρ_0 have the same meaning as in Eq. (2), n_i is the number of atoms at the distance ρ_i from the central atom. For the two types of closest packing of spheres ρ_i is simply related to the nearest neighbor distance by

$$\rho_i = \alpha(i)\, a - d \tag{9}$$

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[10] T. Kihara and S. Koba, J. Phys. Soc. Japan, 14, 247 (1959); S. Koba, ibid. 16, 627 (1961).

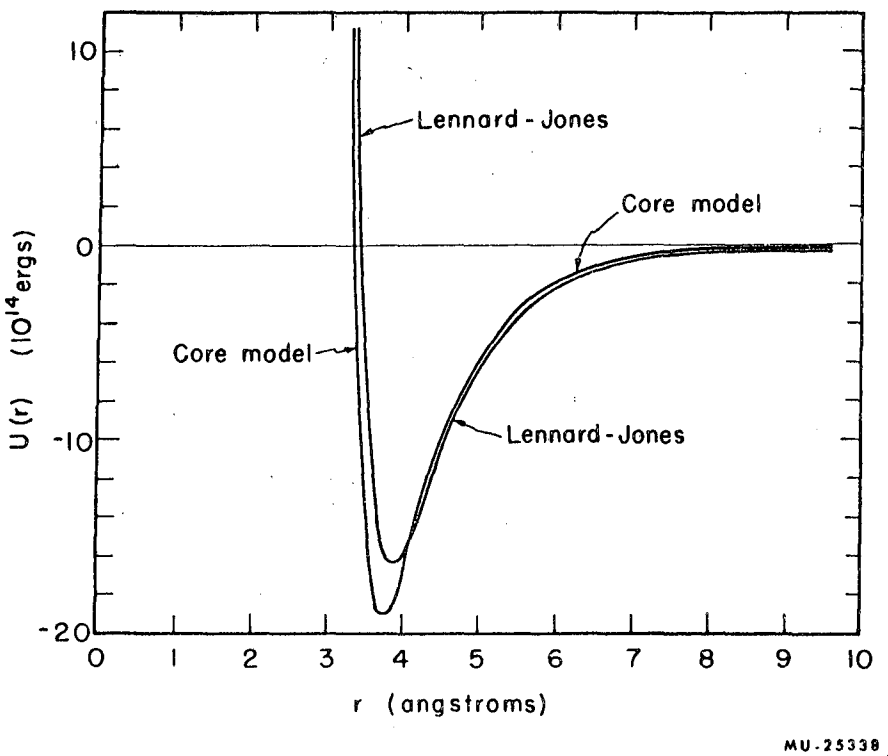

Fig. 2. Intermolecular potential energy functions for argon.

where $\alpha(i)$ is a constant depending on the geometry of the lattice and d the core diameter.

Zero point energy. Corner[11] has made a careful study of the zero point energy effect on the lattice constant and shown that it is by no means negligible.

Following Corner's procedure we evaluated the zero point energy effect for the core model potential. Consider the molecule M in the field of all others. Let R_i be the distance from the center of M to the center of molecule i, r_i be the distance from center of molecule i to the lattice site M_0 of M, and let M be at a distance r from its site in a direction making an angle θ with the radious of the ith molecule as shown in Fig. 3.

Correspondingly we define

$$P_i = R_i - d$$
$$\rho_i = r_i - d$$
$$\rho = r - d$$

so that

$$(P_i+d)^2 = (\rho_i+d)^2 + (\rho+d)^2 - 2(\rho_i+d)(\rho+d)\cos\theta.$$

From here on the treatment is analogous to the one given by Corner,[10] that we omit for the same of brevity.

The final result for the total energy per molecule Φ_z, in the crystal at absolute zero is

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[11] J. Corner, Trans. Faraday Soc. 35, 711 (1939), 44, 914 (1948).

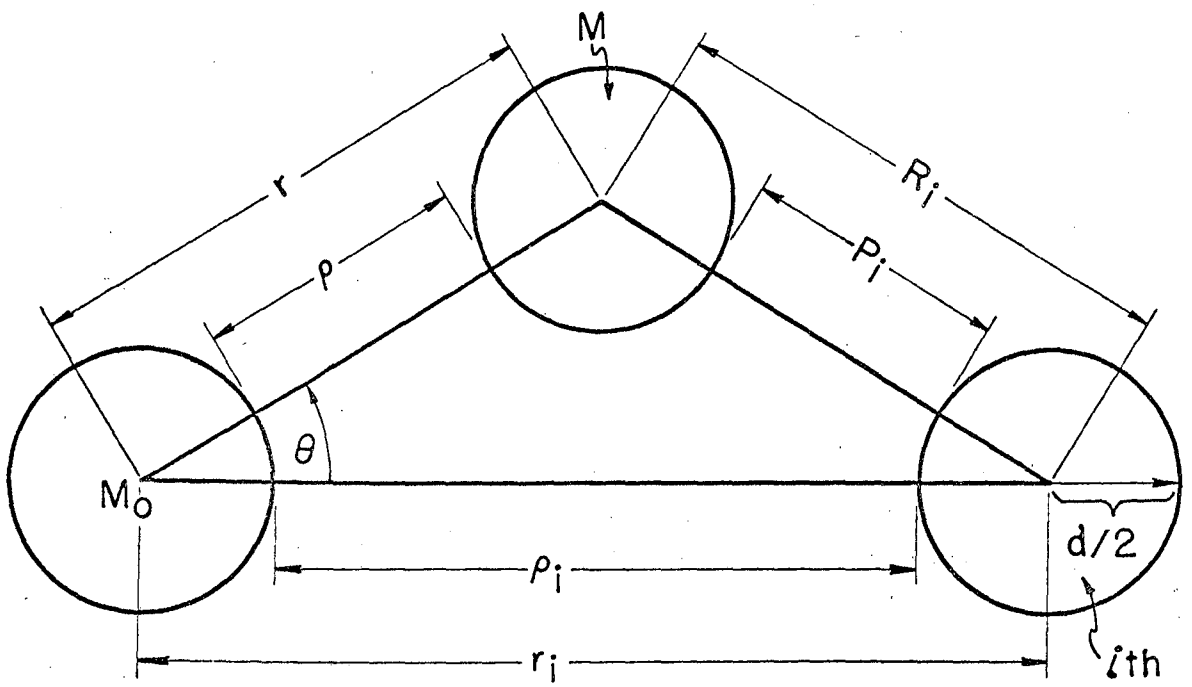

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Fig. 3. Coordinates for the molecules in the crystal.

$$\Phi_z = \frac{U_0}{2} \sum_{i=1}^{\infty} n_i U(\rho_i) + \left(\frac{3h^2}{2\pi^2 m}\right)^{1/2} \left[\sum_{i=1}^{\infty} n_i \left(\frac{1}{\rho_i + d} \cdot \frac{\partial U}{\partial \rho_i}(\rho_i) + \frac{1}{2} \frac{\partial^2 U}{\partial \rho_i^2}(\rho_i)\right)\right]^{1/2} \quad (10)$$

where $U(\rho_i)$ is the pair potential of Eq. (2), n_i has the same meaning as in Eq. (8) and m is the molecular mass.

The cohesive energy per molecule is now given by the minimum of Φ_z as a function of a.

Values of n_i are given in tables prepared by Kihara[12] up to i=65 for the cubic and i=130 for the hexagonal packing. We approximate the rest of the summation by integrating from the last tabulated i value up to infinity. The method is similar to the one used for the Lennard-Jones potential[12] where the n_i are replaced by the mean density of the lattice.

By the use of the model parameters as obtained from the second virial coefficient data and using Eq. (9) we calculated the minimum of Φ_z with respect to a. Calculations were made with the aid of the IBM 704 computer at Berkeley. Results of the calculations of the nearest neighbor distance a and the sublimation energy corrected for the zero point energy H_0, for the face centered cubic lattice are given in Table II. Values obtained for a Lennard-Jones potential are included for comparison.

If, on the other hand, we use the observed values of the nearest neighbor distance a[13] and the sublimation energy corrected for the zero point vibrational energy[14] we obtain a set of values for the parameters of the pair potential. There results $U_0/k = 126.4^{\circ}K$, $\rho_0 = 3.505$ A, d = 0.280 A. These values, however, should not be used in constructing the intermolecular pair potential, because

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12 T. Kihara and S. Koba, J. Phys. Soc. Japan 7, 348 (1952).

13 C. Domb and I.J. Zucker, Nature (London) 178, 484 (1956).

14 E.R. Dobbs and G.O. Jones, Rept. Prog. Phys. 20, 516 (1957).

Table II

Sublimation energy and nearest neighbor distance in solid argon.

	H_0 cal/mole observed value[a] H_0 = 2030	a Angstrom observed value 3.755 (b)	
		Neglecting zero point vibrations	Considering zero point vibrations
Lennard-Jones r_0 = 3.86	2040	3.750	3.80
Core Model ρ_0 = 3.452 $\frac{U_0}{k}$ = 139.0 d=0.276	2229	3.649	3.695

(a) E.R. Dobbs and G.O. Jones, Repts. Prog. Phys. 20 516 (1957).

(b) C. Domb and I.J. Zucker, Nature (London) 178, 484 (1956).

of the dubious validity of the assumption of additivity used in their derivation, as pointed out recently by Alder.[15] Thermodynamic and transport properties at low densities should instead be prefered.

Stability of the crystal structures. We investigated the relative stability of the two lattice type of closest packing, hexagonal and cubic, for the potential under discussion. We tested the program of the calculations by setting the core size equal to zero ($d=0$) and reproducing the values reported in the literature,[16] for the Lennard-Jones potential.

Using the parameters listed in Table I we evaluated the potential energy for both lattices, first neglecting the zero point energy and then considering its effect. In both cases the hexagonal close packing was found to be the more stable one, although the zero point energy effect is slightly more marked for the hexagonal. The results are

$$\frac{\Phi_c(a) - \Phi_h(a)}{\Phi_c(a)} = -2.72 \times 10^{-4} \quad \frac{\Phi_{zc}(a) - \Phi_{zh}(a)}{\Phi_{zc}(a)} = -2.87 \times 10^{-4}$$

where Φ stands for the potential energy per molecule without zero point energy as given by Eq. (8) and Φ_z includes the zero point effect, Eq. (10). The subscripts c and h refer to the type of packing considered. All the functions are evaluated at the nearest neighbor distance a.

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[15] B.J. Alder, Ann. Rev. Phys. Chem. 12, 195 (1961).

[16] J.E. Lennard-Jones and A.E. Ingham, Proc. Roy. Soc. (London) A107, 636 (1925); T. Kihara and S. Koba, J. Phys. Soc. Japan 7, 348 (1952).

CONCLUSIONS

The purpose of this paper has been to develop an improved intermolecular pair potential for argon. Recent precise measurements by Levelt[9] of the second virial coefficient at low temperature together with the old data at higher temperatures[9] permits a much more severe test for the potential than was previously possible. Our results indicate a definite better fit to the observed values than the one obtained for the Lennard-Jones potential. The present results should enable one to make a precise check of the theory of corresponding states in terms of the molecular parameters as has been recently done in terms of the critical properties.[17]

Application of this intermolecular pair potential to the evaluation of properties of the solid argon resulted, however, in a marked deviation from observed values. The many body potential for the crystal was obtained assuming the additivity of the pair potential. It has been shown[18,19] that this assumption is not a very good one for the induced dipole-induced dipole interaction forces so that one expects it to be even worse for the higher multipole terms. The latter contributes about 20 percent of the total attractive potential at the minimum.[20] As shown by Eq. (7) our model potential is mathematically equivalent to including higher inverse power terms.

Further evidence that the assumption of additivity plays an important role is given by the fact that a better pair potential for the gas does not necessarily mean a better many body potential.

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17 This thesis, Section III.

18 B.M. Axilrod and E. Teller J. Chem. Phys. 11, 299 (1943); B.M. Axilrod J. Chem. Phys. 19, 719 (1951).

19 T. Kihara, Advances in Chem. Phys. 1, 267 (1958).

20 K.S. Pitzer, Advances in Chem. Phys. 2, 59 (1959).

The relative stability of the crystal structures is found to be of the same order of magnitude as for the Lennard-Jones potential.[21] The same can be said of the effect of the zero point vibrational energy in both crystal lattices.[22]

It would be desirable to evaluate the core size parameter in a more precise form than the one used in this paper.

It is interesting to point out, however, that from expansion in Eq. (7) one can obtain an independent estimation of this parameter. Quantum mechanical calculations have been made[23] on the coefficients of the higher power attractive terms of the dispersion energy, $\varphi^{(disp.)}$ that can be written as

$$\varphi^{(disp.)} = - \frac{c}{r^6} - \frac{c'}{r^8} - \frac{c''}{r^{10}}$$

By equating the coefficient in expansion (7) to the corresponding one calculated for the theory of dispersion forces, c', one obtains the relationship

$$c' = 42 U_0 \rho_0^6 b^2 \qquad (11)$$

For the present case of spherical cores b equals the core diameter. Using the numerical value for c' as given by Margenau[24] and solving for b, Eq. (11) gives a core radius for argon of 0.148 Angstroms compared to 0.138 Angstroms we used in our calculations.

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21 T.H.K. Barron and C. Domb Proc. Roy. Soc. (London) A227, 447 (1955).

22 L. Jansen and J.M. Dawson, J. Chem. Phys. 23, 482 (1955).

23 J.O. Hirschfelder, C.F. Curtiss and R.B. Bird "Molecular Theory of Gases and Liquids." (J. Wiley and Sons, Inc. New York, 1954) p. 964.

24 H. Margenau, J. Chem. Phys. 6, 897 (1938).

SECTION III

CORRESPONDING STATES THEORY FOR ARGON AND XENON

Abstract

Recent experimental results allow a more precise check than was previously possible on the conformity of argon and xenon to the principle of corresponding states. The data shows agreement within experimental error except at very high pressures where small differences are found for some but not for other measurements.

INTRODUCTION

Precise check on the theory of corresponding states for the rare gases has until recently been limited by the lack of experimental volumetric data for argon at low reduced temperatures. Consequently the recent volumetric measurements of Levelt[1] are of particular interest. Other relevant data will also be considered.

Compressibility Factor

Unfortunately the compressibility factor comparisons of Levelt's results[1] with values for xenon were made in ways which introduced unnecessary inaccuracies from auxiliary data. Consequently it seemed desirable to present the comparison of the compressibility factor data of Ar and Xe on the basis of reduced temperature and pressure. It has been pointed out[2] that the critical temperature and pressure are readily measured with high accuracy hence the selection of these reduced variables introduces little error. By contrast the critical volume is frequently the much less accurately known than the volumetric data at other temperatures and pressures.

The critical properties used in our calculations are as follows:

	Ar	Xe
T_c	150.86°K	289.74°K
P_c	48.34 atm.	57.64 atm.
z_c	0.2913	0.287

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1 J.M.H. Levelt, Physica, 26, 361 (1960); Thesis, Amsterdam (1958).

2 R.F. Curl, Jr., and K.S. Pitzer, Ind. Eng. Chem. 50, 265 (1958), "Thermodynamic and Transport Properties of Fluids", p. 1, Inst. Mech. Engr. London, 1958.

The values for argon are from Levelt's work; those for xenon are from Habgood and Schneider[3] and are the same as Levelt used. The substantial difference in the z_c values is at once apparent. A comparison of compressibility factor of argon with that for xenon at a variety of reduced temperatures and pressures is shown in Table I. These values were obtained by calculating the P_r values corresponding to Levelt's tabulated values of z at even T_r and d_r. These z values were then interpolated to even P_r values.

The results in Table I show essentially perfect conformity to the principle of corresponding states at densities substantially less than critical density. At higher densities, however, z for argon rises from 2 to 3% above that for xenon. These differences are much smaller than those reported by Levelt on the basis of comparison in terms of reduced temperature and density where a difference of about 10% is found at $T_r = 1.05$ and $d_r = 2.0$. This point is near $T_r = 1.05$, $P_r = 6.0$ where Table I shows less than 1% difference.

Second Virial Coefficient

The second virial coefficients of argon and xenon[4] were also compared on the reduced basis $B^* = BP_c/RT_c$. The results are shown in Fig. 1 as differences from values calculated by the empirical second virial equation

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3 H.W. Habgood and W.G. Schneider, Can. J. Chem. 32, 98 164 (1954).

4 J.M.H. Levelt (ref. 1); E. Whalley, Y. Dupien, and W.G. Schneider, Can. J. Chem., 31, 723 (1953); 33, 633 (1955); J.A. Beattie, R.J. Barriault, and J.S. Brierly, J. Chem. Phys., 19, 1222 (1951); A. Michels, H. Wijker, and Herb. Wijker, Physica 15, 627 (1949).

Table I Comparison of reduced compressibility factors for argon and xenon

P_r	T_r = 1.05		1.20		1.45	
	Ar	Xe	Ar	Xe	Ar	Xe
0.9	0.665	0.666	0.860	0.860	0.906	0.906
1.5	.308	.304	.613	.615	.847	.847
3.0	.465	.453	.541	.532	.753	.750
6.0	.816	.809	.809	.791	.857	.842
9.0	-	-	1.095	1.066	1.071	1.046

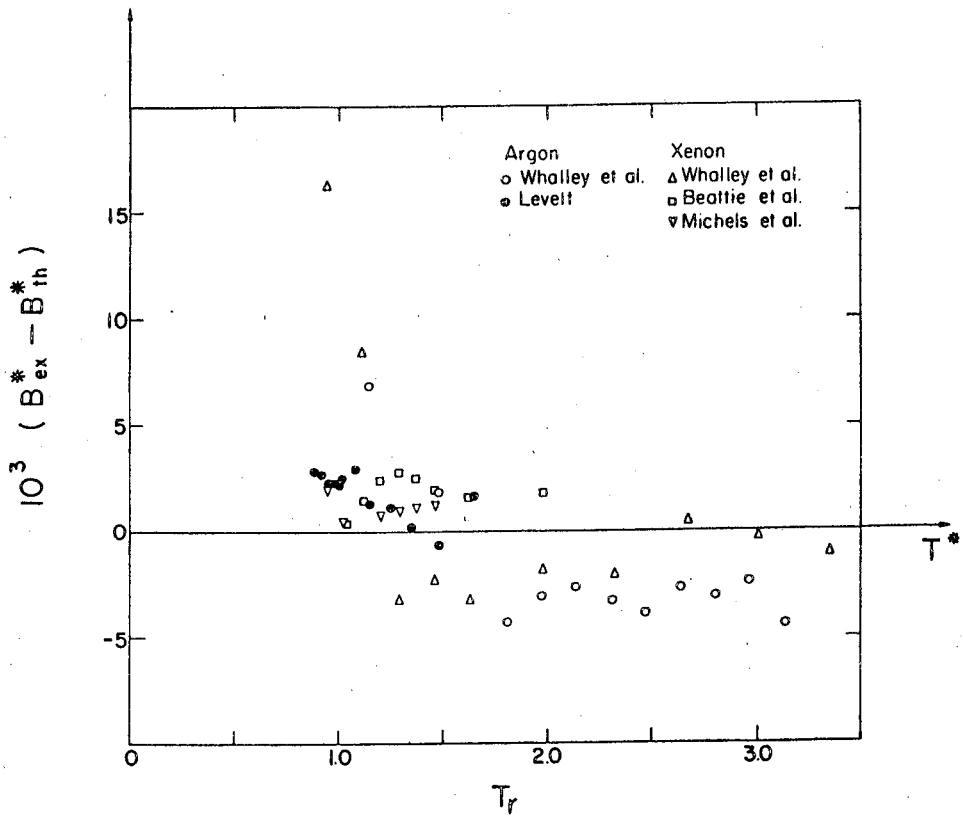

Fig. 1. Reduced second virial coefficients of argon and xenon compared as differences from the empirical equation of Pitzer and Curl.

presented by Pitzer and Curl.[5]

While the xenon values average a little above those for argon at the higher temperatures, the difference appears to be within the experimental uncertainties. Indeed there is a much larger difference between the Ottawa and the Amsterdam measurements at the lowest temperatures where no Ar-Xe differences are found in the data of either laboratory.

While it was not our primary purpose to further test the empirical equation of Pitzer and Curl, we may note that the differences from the empirical equation remain below 0.005 except for the Ottawa measurements near the critical temperature. Thus we find agreement in this respect also within the range of experimental error.

Solid State Properties

Further support for conformity to the principle of corresponding states is obtained from a study of the solid state properties of the noble gases. Guggenheim and McGlashan[6] have recently considered the interaction energy between pairs of argon atoms using experimental data both on the equilibrium properties of the crystalline solid and on the gas phase. The potential function they obtained was then used for the calculation of several thermodynamic properties, e.g. entropy and energy of the crystal as a function of temperature, density of the crystal as a function of temperature and pressure and the temperature dependence of the second virial coefficient.

In a later publication[7] by the same authors, their results on the interaction energy between argon atoms together with the principle of corresponding states are applied to the evaluation of thermodynamic properties of xenon.

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5 K.S. Pitzer and R.F. Curl, Jr., J. Am. Chem. Soc., 79, 2369 (1957).

6 E.A. Guggenheim and M.L. McGlashan, Proc. Roy. Soc., A255, 456 (1960)

7 E.A. Guggenheim and M.L. McGlashan, Mol. Phys., 3, 563 (1960).

They obtained an agreement between calculated and measured values of the entropy and the enthalpy within the limits of the experimental error from the triple point temperature down to about 20°K. For the molar volume the agreement is of the order of 1%. This larger deviation is, however, as these authors point out, not surprising considering that the equilibrium molar volume is determined by minimizing the free energy and a small inaccuracy in the shape of the potential curve would give rise to a much greater inaccuracy in the position of the minimum.

The variation of the melting temperature of argon with pressure was measured by several investigators.[8] There had not been, however, any similar study made for xenon, until very recently Stryland, et al,[9] reported the results of their measurements. This makes possible a comparison of the melting curve for both substances which is shown in reduced form, $P_r = P/P_c$, $T_r = T/T_c$ in Fig. 2. The curve through the single series of xenon points lies within the range of the several series of results for argon. Hence any deviation from corresponding states must be less than present experimental error. Since this comparison extends to 50 times the critical pressure, it is a real test of the correspondence of the repulsive portions of the intermolecular potential curves.

The application of the principle of corresponding states to solid inert gases at very low temperature, where quantum effects have to be considered, has also been made in two recent independent studies by Bernardes[10] and

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8 D.W. Robinson, Proc. Roy. Soc., A225, 393 (1954); P.W. Bridgman, Phys. Rev. 46, 930 (1934); F.E. Simon, M. Ruhemann and N.A.M. Edwards, Z. Phys. Chem., B6, 62 331 (1930).

9 J.C. Stryland, J.E. Crawford and M.A. Mastoor, Can. Jour. of Phys., 38, 1546 (1960).

10 N. Bernardes, Phys. Rev., 120, 807 (1960).

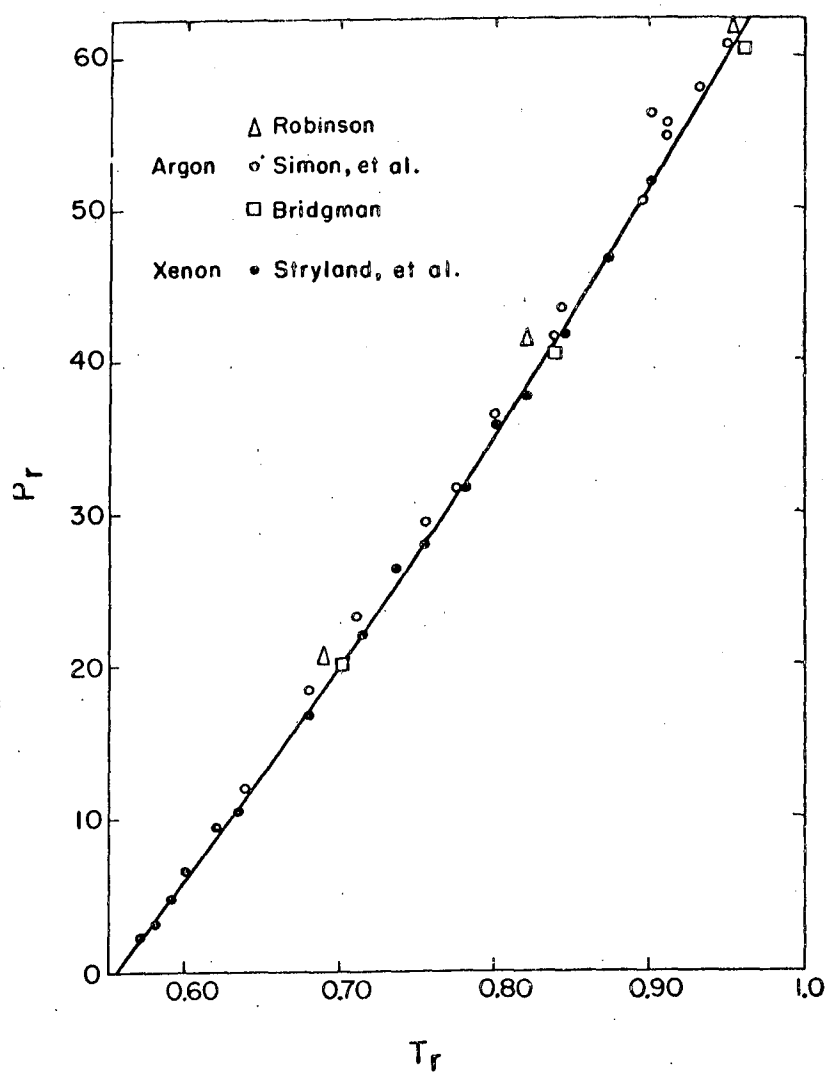

Fig. 2. Melting curve for argon and xenon compared in terms of reduced pressure and temperature.

Zucker;[11] their results also support the general validity of the principle.

[11] I.J. Zucker, Proc. Phys. Soc. (London) 77, 889 (1961).

DISCUSSION AND CONCLUSIONS

We note first that the corresponding states principle (as extended by the acentric factor[12] where applicable) may still be recommended as a reliable basis for estimating volumetric data provided accurate critical temperature and pressure values are available. Since critical volume data are usually relatively inaccurate, comparisons on the basis of reduced volume or reduced density should be avoided.

From the viewpoint of microscopic theory, exact conformity to the corresponding states principle has been shown[13] to follow for the heavier rare gases if their intermolecular potentials are pairwise additive and are given by an expression of the type

$$V = E_o \Phi (r/r_o) \qquad (1)$$

where Φ is a unversal function but E_o and r_o are characteristic energy and distance parameters for each substance. The London theory yields a general inverse sixth power dependence on r at long distances which is in accordance with the concept of a universal function Φ. Unfortunately, the theory of intermolecular interaction at short distances is not precise enough to show whether this assumption of a universal function is exact or merely a good approximation.

The molecular theory also predicts pairwise additivity of potential interactions only as an approximation. It is possible that differences between Ar and Xe with respect to the importance of triple interaction and still higher terms may be significant.

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[12] K.S. Pitzer, J. Am. Chem. Soc., 77, 3427 (1955). For a complete discussion of the properties of fluids in terms of the acentric factor see G.N. Lewis and M. Randall, "Thermodynamics" revised by K.S. Pitzer and L. Brewer, 2nd. Ed., McGraw-Hill Book Co., New York, 1960, App. 1, p. 605.

[13] K.S. Pitzer, J. Chem. Phys., 7, 583 (1939).

The differences in compressibility factor at the highest pressures, which were noted in Table I, may arise from one or more of the sources just noted. However, the data on the melting curve, which shows no significant deviation from corresponding states, extend to even higher pressures and densities than those on the fluid density. Hence further experimental work seems to be indicated before concluding that any deviation of Ar and Xe from corresponding states behavior exists.

SECTION IV

NOTE ON THE CONDENSATION COEFFICIENT

ABSTRACT

A simple theory for the evaluation of the condensation coefficient of liquids is presented. The condensation coefficient is calculated by assuming that the fraction of molecules reaching the surface with a kinetic energy higher than the emission energy, is able to leave the surface. The emission energy is obtained from the internal heat of vaporization. The agreement with the experimental data is satisfactory.

INTRODUCTION

The condensation coefficient, introduced on studying the rate of evaporation from liquid and solid surfaces, is defined as the ratio of the observed rate of evaporation to the maximum possible rate, or, what is equivalent, as the ratio of the number of molecules sticking to the surface, n_s, to the number of molecules hitting it from the gaseous phase.

$$\alpha = \frac{n_s}{n_h} \tag{1}$$

We shall restrict our study to evaporation from liquid surfaces. From kinetic theory of gases,[1] the number of molecules colliding against a wall, n_h, per unit area and per unit time is given by

$$n_h = \frac{1}{4}\int_0^\infty v\,dn_v$$

where v is the molecular speed and

$$dn_v = \frac{4n_g}{\sqrt{\pi}}\left(\frac{m}{2kT}\right)^{3/2} v^2\, e^{-mv^2/2kT}dv$$

is the distribution function giving the number of molecules per unit volume with speed between v and v + dv, other symbols having the usual meaning. Putting this value for dn_v and performing the integration we get

$$n_h = n_g\left(\frac{kT}{2\pi m}\right)^{1/2} \tag{2}$$

At equilibrium conditions the number of molecules, n_ℓ, leaving the liquid surface is equal to the number of molecules coming from the gaseous phase

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[1] See, for instance: R.D. Present, "Kinetic Theory of Gases," McGraw Hill Book Co., Inc., New York, 1958.

sticking to the surface, n_s.

$$n_s = n_\ell \tag{3}$$

We present a method, based on a simple idea, for evaluating this number n_ℓ, and consequently α. Consider the molecules in the liquid phase: their Hamiltonian will in general be given by $H = V(x,y,z) + T(px,py,pz) + I(q_4 \ldots q_r, p_4 \ldots p_r)$ where the potential energy, $V(x,y,z)$, is a function of position only, the kinetic energy, $T(px,py,pz)$, is a function of momentum only and $I(q_4 \ldots q_r, p_4 \ldots p_r)$, is the internal energy depending on the remaining coordinates and momenta (internal degrees of freedom).

If we now assume that there are no crossed (or coupling) terms in the Hamiltonian, then it can be shown that the distribution functions corresponding to each term of the separable Hamiltonian can be regarded as independent[2] and so we can set up these distribution functions for the liquid phase. We calculate the number of molecules n_i hitting the surface from inside per unit area and per unit time, making the additional assumption that the interface can be thought of as an ideal surface, (a geometrical plane).

We then evaluate the fraction of molecules having high enough kinetic energy to overcome the binding energy in the liquid and so be able to jump out to the gaseous phase. This gives us n_ℓ.

Consider the molecules with a given velocity component v_z, the z axis being taken normal to the surface. The number striking the surface per unit area and unit time is given by

$$dn_{v_z} = \frac{n}{\sqrt{\pi}} \left(\frac{m}{2kT} \right)^{1/2} v_z \, e^{-mv_z^2 / 2kT} \, dv_z$$

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2 See R.C. Tolman, "The Principles of Statistical Mechanics", Chap. IV, Paragraph 33. Oxford University Press, London, 1938.

and the fraction with kinetic energy higher than the value of the emission energy j, is

$$n_e = \frac{n}{\sqrt{\pi}} \left(\frac{m}{2kT}\right)^{1/2} \int_{v_{z,j}}^{\infty} v_z \, e^{-mv_z^2/2kT} \, dv_z \qquad (4)$$

Setting $u^2 = \frac{mv_z^2}{2kT}$, and correspondingly $v_{z,j} = (\frac{2j}{m})^{1/2} = (\frac{2kT}{m})^{1/2} u_j$ and performing the integration we get:

$$n_e = n_v \left(\frac{kT}{2\pi m}\right)^{1/2} e^{-u_j^2} \qquad (5)$$

HEAT OF VAPORIZATION AND INTERFACIAL ENERGY RELATIONS

W.D. Harkins and his coworkers have paid considerable attention to the study of interfacial energy relations.[3] The discussion here follows their ideas. Vaporization process can be considered as made up by two different steps: i) surface formation and, ii) jumping out of the molecules from the liquid surface into the vapor. Energy for i) is supplied partly as heat - latent heat of surface formation - and partly in mechanical form that gives rise to the surface free energy.

In evaluating these two quantities per molecule, the number of them per unit area of the surface is required. This number is proportional to the 2/3 power of the concentration in the bulk of the liquid. They made the assumption - proved justified later in their own calculations - that the constant of proportionality is just unity.

$$n_s = \beta\, n_v^{2/3} \text{ with } \beta = 1$$

However, there is some evidence from the study of insoluble films - pointed out by Harkins himself - and from the type of molecular packing, that the factor is slightly less than one.

Assuming cubic closest packing of the molecules, that is a face-centered cubic lattice, a simple calculation shows the relationship between volume and surface concentration. If the 1.0.0 face is exposed to the surface then:

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3 W.D. Harkins: "The Physical Chemistry of Surface Films". Reinhold Pub. Corp., New York, 1952.
W.D. Harkins et al: J. Am. Chem. Soc. 39, 541 (1917), ibid, 44 (1922).
Colloid Symposium Monograph V. New York (Chem. Cat. Co.) 1927.
Z. Physik Chem. A139, 647 (1928).

$$n = 4\frac{v}{a^3}, \quad n_v = \frac{4}{a^3} \text{ and } n_s = \frac{2}{a^2} \quad \frac{2n_v^{2/3}}{4^{2/3}} = 0.79\, n_v^{2/3}$$

where n is the number of molecules in volume v, a is the edge of the elementary cell and n_s is the number of molecules per unit area of the surface. If the 1.1.1 face is exposed

$$n_s = \frac{4}{\sqrt{3}a^2} = \frac{2^{2/3}}{3^{1/2}} n_v^{2/3} = 0.92\, n_v^{2/3}$$

This gives an idea of the range of variability of the parameter β for approximate spherical molecules, it being around the lower end for polar molecules - the electrostatic repulsion opposing to their packing very closely - and toward the upper end for the non-polar, though of course not a strong significance can be assigned to these numbers.

Now, if

ΔH_v = latent heat of vaporization per mole

N_A = Avogadro's number

Γ = Surface free energy per square cm

n_s = concentration of molecules at the surface

L_s = latent heat of surface formation per square cm

E_s = total energy of the surface per square cm

then

$$\frac{\Delta H_v}{N_A} = \lambda, \frac{\Gamma}{n_s} = \gamma, \frac{L}{n_s} = \ell, \quad \gamma + \ell = \frac{E}{n_s} = e$$

$\lambda - kT = \lambda_i$ energy of vaporization per molecule

$\lambda_i = e + j$ $\quad$ j = energy of thermal emission from the liquid surface to the gaseous phase.

It can be shown[3,4] that the latent heat of the surface formation is

[4] N.K. Adam, "The Physics and Chemistry of Surfaces", Third Edition, p. 12, Oxford Univ. Press (London) 1941.

given by $\ell = -T\left(\frac{\partial\gamma}{\partial T}\right)_{T = T}$ so that we can write

$$e = \gamma \quad T\left(\frac{\partial\gamma}{\partial T}\right) \text{ and } j = \lambda_i - \gamma + T\left(\frac{\partial\gamma}{\partial T}\right)_T$$

j/λ_i gives the fraction of the total energy of vaporization which a molecule must have to be able to jump out to the gaseous phase. This ratio is a function of the temperature and it is much higher for polar molecules (CH_5OH, H_2O) than for non polar ones (C_6H_6, CCl_4) but the values in the two groups approach each other as the temperature is increased, this being a consequence of the decrease in orientation at the surface for the polar ones.

This value j, of the emission energy, is a threshold of energy which determines our lower limit of integration in Eq. (4). Introducing the values of n_h from Eq. (2), n_e from Eq. (5) and using Eq. (3) we get as an expression for the condensation coefficient

$$\alpha = \frac{n_v}{n_g} \; e^{-j/kT} \tag{7}$$

n_v and n_g being the densities, in molecules per unit volume, in the bulk of the liquid and in the gaseous phase respectively.

It should be pointed out that n_v, n_g, and j through λ_i are all functions of the temperature, so the temperature dependence of α is naturally introduced.

Notice that if T goes to critical temperature Tc, the heat of vaporization λ, the surface tension γ, and $\frac{d\gamma}{dT}$ will all go to zero, so that from Eq. (6) the emission energy goes to zero, and $e^{-j/kT}$ goes to 1. As $T \to Tc$, the densities of liquid and gaseous phase approach one another, $n_v \to n_g$, so $\alpha \to 1$.

Results obtained with the application of formula (7) are shown in Table I. They can be regarded as satisfactory if the simplicity of the theory is taken into account.

TABLE I

Comparison of Calculated and Observed Condensation Coefficients

	T^oK	j/λ_i	β	α calc	α obs	Reference
Carbon tet.	273.1	0.62	0.92	1.01	1.0	a,b,c
Benzene	273.1	0.625	0.95	0.92	0.85, 0.95(6^oC)	d
Chloroform	273.1	0.685	0.89	0.17	0.16 (2^oC)	d
Ethyl Alcohol	286.2	0.81	0.76	0.014	0.02, 0.024	d-e
	323.1	0.78	0.76	0.179		
Methyl Alcohol	273.1	0.84	0.76	0.023	0.045	d
	313.1	0.82	0.76	0.040		
Water	273.1	0.81	0.83	0.051	0.04 (-8 to +15^oC)	f
	323.1	0.79	0.83	0.738		
Toluene	273.1	0.65	0.90	0.59	0.45-0.85 room temp.	d

a. T. Alty and F.H. Nicoll, Can. J. Research 4, 547 (1931).

b. T. Alty, Phil. Mag. 15, 82 (1933).

c. W. Pruzer, Z. Physik 115, 202 (1940).

d. M. Baranaev, J. Phys. Chem. (USSR) 13, 1035 (1939).

e. H. Bucka, Z. Physik. Chem. 195, 260 (1950).

f. R.S. Bradley and A.D. Shellard, Proc. Roy. Soc. (London) A206, 65 (1951).

It is interesting to compare the values of the ratio j/λ we obtained against the values predicted by the Stefan's law of $j/\lambda = 1/2$, which does not take into account temperature dependence, molecular symmetry and dipole moment.

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