
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 77

JULY 16, 1955

NUMBER 13

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA,
BERKELEY]

The Volumetric and Thermodynamic Properties of Fluids. I. Theoretical Basis and Virial Coefficients¹

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RECEIVED JANUARY 21, 1955

The basic theory of the volumetric and thermodynamic properties of fluids is examined in relation to the statistical mechanical proof of the theory of corresponding states. It is shown that the general range of non-polar or slightly polar "normal" liquids cannot be expected to conform to the hypothesis of corresponding states but may well conform to a slightly more complex equation involving just one additional parameter. Rigorous theoretical test can be made only for the second virial coefficient. There it is found that linear and globular non-polar molecules fit this theory very exactly and that slightly polar molecules also conform in reasonable approximation.

The quantitative representation of the volumetric behavior of fluids over both gas and liquid regions has proven to be an unusually difficult problem. It is now over eighty years since van der Waals² first proposed his famous equation of state. Yet today we are still in serious need of improvements in the prediction and correlation of the volumetric properties of fluids. This situation is in marked contrast to the extensive theoretical advances with respect to the thermodynamic properties of ideal gases.

Our understanding of the forces operating between molecules has developed rapidly since the emergence of a satisfactory quantum theory in 1926. Particularly important is the work of London on the attractive forces between molecules. Also it became clear that certain anomalous properties of hydrogen and helium arise from quantum effects in the translational motion of those molecules. However, our understanding of intermolecular forces also indicated a bewildering complexity of effects which probably tended to discourage attempts at systemization.

The most generally useful method of prediction of the volumetric properties of fluids is the hypothesis of *corresponding states*, which also came originally from van der Waals. Engineers have used this method extensively to obtain estimated properties for design purposes, and many authors have presented charts of both volumetric and related thermodynamic properties on the basis of correspond-

ing states. Hougen and Watson³ give a particularly extensive discussion of this method, together with estimates of the accuracy to be expected. They indicate that the maximum error in predicted volume is about 15% while errors in other predicted properties range from 5 to 35%. These percentages indicate the degree to which actual substances conform to the hypothesis of corresponding states.

It is the purpose of this series of papers to present a correlative and predictive scheme which is only slightly more complex but which yields results about one order of magnitude more accurate. This scheme involves one parameter in addition to the critical constants for each substance. It is postulated that any group of substances having the same value of this additional parameter will conform within the group to the corresponding states principle.

The possibility of a scheme of this type has been mentioned on several past occasions. Nernst suggested it in the 1907 edition of "Theoretischen Chemie"⁴ but dropped it in later editions. Recently Meissner and Seferian⁵ discussed such a scheme, but we shall see that their attempt to include highly polar substances such as water necessarily impaired the accuracy of the results. However, Riedel⁶ has discussed vapor pressures on a basis very similar to that which we have selected.

(3) O. A. Hougen and K. M. Watson, "Chemical Process Principles, Part Two, Thermodynamics," John Wiley and Sons, Inc., New York, N. Y., 1947, Chapter VII.

(4) See quotation in ref. 6.

(5) H. P. Meissner and R. Seferian, *Chem. Eng. Progress*, **47**, 579 (1951).

(6) L. Riedel, *Chem. Ing. Tech.*, **26**, 83 (1954).

(1) This research was a part of the program of Research Project 50 of the American Petroleum Institute.

(2) J. H. van der Waals, Dissertation, Leiden, 1873.

He excluded highly polar or associated liquids and the quantum liquids (H_2 and He) and showed that the remaining *normal* liquids had reduced vapor pressure curves falling accurately into a single family. We shall return to Riedel's work in a later paper when other properties of the two phase region are discussed. Rowlinson⁷ has also presented certain theoretical work which yields a correlation scheme similar to the present one.

In this paper we present the theoretical background in terms of modern molecular data and discuss theoretical second virial coefficients calculated from appropriate models.

Classification of Substances; Intermolecular Forces

Simple Fluids.—Our present theoretical knowledge is of great aid in selecting the substances which may reasonably be expected to conform to a particular equation. The theoretical requirements for conformity to the postulate of corresponding states have been given in several places including a paper by the present author⁸ which includes a more detailed presentation of several topics essential to the present development. The simplest class of substances following corresponding states behavior comprises the heavier rare gases (Ar, Kr, Xe) and methane. The principal characteristics are *spherical shape* (which methane gains by rapid and relatively free rotation) and an *inverse sixth power attractive potential*. London's theory yields this force law and applies to cases where the valence shells of all atoms are filled. We shall adopt the term *simple fluid*⁹ for this class of substances.

Since the intermolecular potential curve is of primary importance, it is wise to discuss it a little further. We distinguish between time average or permanent electric moments (the usual dipole moments) and instantaneous moments arising from the momentary location of the electrons. The inverse sixth power attractive term arises from the interaction of instantaneous dipole moments. Higher power terms arise from higher electrical moments, but these are small and their effect may be absorbed in our ignorance of the repulsive potential. We know that molecules repel one another on close approach, that this repulsion arises very suddenly, and that it is a manifestation of the Pauli exclusion principle. However, we do not have a good simple mathematical expression for this repulsive effect. While exponential terms are believed to be somewhat superior expressions of this repulsive potential, inverse power terms are much easier to use and have proven almost as satisfactory. The best compromise of accuracy and simplicity is probably the Lennard-Jones or 6-12 potential given by the expression

$$\epsilon(r) = \epsilon_0 \left[\left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^6 \right] \quad (1)$$

where ϵ_0 is the depth of the potential minimum, r is the intermolecular distance, and r_0 its value at the

(7) J. S. Rowlinson, *Trans. Faraday Soc.*, **50**, 647 (1954).

(8) K. S. Pitzer, *J. Chem. Phys.*, **7**, 583 (1939). The symbols E , A and R_0 of that paper become ϵ , ϵ_0 and r_0 in the present text.

(9) In the earlier paper⁸ the term perfect liquid was used. Extension of the treatment to the imperfect gas region makes a change obviously desirable.

minimum. We shall also define σ as the collision diameter which is the point of zero energy on the repulsive branch of the curve. Its value is

$$\sigma = (2^{-1/6})r_0$$

The curve of equation 1 is shown as the solid line in Fig. 1.

Another important characteristic of London forces is their additivity. To a first approximation, equation 1 may be applied to each intermolecular distance in a large assemblage of molecules. The accuracy of this approximation has been studied by Axilrod.¹⁰

We have assumed a simple fluid to be one having an intermolecular potential essentially like equation 1. Each substance has its own value of ϵ_0 and r_0 . These are related to the critical temperature and critical volume, respectively. But the shape of the curve is the same for all simple fluids.

An additional limitation on the simple fluid is the absence of quantum effects for molecular translation. Helium and hydrogen must be excluded on this account. Neon also deviates at low temperatures from the simple fluid behavior for this reason. Since we have already named all of the substances likely to deviate because of quantization of molecular translation, there is little need to extend general correlation schemes to cover this area. The volumetric behavior of these substances is known and does not need to be predicted from a practical point of view. We shall ignore quantum fluids hereafter and turn our attention to other types.

Globular Molecules.—Next let us consider large molecules of nearly spherical shape, globular molecules. Neopentane, $C(CH_3)_4$, is a simple example. The attractive forces are still of the London type but now the effective centers are the peripheral atoms or the methyl groups. The intermolecular potential may be taken as the sum of inverse sixth power terms summed over the various distances between methyl groups and is no longer an inverse sixth power potential between molecular centers. This effect is probably responsible for most of the deviation of neopentane from simple fluid behavior, but there is also probably some deviation from spherical shape.

Figure 1 shows the effect of this globular character on the intermolecular potential curve. Two approximations are given. The dashed line is based on the core model of Kihara.¹¹ He assumes a core inside each molecule and then takes the Lennard-Jones potential for the shortest distance between molecular cores. The potential is thus

$$\epsilon = \epsilon_0 \left[\left(\frac{\rho_0}{\rho} \right)^{12} - 2 \left(\frac{\rho_0}{\rho} \right)^6 \right] \quad (2)$$

where ρ is the shortest distance between the cores, ρ_0 , this distance at the potential minimum, and a is the radius of the spherical core. In the present case of spherical cores, $\rho = r - 2a$. For the curve in Fig. 1 we take a spherical core of diameter equal to one fourth of the intermolecular distance at the potential minimum, *i.e.*, $a = 0.125r_0 = 0.167\rho_0$.

Since attractive effects between the more distant parts of the molecule are not negligible, al-

(10) B. M. Axilrod, *J. Chem. Phys.*, **19**, 719, 724 (1951).

(11) T. Kihara, *Rev. Mod. Phys.*, **25**, 831 (1953); and earlier papers there cited; see also J. S. Rowlinson, *J. Chem. Phys.*, **20**, 337 (1952).

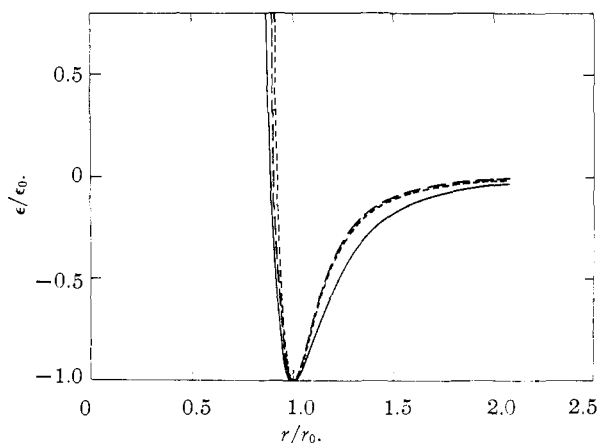


Fig. 1.—The intermolecular potentials for globular molecules; see text for details.

though repulsive effects presumably are, we also investigate additional models. Repulsion will be taken as the inverse twelfth power of the minimum distance between the surfaces of spherical cores, like the Kihara model. The attractive force will be taken as arising from centers distributed equally on the surface or through the volume of the spherical core. By expanding the integral for the attractive potential in a Maclaurin series in the radius of the core, a , the following expressions result. They may be arranged as

$$V(r) = -cr^{-6}\psi(a/r) \quad (3)$$

where the surface model yields

$$\psi_s = 1 + 10 \left(\frac{a}{r}\right)^2 + \left(\frac{148}{3}\right) \left(\frac{a}{r}\right)^4 + 480 \left(\frac{a}{r}\right)^6 \quad (4)$$

and the volume model yields

$$\psi_v = 1 + 6 \left(\frac{a}{r}\right)^2 + \left(\frac{148}{7}\right) \left(\frac{a}{r}\right)^4 + 160 \left(\frac{a}{r}\right)^6 \quad (5)$$

The complete potential becomes

$$\epsilon = \frac{c_1}{(r-2a)^{12}} - \frac{c_2}{r^6} \psi(a/r) \quad (6)$$

where c_1 and c_2 are constants which can be evaluated in terms of ϵ_0 and r_0 for any particular value of a/r_0 .

In the important region near the potential minimum these two models give similar results provided the core radius of the surface model is taken as about 0.8 of that for the volume model. The dotted curve in Fig. 1 shows the potential for the surface model with $a = 0.2r_0$. The nearly equivalent volume model would have $a = 0.25r_0$. It is apparent from Fig. 1 that the Kihara model with $a = 0.125r_0$ is very similar in its net effect—a little steeper outside the minimum and a little less steep inside. Thus there seems little need to pursue these additional models further except to note that the Kihara core radius should be taken considerably smaller than that of the polarizable electron cloud.

The important effect of the globular character of a molecule on its potential function, as is evident from any of the models, is a narrowing of the potential minimum. This decreases the probability of any given clustering of molecules at a given ratio, ϵ_0/kT , of the intermolecular potential energy to

thermal energy. In statistical mechanics probabilities are proportional to volumes in phase space, and in this case the important dimension is the range of intermolecular distance within the potential curve at a height approximately kT above the minimum. Likewise decreased probabilities lead to decreased entropies. Thus we expect the decrease in entropy from the ideal gas state to some comparable state in the imperfect gas or liquid region to be greater for globular molecules than for those of simple fluids.

Since the liquid state represents the essentially complete clustering of the molecules, the vapor-liquid equilibrium should give the most marked manifestation of the effect just mentioned. With a greater decrease in entropy on condensation for globular molecules, the temperature must be lower, relatively, before condensation takes place. Also the change in vapor pressure with temperature will be more rapid for substances with globular molecules than for simple fluids. This is shown in Fig. 2. Eventually, we shall take this increase in slope of the vapor pressure curve over that of a simple fluid as the essential third parameter of our theory.

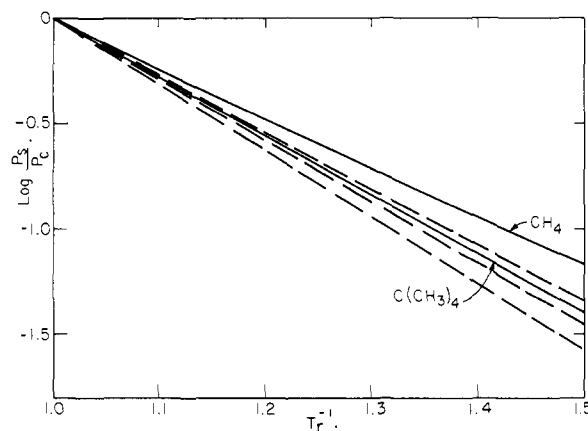


Fig. 2.—Reduced vapor pressure curves (P_a is the sat. vapor pressure). The dashed curves are, from the top, for propane, n -pentane and n -heptane, respectively.

The derivation of the theory of corresponding states for simple fluids is easily extended to substances with globular molecules.¹² The essential requirement is that the shape of the intermolecular potential curve be the same for all substances in the class which is to conform to the theory. Thus on any one of the core models, if the ratio of the core radius to the intermolecular distance at the potential minimum (a/r_0) is the same for a group of substances, then that group will follow corresponding states behavior. The behavior of this group will differ, however, from that of simple fluids where the core radius is zero.

Alternatively, we may say that the volumetric behavior of a fluid with globular molecules is a function of three variables: (1) the depth of the potential minimum ϵ_0 , (2) the intermolecular distance at the minimum r_0 , and (3) the relative core size a/r_0 . Simple fluids form the special case with $a/r_0 = 0$. In terms of macroscopic properties one

(12) See ref. 8. There is now a different function φ but the proof is exactly the same.

may identify the critical temperature, the critical volume and the surplus slope of the vapor pressure curve (over that of a simple fluid) as yielding the equivalent information.

Our general correlation scheme is essentially that defined in the preceding paragraph. However, to be useful it must apply to a broader class of substances than have been considered so far.

Non-spherical, Non-polar Molecules.—Let us turn now to non-polar molecules of irregular shape. Kihara¹¹ has extended his core model to such cases by taking cores of non-spherical shape. We shall show later that the first-order effect of the introduction of a core on the second virial coefficient is the same for all shapes of core. This arises because the essential effect is a narrowing of the potential minimum even though it must now be studied in multidimensional space.

The Kihara model assumes the same minimum energy for a pair of molecules at their optimum separation regardless of their orientation. This is probably an oversimplification. Thus it seems likely that two long molecules exert greater attraction when lying side by side at the optimum distance apart than when they are oriented end to end. However, the introduction of this effect will again merely further narrow the potential curve in this generalized sense. In other words, the minimum energy is attainable only for optimum orientation as well as linear separation. Consequently, the volume in multidimensional configuration space just above the minimum (by the order of kT) is relatively smaller than it would be for a spherical molecule.

It is not pretended that the exact effect of non-spherical shape is the same for every shape or the same as for globular character. However, the macroscopic properties are calculated by averaging appropriate functions over all space and are frequently insensitive to details. Consequently it seems likely that the behavior of a substance with non-polar molecules of non-spherical shape will conform closely to that of globular molecules with some value of the (a/r_0) parameter. This postulate will be tested in the comparisons to follow.

Polar Molecules.—The interaction potential of permanent dipoles of fixed orientation varies as the inverse third power of the distance between their centers. Also it is highly dependent on their orientation—indeed it is repulsive for half of the possible solid angle. Consequently, it is apparent that a cluster of non-rotating dipolar molecules will have properties significantly different from those of non-polar molecules.

If the dipolar effects are small compared to thermal energies, then one does obtain an inverse sixth power interaction potential because of a partial excess of favorable orientations. The formula for this "orientation effect" is

$$\epsilon_{\mu} = -\frac{2}{3} \frac{\mu^4}{kT r^6} + \dots \quad (7)$$

where μ is the dipole moment.

For many substances the interaction of their permanent dipole moments constitutes only a small perturbation to the London force already present. Examples include H_2S , CH_3Cl and HCl . Even in HCl the calculations indicate that the orientation

effect constitutes less than 20% of the total interaction energy at room temperature.¹³ In such cases the effect of the permanent dipole on the intermolecular potential function is again that of a narrowing. Just as for non-spherical, non-polar molecules, the lowest energy arises only in the most favorable angular orientation. Thus the relative volume in a general configuration space just above the potential minimum will be reduced in the polar case as compared to that for a spherical non-polar molecule. We will leave it to later comparisons to show the degree of similarity in the effect on volumetric properties of small dipole moments and of non-polar types of deviation (*i.e.*, globular or non-spherical).

Virial Coefficients

While it is impractical at the moment to carry our general theoretical studies much further, the second virial coefficient has been calculated for several of these models. We shall draw chiefly upon the work of Kihara¹¹ on his core models and that of Hirshfelder, McClure and Weeks¹⁴ and that of Rowlinson¹⁵ on molecules with permanent dipoles in addition to a Lennard-Jones 6-12 potential. The latter potential is

$$\epsilon = \epsilon_0 \left[\left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^6 \right] - \frac{\mu^2}{r^3} (2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \varphi) \quad (8)$$

Here it must be remembered that ϵ_0 and r_0 have lost the precise significance they had in the non-polar case; also θ_1 and θ_2 are the angles the dipoles make with the axis connecting them while φ is the difference in their azimuthal angle.

Kihara's final formula¹¹ for all of his core models gives for the second virial coefficient

$$B = \frac{2\pi}{3} N_0 \rho_0^3 F_3(Z) + M_0 \rho_0^3 F_2(Z) + \left(S_0 + \frac{M_0^3}{4\pi} \right) F_1(Z) + \left(V_0 + \frac{M_0 S_0}{4\pi} \right) \quad (9)$$

where $Z = (\epsilon_0/kT)$, ρ_0 is the core separation for minimum energy, see eq. 2, and M_0 , S_0 and V_0 are the mean curvature, the surface area and the volume of the core, respectively. He gives expressions for many shapes of cores. We shall use only the two extreme shapes, as follows

thin rod of length l :

$$M_0 = \pi l, S_0 = V_0 = 0$$

sphere of radius a :

$$M_0 = 4\pi a, S_0 = 4\pi a^2, V_0 = 4\pi a^3/3$$

For these two cases the virial coefficient formulas become

Thin rod:

$$B = \frac{2\pi}{3} \rho_0^3 \left[F_3(Z) + \frac{3}{2} \left(\frac{l}{\rho_0} \right) F_2(Z) \right] \quad (10a)$$

Sphere:

$$B = \frac{2\pi}{3} \rho_0^3 \left[F_3(Z) + 6 \left(\frac{a}{\rho_0} \right) F_2(z) + 12 \left(\frac{a}{\rho_0} \right)^2 F_1(z) + 8 \left(\frac{a}{\rho_0} \right)^3 \right] \quad (10b)$$

(13) F. London, *Trans. Faraday Soc.*, **33**, 8 (1937).

(14) J. O. Hirshfelder, F. T. McClure and I. F. Weeks, *J. Chem. Phys.*, **10**, 201 (1942). This paper uses r_0 for the collision diameter which is here designated σ .

(15) J. S. Rowlinson, *Trans. Faraday Soc.*, **45**, 974 (1949).

In the absence of a core, ρ_0 becomes r_0 , and F_3 gives the virial coefficient for a Lennard-Jones gas which is our "simple fluid." It is evident that, for small values of l or a , the effect in each case is to introduce a small component of F_2 . All shapes of core give this same result for the first order deviation

$$B = \frac{2\pi}{3} N_0 \rho_0^3 [F_3(Z) + xF_2(Z)] \quad (11)$$

Turning now to the permanent dipole molecules, the second virial coefficient is¹⁴

$$B = \frac{2\pi}{3} N_0 \rho_0^3 [F_3(Z) + yH(Z) + y^2J(Z) \dots] \quad (12)$$

where¹⁶ r_0 is the distance at the minimum in the non-polar part of the potential function, see equation 8, and $y = \mu^4/\epsilon_0^2 r_0^6$ is the parameter which measures the relative importance of the dipole. This is a series and additional terms are available but are not needed for our purposes.

For ease in our calculations we fitted third-order equations to the tabulated values of the virial coefficient functions over the range from the lowest useful temperatures to about four times the critical temperature. Our four-constant expressions for the various functions are

$$F_3 = 0.5188 - 1.6223Z - 0.5235Z^2 - 0.1684Z^3 \quad (13a)$$

$$F_2 = 0.6426 - 0.7237Z - 0.3677Z^2 - 0.0936Z^3 \quad (13b)$$

$$F_1 = 0.8007 - 0.2443Z - 0.1993Z^2 - 0.0372Z^3 \quad (13c)$$

$$H = 0.0168 - 0.165Z - 0.119Z^2 - 0.630Z^3 \quad (13d)$$

$$J = 0.0135 - 0.119Z + 0.319Z^2 - 0.302Z^3 \quad (13e)$$

No unusual effort was made to maximize the accuracy of these expressions, since the original functions are available for precision work. It is believed that they are accurate to at least 1% or 0.001 (whichever is larger) in the range $0.2 < Z < 2$ for F_1 , F_2 and F_3 and $0.2 < Z < 1$ for H and J . Rowlinson¹⁵ gives tables for dipolar molecules in the range $Z > 1$.

Our interest is to determine the extent to which shape or dipole factors cause deviation from the postulate of corresponding states. Since the critical properties have not been calculated for these models we shall use the Boyle point as the reference point for reduced variables. However, to avoid possible confusion with the usual reduced variables we shall always write the explicit ratios, T/T_B , Z/Z_B , B/v_B , etc. We take the reference volume to be

$$v_B = \left(T \frac{\partial B}{\partial T} \right)_{T=T_B} = - \left(Z \frac{\partial B}{\partial Z} \right)_{Z=Z_B} \quad (14)$$

in accordance with Kihara.

Since the addition of functions F_2 and H in equations 11 and 12 affects the reference points, the final reduced equation had to be corrected for this effect. To the first order, the result is

$$\begin{aligned} \frac{B}{v_B} &= \left[\frac{B}{v_B} \right]_0 + x \left[\frac{\partial}{\partial x} \left(\frac{B}{v_B} \right) \right]_0 + y \left[\frac{\partial}{\partial y} \left(\frac{B}{v_B} \right) \right]_0 \quad (15) \\ \left[\frac{B}{v_B} \right]_0 &= 0.908 - 0.824 \left(\frac{T_B}{T} \right) - 0.0771 \left(\frac{T_B}{T} \right)^2 - \\ &\quad 0.00720 \left(\frac{T_B}{T} \right)^3 \quad (15a) \end{aligned}$$

(16) Note that our functions are related to those of reference 14 as follows: $y = x/2$, $F_3 = F_{12}/\sqrt{2}$, $H = \sqrt{2} H_{12}$, $J = 2\sqrt{2} J_{12}$. These changes were made for consistency with Kihara's equations.

$$\left[\frac{\partial}{\partial x} \left(\frac{B}{v_B} \right) \right]_0 = -0.079 + 0.148 \left(\frac{T_B}{T} \right) - 0.0597 \left(\frac{T_B}{T} \right)^2 - 0.0096 \left(\frac{T_B}{T} \right)^3 \quad (15b)$$

$$\left[\frac{\partial}{\partial y} \left(\frac{B}{v_B} \right) \right]_0 = -0.0444 + 0.065 \left(\frac{T_B}{T} \right) + 0.0039 \left(\frac{T_B}{T} \right)^2 - 0.0244 \left(\frac{T_B}{T} \right)^3 \quad (15c)$$

The effect of the reduction is to make each function zero at $T = T_B$. The slope of the base function is unity at this point while the slope of each derivative function is zero. The range of validity of these equations is for (T_B/T) from 0.7 to 6 for (15a and b) and to 3.5 for (15c).

While the derivative functions 15b and 15c do not look very much alike in equation form, it is apparent from Fig. 3 that they are actually quite similar. It is a coincidence, of course, that x and y have been defined in a manner that these two functions have similar magnitude as well as the same shape.

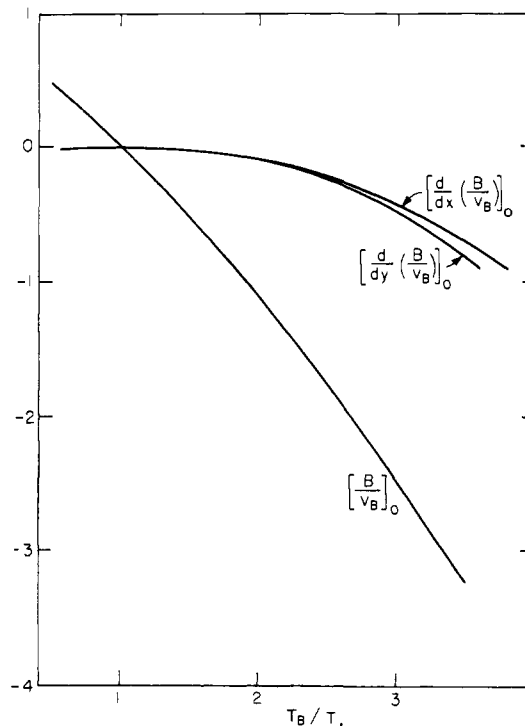


Fig. 3.—Reduced second virial coefficient functions.

Our basic correlation scheme as stated above is to involve just one variable in addition to the energy and distance parameters. For the moment we take this variable to be the x defined by equation 11 for the core model. Now we may determine the extent to which dipole effects may be substituted for core effects without exceeding some limit of error. Let us consider a limit such as 1%, which is a high accuracy for virial coefficients, and take the range of temperature above $T_B/3.5$. We find that the two effects are interchangeable within the limit of validity of the first-order equation 15. We turn, therefore, to a comparison of curves for finite values of the parameters for linear, spherical and dipolar molecules. Such a set of curves is shown in Fig. 4. A more sensitive comparison is given in Fig. 5

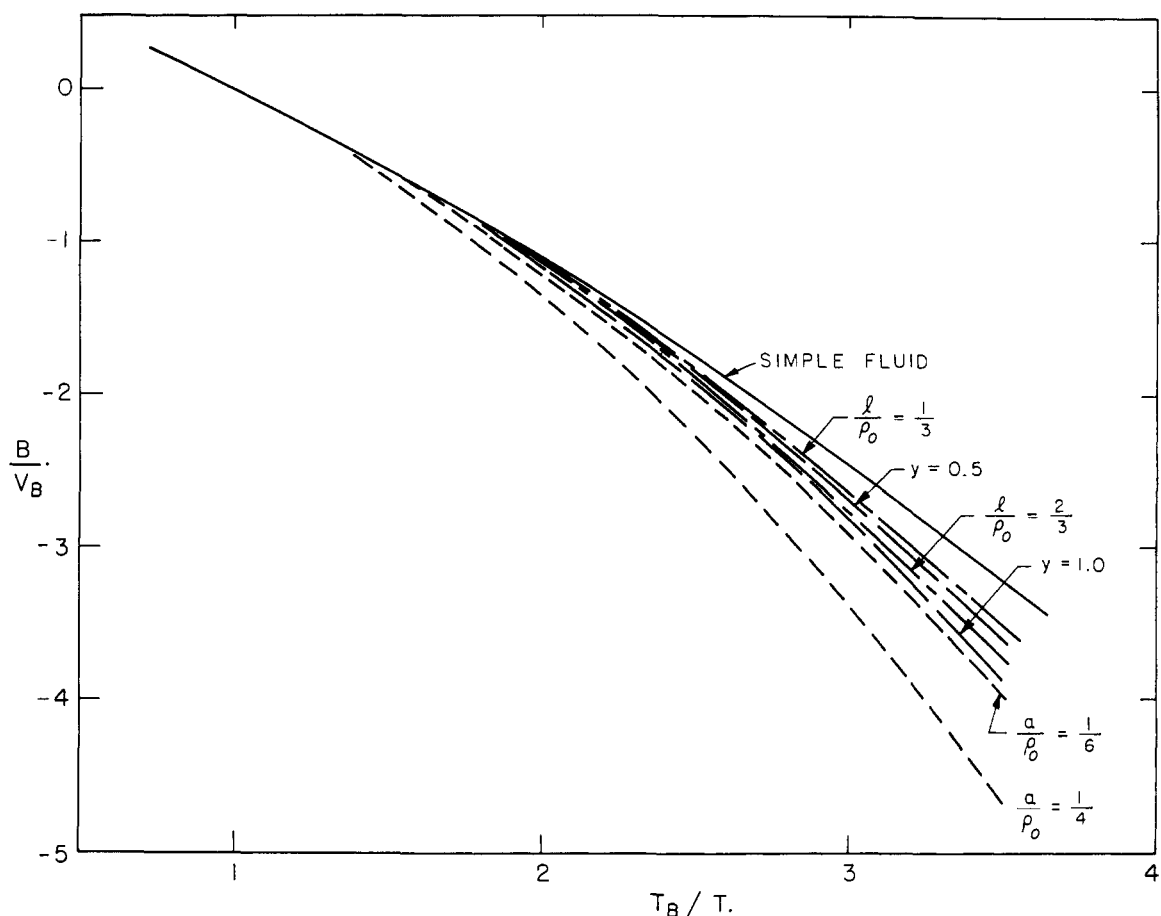


Fig. 4.—Reduced second virial coefficients for several models.

where the reduced virial at $T_B/T = 3.5$ is plotted against the value at $T_B/T = 2$ for various models. It is apparent that the points for linear and spherical core molecules fall on the same curve within very small limits. The points for dipolar molecules are on a definitely different curve. However, y can have values up to about 0.7 before a 1% difference is exceeded at each temperature.

The available experimental second virial coefficients were examined in terms of these effects. While the data generally conformed to these families of theoretical curves, the experimental accuracy is not high enough to allow precise determinations of the parameters related to the core or the dipole moment. Kihara assumed reasonable cores and obtained agreement with the experimental virial coefficients—a result consistent with this conclusion. For dipolar molecules meaningful values of the parameter y can be obtained by use of the dipole moment value in addition to the virial coefficient data provided the latter cover a wide enough temperature range. Rowlinson¹⁵ has made such analyses in a number of cases. For example he finds for ammonia values yielding $y = 4$ which is far above the limit of 0.7 for conformity to our scheme within 1%. By contrast the y value for chloroform is only 0.04 and that for ethyl chloride is 0.16.

In conclusion, we have shown that for non-polar molecules of various shapes and for molecules with modest dipoles ($y \leq 0.7$), the theoretical second

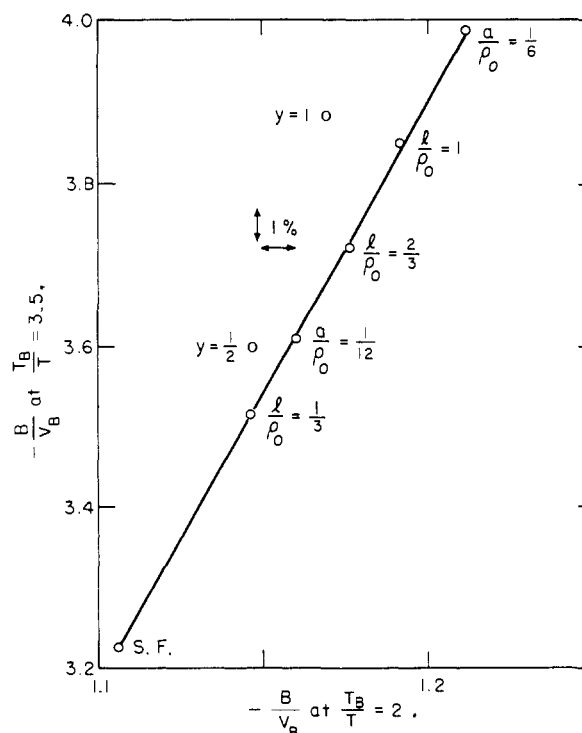


Fig. 5.—Deviation plot of the data of Fig. 4. Deviations from the simple fluid (S.F.) at $(T_B/T) = 3.5$ and 2, respectively, are compared.

virial coefficients conform within about 1% to the theory we are proposing for volumetric and thermodynamic properties generally. In later papers we

shall test this scheme against various experimental data and present general tables.

BERKELEY, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Volumetric and Thermodynamic Properties of Fluids. II. Compressibility Factor, Vapor Pressure and Entropy of Vaporization¹

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RECEIVED JANUARY 21, 1955

The theoretical considerations of Part I suggested that the compressibility factor of a normal liquid in either gas or liquid state should be expressible as a function of just one parameter in addition to the reduced temperature and reduced pressure. The additional parameter is defined in terms of the vapor pressure at $T_r = 0.7$. This third parameter is required because the intermolecular force in complex molecules is a sum of interactions between various parts of the molecules—not just their centers—hence the name *acentric factor* is suggested. The theory requires that any group of substances with equal values of the acentric factor should conform among themselves to the principle of corresponding states. This result is verified with relatively high accuracy. While a completely analytical expression for the compressibility factor was not obtained, power series expressions in the acentric factor proved satisfactory and the coefficients are tabulated for a wide range of reduced temperature and pressure. The reduced vapor pressure and the entropy of vaporization are also treated similarly. Agreement is obtained to 0.5% over most regions with maximum deviations of about 2%.

A general introduction together with discussion of the theoretical basis for the correlation scheme has been presented in Part I of this series.³ Although exact theory was available only for the second virial coefficient, those results together with general arguments indicated that a three parameter correlation might well yield at least a factor of ten greater accuracy than is obtained from the simple hypothesis of corresponding states. As was indicated in Part I, we take two critical constants for two of our three independent parameters for each substance. The critical temperature is readily selected as the first parameter which characterizes the intermolecular interaction energy.

While the critical volume would be the simple measure related to intermolecular distance, it is unsatisfactory from the empirical viewpoint. The differential compressibility is infinite at the critical point. Consequently the critical volume is not directly measureable with any accuracy. The values commonly given are extrapolated. The critical pressure is a much more accurately determinable quantity and it suffices just as well for correlation purposes. Hence we choose the critical pressure as our second parameter.

The third parameter is to measure the deviation of the intermolecular potential from that of a simple fluid. An important deviation arises from the fact that the sum of the inverse sixth power terms applying to the various portions of a pair of complex molecules cannot be replaced by a single inverse sixth power term in the distance between molecular centers. Since these forces between non-central portions of the molecules must be considered, the term *acentric factor* is suggested.

The most convenient empirical quantity is the reduced vapor pressure at a point well removed

from the critical point. This in effect gives the slope of the vapor pressure curve, see Fig. 2, Part I. For a *simple fluid*³ (e.g., A, Kr, Xe, CH₄) the reduced vapor pressure is almost precisely 0.1 at a reduced temperature of 0.7. This point is well removed from the critical yet above the melting point for almost all substances. Consequently it is convenient to take 0.7 as our standard value of reduced temperature for the determination of the *acentric factor* which we define as

$$\omega = -\log P_r - 1.000$$

with P_r the reduced vapor pressure (P/P_c) at $T_r = 0.7$.

The slope of the vapor pressure curve is, of course, closely related to the entropy of vaporization. Thus we may regard our acentric factor as a measure of the increase in the entropy of vaporization over that of a simple fluid. It was also shown in Part I that the acentric factor would depend upon the core radius of a globular molecule, the length of an elongated molecule, or the dipole moment of a slightly polar molecule.

Table I lists the essential parameters for the various substances which were given substantial consideration in our correlations. On the basis of the arguments in Part I it was not expected that the highly polar molecules, ammonia and water, would conform to our scheme. Points for these substances are included on some graphs to illustrate the magnitude of the deviations; however, these points were given no weight in preparing the final tables. The references to Table I include the sources of data for the respective substances for the other tables of this paper.⁴

Compressibility Factor.—The compressibility factor was interpolated graphically to even values

(1) This research was a part of the program of Research Project 50 of the American Petroleum Institute.

(2) A portion of this paper is abstracted from the Ph.D. Dissertation of David Z. Lippmann, University of California, 1953.

(3) K. S. Pitzer, *THIS JOURNAL*, **77**, 3427 (1955).

(4) In addition to the substances listed in Table I, supplementary use was made of data for *n*-hexane in certain areas. The sources are S. Young, *Scient. Proc. Roy. Dub. Soc.*, New Series **12**, 374 (1909-1910); E. A. Kelso with W. A. Felsing, *Ind. Eng. Chem.*, **34**, 161 (1942); E. A. Kelso with W. A. Felsing, *THIS JOURNAL*, **62**, 3132 (1940).