DIRECT METHOD FOR DETERMINING PARAMETERS IN INTERMOLECULAR PAIR POTENTIALS FROM PVT DATA AND FROM THERMODYNAMIC PROPERTIES OF DILUTE GASES. I. CALCULATION OF PARAMETERS FROM *PVT* DATA

A.MALIJEVSKÝ, P.VOŇKA and J.P.NOVÁK

Department of Physical Chemistry
Institute of Chemical Technology, 166 28 Prague 6

Received May 18th, 1972

A new method was proposed for calculating parameters in intermolecular pair potentials. The method uses *PVT* data which can be represented by the virial expansion with the second and third virial coefficients. The procedure is tested on the Lennard–Jones 12–6 potential and *PVT* data of argon. The results are discussed and existing methods for calculating the parameters are criticized.

The use of statistical thermodynamics relations for calculating thermodynamic properties stipulates knowledge of interactions among the particles in the system. Potentials used for the description of intermolecular interaction are empirical or semiempirical functions of mutual distances and orientations of the molecules and contain therefore adjustable parameters. When statistical thermodynamics calculations are applied to real systems, numerical values of these parameters must be known, often with high accuracy. Intermolecular potential parameters are determined most often from low-density *PVT* data of gases represented by second virial coefficients. However, this currently used method is not suitable with regard to the desired accuracy. We propose a modification of this method which has been rid of its several drawbacks and which uses available experimental material on the properties of gases to a much larger extent.

In the first part of our work we demonstrate the method on the Lennard–Jones 12 – 6 potential and on *PVT* data of argon which can be described by the virial expansion with the second and third virial coefficients. In the second part, further thermodynamic data will be used in the calculations and these will be extended to more substances.

THEORETICAL

Critique of the Method for Determining Interaction Parameters from Second Virial Coefficients.

The volumetric behaviour of gases may be described by the virial expansion

$$z = 1 + \sum_{i=2}^{\infty} B_i d^{i-1}\,, \tag{1}$$

where z is the compressibility factor, B_i the i-th virial coefficient, and d molar density. The virial coefficients are known temperature functions which include intermolecular potentials. For example, it holds for the second and third virial coefficients[1]

$$B_2 = -\,2\pi N \int_0^{\infty} f(r)\, r^2\, \mathrm{d}r\,, \tag{2}$$

$$B_3 = -8\pi^2 N^2 \int_0^{\infty} \int_0^{r_1} \int_{r_1 - r_2}^{r_2} f(r_1) f(r_2) f(r_3)\, r_1 r_2 r_3\, \mathrm{d}r_3\, \mathrm{d}r_2\, \mathrm{d}r_1\,, \tag{3}$$

where $f(r) = \exp\left[-u(r)/kT\right] - 1$, N is Avogadro's constant, k Boltzmann's constant, Tabsolute temperature and $u(r)$ is the potential energy (potential) of a molecular pair whose centres are separated by a distance r (for simplicity we write Eqs (*2*) and (*3*) for an angularly independent potential).

The currently used method for determing parameters in a pair potential $u(r)$ may be divided into two steps: *1*) Calculation of values of the second virial coefficient from experimental *PVT* data. Usually it is performed by extrapolating from the relation

$$B_2 = \lim_{d \to 0} (z - 1)/d\,. \tag{4}$$

Other methods for calculating B_2, *e.g.* a minimization of squares of deviations of the expression on the rhs of Eq. (*1*) from experimental z values, are less justifiable. *2*) Calculation of the interaction parameters from "experimental" B_2 values. Generally the function

$$F_B = \sum_j \left\{ B_2(T_j)_{\exp} - 2\pi N \int_0^{\infty} \left[1 - \exp\left(-u(r)/kT_j\right)\right] r^2\, \mathrm{d}r \right\}^2 \tag{5}$$

is minimized with respect to parameters contained in $u(r)$.

Error in numerical values of the parameters determined by the classical method is estimated[2] to 2%, which is insufficient for some purposes. The main disadvantage of the method consists in the fact that it does not make use of all available experimental material on dilute gases. It is harmful to disregard the large part of the information yielded by experiments, especially in connection with the known fact that the second virial coefficients are very little sensitive to values of the interaction parameters.

At low temperatures, the sensitivity of B_2 is higher, however, few good experimental data are found in this region.

To increase the accuracy of the parameters, it would be basically possible to minimize simultaneously the deviations in both the second and third virial coefficients. The accuracy of third virial coefficients obtained from experimental data is, however, so low that such an experiment would most probably collapse. Fig. 1 may serve as an illustrative example of the scatter in "experimental" values of B_3.

A further disadvantage of the cited method of the calculation of the parameters consists in its division into two steps. The second virial coefficients are laden with a larger error than experimental data from which they were determined. As will be shown later on, it is possible to avoid the preliminary determination of B_2 and thus both to increase the accuracy and to decrease the laboriousness of the whole procedure.

Principle of the Proposed Method

The interaction parameters may be obtained by minimizing the function

$$F_n(a_1, a_2, \ldots, a_p) = \sum_j V_j[z_j - 1 - \sum_{i=2}^{n} B_i(a_1, a_2, \ldots, a_p, T_j)\, d_j^{i-1}]^2\,, \qquad (6)$$

with respect to the interaction parameters $a_1, a_2, \ldots, a_p$. For B_i it is necessary to substitute statistical thermodynamics expressions containing temperature and through $u(r)$ also the parameters $a_1, a_2, \ldots, a_p$[9]. The summation is performed over all experimental points (z_j, T_j, d_j). The symbol V_j stands for the weight of the j-th point which has been chosen so as the distances of the experimental points (z_j, T_j, d_j) in relation (*6*) from the $z = z(T, d)$ surface defined by Eq. (*1*) be minimized. For the weight defined in this manner, it is possible to deduce easily from geometric considerations an approximative expression (see Appendix)

$$V_j = [1 + (\partial z/\partial T)_j^2 + (\partial z/\partial d)_j^2]^{-1}\,. \qquad (7)$$

In relation (*6*) we use the virial expansion (*1*) with first n virial coefficients. Therefore it is impossible to employ during the calculations data requiring $n + 1$ and/or more terms in Eq. (*1*). As we cannot assess the behaviour of the residue of series (*1*), *i.e.* of the sum B_{i+1} from $i = n$ to ∞, we use as a test for the choice of acceptable experimental points the inequality

$$|B_{n+1}(a_1, a_2, \ldots, a_p, T)|\, d^n < \delta\,, \qquad (8)$$

where δ is an estimate of the average scatter in experimental values of the compressibility factor. This test fails for B_{n+1} approaching zero. In this case it is necessary to use

$$B_{n+2}(a_1, a_2, \ldots, a_p, T)\, d^{n+1} < \delta\,,$$

supposing that $B_{n+2} \neq 0$.

In our calculations we have employed relation (*6*) for $n = 2$ and $n = 3$. For $n = 3$, the coefficient B_3 was calculated from relation (*3*). However, this relation holds only for a pairwise additive intermolecular energy. It is well-known that this condition for the intermolecular interaction is not fully satisfied. If we use relation (*3*) in spite of this fact, we calculate some effective values of the pair potential parameters. Because the validity of the pairwise additivity is assumed in most molecular theories of the fluid state, our calculated effective parameters are just those which are usually required.

RESULTS

All calculations were performed for the Lennard–Jones[10] 12–6 potential

$$u(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6] \tag{9}$$

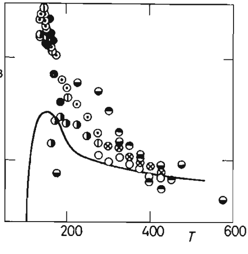

FIG. 1

Values of the Third Virial Coefficient of Argon[3]

● Ref.[4], ⊖ ref.[5], ◓ ref.[6], ⊗, ○ ref.[7], ◑, ⊙ ref.[8], ⦶ ref.[9], — course of the third virial coefficient calculated from the Lennard–Jones 12–6 potential with parameters $\varepsilon/k = 118{\cdot}6$ K, $\sigma = 3{\cdot}405$ Å; for the calculation of values denoted by ⊗, ⊙, only low-density data were used; C in $\text{cm}^6\,\text{mol}^{-2}$, T in K.

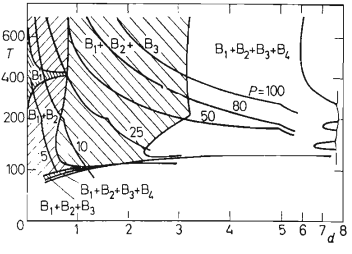

FIG. 2

Regions of Validity of the Virial Equation for Deviations in the Compressibility Factor of Argon Lower than 0·0005

The regions were determined for the Lennard–Jones 12–6 potential $\varepsilon/k = 118{\cdot}6$ K, $\sigma = 3{\cdot}405$ Å. The values of the virial coefficients are from ref.[19,20]. T in K, d in mol dm^{-3}.

and for *PVT* data of argon. We have employed the data by Holborn and coworkers[5] (temperature range 173–673 K); Whalley and coworkers[11,12] (173–873 K); Michels and coworkers[7,8] (133–423 K); Rogovajova and coworkers[13] (190–248 K). The following authors have published only the values of the second virial coefficients: Fender and coworkers[14] (84–124 K); Weir and coworkers[15] (80–190 K); Byrne and coworkers[16] (84–271 K). From these data we have calculated corresponding values of the compressibility factor for selected densities satisfying inequality (*8*). The quantity δ in inequality (*8*) necessary for the selection of acceptable data was taken equal to $5 \cdot 10^{-4}$ taking into account the scatter in the values of the compressibility factor reported by different authors. Data acceptable for the calculations lie in the temperature range 80–873 K. The density range is determined by inequality (*8*).

In Fig. 2 lines are drawn separating temperature and density regions in which the virial expansion (*1*) may be used with first and second, first to third, and first to fourth coefficients. The errors in the compressibility factor do not exceed the value of 0·0005 inside these regions. Several isobars are also shown for a quicker orientation in the figure.

The minimum in function F_n defined by relation (*6*) was being searched for by a simple grid search method. Virial coefficients necessary for the calculations may be determined from Eqs (*2*) and (*3*). However, the numerical integration would be very time-consuming. Therefore we have calculated B_2 from an expansion developed by Jones[10], which can be written for a Lennard–Jones 12–6 potential in the form

$$B_2 = b_0 \sum_{j=0}^{\infty} b_{(j)}(\varepsilon/kT)^{(2j+1)/4}\,, \tag{10}$$

with $b_0 = 2/3\pi N\sigma^3$. The coefficients $b_{(j)}$ ($j = 0, 1, \ldots, 40$) were taken from a monograph by Hirschfelder and coworkers[1].

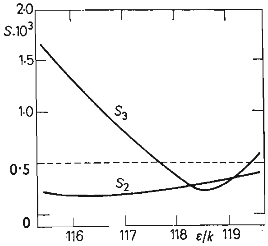

FIG. 3

Dependence of the Standard Deviations S_2 and S_3 on ε/k

Kihara[17] obtained for B_3 a similar expansion. By comparison with B_3 values determined by numerically integrating[18] Eq. (*3*) and with those tabulated by Hirschfelder and coworkers[1] we have found out that the numerical values of the coefficients in the Kihara's expansion are not sufficiently accurate for our purposes. From that reasons we have proposed for B_3 an empiric expansion

$$B_3 = b_0^2 \sum_{i=1}^{r} c_i (\varepsilon/kT)^{i/2}\,, \tag{11}$$

whose coefficients c_i were determined by minimizing squares of deviations from tabulated B_3 values. For a choice $r = 10$ we have obtained the following coefficients

$c_1 = 1{\cdot}7499$ $c_2 = -\ 3{\cdot}9020$ $c_3 = 10{\cdot}154$ $c_4 = -\ 52{\cdot}116$
$c_5 = 188{\cdot}62$ $c_6 = -410{\cdot}30$ $c_7 = 560{\cdot}84$ $c_8 = -471{\cdot}13$
$c_9 = 223{\cdot}38$ $c_{10} = -\ 46{\cdot}861$

The standard deviation from the tabulated values was $8{\cdot}7 \,.\, 10^{-5}$ and the maximum deviation $3{\cdot}3 \,.\, 10^{-4}$ whereas the authors[18] give a maximum error of $2 \,.\, 10^{-4}$ for their tabulated values.

By choosing $n = 3$ in Eq. (*6*) it was necessary for the selection of data with the help of inequality (*8*) to know the temperature dependence of the fourth virial coefficient. The values of the fourth virial coefficient for a Lennard–Jones 12–6 potential were calculated by Barker and coworkers[19,20]. The temperature dependence of B_4 was obtained by correlating these values with a 3-constant expansion of type (*11*). Although the accuracy of this correlation was low, it was fully sufficient for the selection among the data by inequality (*8*).

The values of the interaction parameters ε, σ have been determined by minimizing Eq. (*6*) for $n = 2$ and $n = 3$. At $n = 2$, *i.e.* for data which can be described by the virial expansion with the second virial coefficient, 158 literature data points (z_j, T_j, d_j) satisfying inequality (*8*) have been used. For the values of the parameters we have obtained $\varepsilon/k = 116{\cdot}1$ K and $\sigma = 3{\cdot}456$ Å. The standard deviation has been determined as $S_2 = \sqrt{(F_2/\sum V_j)} = 1{\cdot}8 \,.\, 10^{-4}$.

At $n = 3$, *i.e.* for data which can be described by Eq. (*1*) with second and third virial coefficients, 325 points satisfying inequality (*8*) were found. The following values have been obtained: $\varepsilon/k = 118{\cdot}6$ K, $\sigma = 3{\cdot}405$ Å, and the standard deviation $S_3 = \sqrt{(F_3/\sum V_j)} = 2{\cdot}2 \,.\, 10^{-4}$.

Occasionally, statements may be found that data on the third virial coefficient are not represented with the Lennard–Jones 12–6 potential with sufficient accuracy. We do not consider this as well established because the standard deviations S_2 and S_3 are lower than the estimated value of the scatter in the experimental values of the compressibility factor ($\delta = 5 \cdot 10^{-4}$); these data cannot be therefore used for an estimate of the extent to which the Lennard–Jones potential described interactions between the molecules. It is obvious from Fig. 1 that discrepances between the calculated B_3 values and those calculated from the experimental data are rather due to inaccuracy of the "experimental" B_3 values.

For comparison we give here also value of ε and σ obtained from viscosity data: $\varepsilon/k = 116$ K; $\sigma = 3{\cdot}465$ Å, and from "experimental" second virial coefficients: $\varepsilon/k = 119{\cdot}8$ K; $\sigma = 3{\cdot}405$ Å as published by Hirschfelder and coworkers[1]. The remarkable coincidence between the values obtained from the viscosity measurements and our values for $n = 2$ and good agreement between the constants determined from the second virial coefficients and our values for $n = 3$ are fortuitous. It follows from the subsequent discussion that all four pairs of values of ε, σ are equivalent with regard to the accuracy of the experimental data.

DISCUSSION

Two variants were tried for the calculation of ε and σ from *PVT* data of argon. For the first one ($n = 2$), the minimized function F_2 is very little sensitive to the values of the parameters similarly as B_2 in the classical procedure. This fact is documented by a considerable flatness of the standard deviation S_2 in the vicinity of the minimum. We shall examine the flatness of the function $S_2 = S_2(\varepsilon, \sigma)$ by the following method: in the vicinity of the minimum we choose a value of ε and search for such σ which would minimize S_2. The function $S_2 = S_2[\varepsilon, \sigma(\varepsilon)]$ constructed int this way is plotted in Fig. 3 in dependence on ε/k. We can change ε/k in the vicinity of the minimum in the range $111-121$ K and we would still find such σ that the standard deviation S_2 would be lower than the estimated scatter in the experimental values of the compressibility factor. The corresponding σ is in the range $3{\cdot}35-3{\cdot}55$ Å. Calculated values of ε and σ are thus laden with a 5% error. With regard to the foregoing analysis we consider the usually reported 98% accuracy in determining the parameters from the second virial coefficients as exaggerated.

By including experimental data which can be described by the virial expansion with the third virial coefficient, the accuracy of the calculation of the parameters ε and σ has been increased considerably. This may be seen from Fig. 3, where the dependence of $S_2 = S_2[\varepsilon, \sigma(\varepsilon)]$ on ε/k is plotted simultaneously with the function $S_3 = S_3[\varepsilon, \sigma(\varepsilon)]$. The function S_3 is substantially steeper in the neighbourhood of the minimum. The scatter in the constants has decreased to $117{\cdot}5-119{\cdot}5$ in ε/k and $3{\cdot}35-3{\cdot}45$ in σ, *i.e.* the error of constants dropped to 1%.

Even a 99% accuracy is not sufficient for some applications. By including further terms of the virial expansion into the calculations, *i.e.* by choosing $n = 4, 5, \ldots$ in Eq. (*6*), we would probably obtain constantly improving results. Good experimental data are usually plentiful even at higher densities. However, we cannot follow this way too far, as the calculation of higher virial coefficients from statistical thermodynamics relations would become unacceptably lengthy and laborious. It seems to us much more hopeful to use experimental data on enthalpy, heat capacity, Joule–Thomson coefficient and sound velocity together with *PVT* data of rarefied gases. We are going to report calculations employing these data in Part II of this work.

APPENDIX

We shall elucidate the derivation of Eq. (*7*) on a simple example. Let (x_j, y_j) $j = 1, 2, \ldots, n$ be n points through which a curve $y = f(c_1, c_2, x)$ is to pass, where c_1 and c_2 are adjustable parameters. If we proceeded by the classical method of least squares, we would minimize the deviation Δy between experimental and calculated functional values, whereas a minimization of Δz values, *i.e.* of distances between experimental points and the curve $y = f(c_1, c_2, x)$, is more correct. It may be proved easily that

$$(\Delta z)^2 \approx (\Delta y)^2 \, [1 + (\mathrm{d}f/\mathrm{d}x)^2]^{-1} \, . \tag{D-1}$$

From this it follows

$$\sum_{j=1}^{n} (\Delta z_j)^2 = \sum_{j=1}^{n} V_j (\Delta y_j)^2 \, , \tag{D-2}$$

where

$$V_j \approx [1 + (\mathrm{d}f/\mathrm{d}x)^2_{x=x_j}]^{-1} \, . \tag{D-3}$$

The proposed procedure may be simply extended to functions

$$y = f(c_1, c_2, \ldots, c_p, x^{(1)}, x^{(2)}, \ldots, x^{(k)}) \, . \tag{D-4}$$

In this case, the relation analogical to (*D-3*) has the form of

$$V_j = [1 + \sum_{i=1}^{k} (\partial f/\partial x^{(i)})^2_{x=x_j}]^{-1} \, . \tag{D-5}$$

REFERENCES

1. Hirschfelder J. O., Curtiss C. F., Bird R. B.: *Molecular Theory of Gases and Liquids.* Wiley, New York 1954.
2. Rowlinson J. S.: *Liquids and Liquid Mixtures.* Butterworths, London 1969.
3. Dymond J. H., Smith E. B.: *The Virial Coefficients of Gases,* Clarendon Press, Oxford 1969.
4. Kamerlingh-Onnes H., Cromelin C. A.: Communs. Phys. Lab. Univ. Leiden *1910,* 118.
5. Holborn L., Otto J.: Z. Physik *33,* 1 (1925).
6. Tanner C. C.: Mason I.: Proc. Roy. Soc. (London) *A 126,* 268 (1930).
7. Michels A., Wijker H., Wijker H.: Physica *15,* 627 (1949).
8. Michels A., Levelt J. M., de Graaff W.: Physica *24,* 659 (1958).
9. Michels A., Levelt J. M., Wolker G. J.: Physica *24,* 769 (1958).
   Crain R. W., Sonntag R. E.: Advan. Cryogen. Eng. *11,* 379 (1966).
10. Jones J. E.: Proc. Roy. Soc. (London) *A 106,* 463 (1924).

11. Whalley E., Lupien Y., Schneider W. G.: Can. J. Chem. *31*, 722 (1953): Can. J. Technol. *33*, 111 (1955).
12. Landolt-Börnstein: *Zahlenwerte und Funktionen, Eigenschaften der Materie in ihren Aggregatzuständen*, I. *Mechanisch-thermische Zustandgrössen*, 6. Aufl., Bd. II, 1. Springer, Berlin 1971.
13. Rogovaja I. A., Kaganer M. G.: Ž. Fiz. Chim. *35*, 2135 (1961).
14. Fender B. E., Halsey G. D.: J. Chem. Phys. *36*, 1881 (1962).
15. Weir R. D., Wynn Jones I., Rowlinson J. S., Saville G.: Trans. Faraday Soc. *63*, 1320 (1967).
16. Byrne M. A., Jones M. R., Staveley L. A. K.: Trans. Faraday Soc. *64*, 1747 (1968).
17. Kihara T.: Rev. Mod. Phys. 25 (*4*), 831 (1953).
18. Bird R., Spotz R. L., Hirschfelder J. O.: J. Chem. Phys. *18*, 1395 (1950).
19. Barker J. A., Monaghan J. J.: J. Chem. Phys. *36*, 2564 (1962).
20. Barker J. A., Leonard J. P., Pompe A.: J. Chem. Phys. *44*, 4206 (1966).

Translated by K. Hlavatý.