Molecular Physics, 1986, Vol. 58, No. 6, 1137–1148

Response of second virial coefficients and intermolecular potential parameters to the adsorption and impurity perturbations

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(*Received 23 January 1986 ; accepted 26 March 1986*)

A common method for the estimation of uncertainties introduced by surface and impurity effects into experimental measurements of virial coefficients is described. The sign and the amplitude of the second virial coefficient response to perturbation caused by adsorption of molecules on the internal surface of the vessel have been determined. It has been shown that the magnitude of the second virial coefficient distortion depends on such competing factors as adsorption–impurity perturbation parameter, mixture composition which has been corrected taking into account this perturbation, and the nature of the impurity expressed in terms of its second virial coefficient and of the solvent–impurity cross second virial coefficient. The character of the Lennard-Jones 12-6 potential parameters perturbation, caused by the adsorption–impurity effects, is determined using second virial coefficient data inversion technique. Numerical estimates are made for nitrogen, helium, argon, xenon, their binary mixtures, and also for krypton–sulphur hexafluoride gaseous mixtures.

1. Introduction

In recent years experimental thermophysical data for gases and gaseous mixtures have been used to obtain information about the intermolecular potential energy functions. Original iterative methods have been devised by which transport properties [1] and second virial coefficient [1, 2] data may be inverted to give the potential energy function. Smith and coworkers [3, 4] have recently developed the new iterative procedure which enables the full potential energy functions to be obtained with considerable accuracy from the virial equation of state

$$z = PV/RT = 1 + \sum_{n=1}^{\infty} B_{n+1}(T)/V^n. \tag{1}$$

In (1) z is the compressibility factor, P is the pressure, V is the molar volume, R is the gas constant, T is the temperature, and $B_{n+1}(T)$ are the corresponding virial coefficients.

As a rule [5], the virial coefficients are calculated by the computational method of Michels or determined by extrapolation of experimental gaseous isotherms to zero density in Keyes's coordinates for $n = 1$

$$B_2(T) = \lim_{V^{-1}\to 0} [V(z-1)]_T, \tag{2}$$

and for $n \geqslant 2$:

$$B_{n+1}(T) = \lim_{V^{-1}\to 0} \left\{ V^n \left[z - 1 - \sum_{n=2}^{n} B_n(T)/V^{n-1} \right] \right\}_T, \quad n \geqslant 2. \tag{2'}$$

The important advantage of the virial equation of state of gases lies in that fact that there is a direct connection between virial coefficients and intermolecular forces. In some cases, on the basis of good quality data, this connection allows us to estimate the parameters of the model potential energy function chosen, and thereby to calculate a large number of thermophysical properties of gaseous systems [6]. On the other hand, (1) enables us to interpret the deviation from ideality of any equilibrium property of nonideal gaseous system being studied in terms of intermolecular interactions. Clearly, definitive information about the intermolecular parameters can only be obtained from virial coefficient and its temperature derivative measurements that meet the criteria of high precision and are free from systematic errors. Recently, the investigation of finite size effects in a thermodynamic system have been made and a general approach to the problem of the finite-size corrections to the compressibility factor, the second virial coefficient and its temperature derivative have been provided for spherical conditions [7, 8]. However, no account is taken in these studies of interactions of molecules with a real boundary of a system, i.e. with a wall of a vessel. If such an interaction does not take place the finiteness effects are significant only in systems with a few dozen of particles. One of us has shown [9, 10] that the configuration of the thermodynamic state surface of real gaseous macroscopic system may have the essential experimental distortion caused by surfaces and impurities effects. This is mostly exposed in the range of parameters near the first-order phase transition points. These effects shift the transition points and the values of displacement cannot be neglected. Exclusion of the range of pretransitional phenomena, however, allows the experimental data obtained in different laboratories to be in a good agreement [11]. Virial coefficient measurements, for example [12, 13], showed that the results of Butcher and Dadson for carbon dioxide obtained at low pressures ($P \leqslant 0{\cdot}2$ MPa) and the results of Michels and coworkers obtained at high pressures reveal a discrepancy exceeding the uncertainty of experimental data. Certain difficulties in using equation (2) for precise determination of helium and of nitrogen second virial coefficients from P, V, T-measurements at very low pressures were noted in [14]. It was observed that the isotherms both for helium and for nitrogen varied in a nonlinear manner in Keyes's coordinates at sufficiently large molar volumes of gases. We assume that the above anomalies and differences between the virial coefficients derived from low pressure experimental data as well as in the case of high pressure measurements may be seen as resulting from adsorption encounted in the traditional volumetric method, impurity effects, and the selective adsorption of major component or of impurity cross-effects. Therefore it is necessary to take into account the sign and the amplitude of the intermolecular potential function parameters response to perturbations introduced by these heterogeneous external effects into results of second virial coefficients measurements.

Let us consider the role of each of these perturbation factors under typical conditions of volumetric experiment in consecutive order.

2. THE METHOD

We now consider the case in which N gaseous molecules are contained in a vessel of constant volume V_0 at a given temperature and pressure. The number of molecules adsorbed on the minimum geometrical inside surface area $S_0 \sim V_0^{2/3}$ of the vessel we denote as N_a ($N_a \ll N$). Speaking about the geometrical surface area we take into account that inner vessel walls even very carefully polished have some roughness. In practice they exclude mirror reflection of falling molecules: for gaseous hydrogen it was shown [15] that at room temperature and roughness height $\leqslant 10^{-7}$ m reflection occurred only for those molecules which had an angle of incidence $>89° 56'$. According to [15] the value of $N_a/V_0^{2/3}$ is defined as the product of the molecular flow on the wall

$$\bar{n} = 8{\cdot}33 \times 10^{22} P(MT)^{1/2} \tag{3}$$

and the average settled lifetime of molecules on the solid surface

$$\tau = \tau_0 \exp (Q_a/RT). \tag{4}$$

In the above equations $\bar{n}$ is the number of molecules striking upon 1 m^2 of the surface in 1 s, P is pressure in Pa, M is the molar mass of investigated gas in kg mol^{-1}, $\tau_0 \simeq 10^{-13}$ s and represents the reverse value of oscillation frequency of solid surface atoms, and Q_a is the heat of adsorption in J mol^{-1}. Then

$$N_a = 6{\cdot}93 \times 10^{10} V_0^{2/3} \left[1 + \sum_{n=1}^{\infty} B_{n+1}(T)/V^n \right] (T/M)^{1/2} \exp (Q_a/RT)/V. \tag{5}$$

Due to adsorption the initial number of gaseous molecules in the volume V_0 changes and becomes equal to the value defined by

$$\Delta N = N - N_a = (N_A V_0 - N_a V)/V, \tag{6}$$

where N_A is Avogadro number. The value of ΔN may be interpreted as an increase of the molar volume of gaseous phase:

$$\Delta N = N_A V_0/(V + \Delta V), \quad \Delta V \geqslant 0, \tag{6$'$}$$

whence

$$\Delta V = N_a V/(N - N_a), \tag{7}$$

and under the conditions of $N_a \ll N$, $z - 1 \ll 1$ which correspond to sufficiently large volume (for the virial equation truncated after the second virial coefficient the last condition is equivalent to $B_2(T) \ll V$)

$$\Delta V \simeq N_a V/N = tV, \tag{7$'$}$$

where t can be called as the adsorption perturbation parameter and determined by

$$t = A(T/M)^{1/2} \exp (Q_a/RT)/V_0^{1/3}. \tag{8}$$

In equation (8) $A = 1{\cdot}15 \times 10^{-13}$. Then the molar volume perturbed by adsorption may be defined as

$$V^* = (1 + t)V, \quad 1 \gg t > 0. \tag{9}$$

Comparing equation (1) with that for perturbed system at the same temperature

$$z^* = P^* V^*/RT = 1 + \sum_{n=1}^{\infty} B_{n+1}(T)/V^{*n} = 1 + \sum_{n=1}^{\infty} B^*_{n+1}(T)/V^n, \tag{1$'$}$$

we obtain the correlation between compressibility factors determined taking into account adsorption perturbation or not considering it

$$\Delta z = z^* - z = -\sum_{n=1}^{\infty} [1 - (1 + t)^{-n}] B_{n+1}(T)/V^n. \tag{10}$$

In the same manner we can obtain the correlation for virial coefficients

$$B^*_{n+1}(T) = B_{n+1}(T)/(1 + t)^n. \tag{11}$$

In the case of the virial equation of state truncated after the second term ($n = 1$) equation (10) is reduced to

$$\Delta z_{n=1} \simeq -tB_2(T)/V. \tag{10'}$$

Equation (10′) yields the next (figure 1) qualitative results:

$$z^* = \begin{cases} \leqslant z, & T > T_B, \\ = z, & T = T_B, \\ \geqslant z, & T < T_B, \end{cases} \tag{12}$$

where T_B is Boyle temperature. According to the same approximation ($n = 1$) and using equation (11) we find that the adsorption effects in the individual gaseous system make the curve of the second virial coefficient temperature dependence turn clockwise round the Boyle temperature value being a pole (figure 2).

The results obtained from equation (11) show that positive ($V_1(z_1 - 1) - V_2(z_2 - 1) > 0$ at $V_1 > V_2$ and $T = \text{const.}$) deviations of helium second virial coefficient at $T > T_B$ observed in [14] cannot be explained by adsorption of the gas being studied (experimental data for nitrogen [14] are in qualitative accordance with equation (11)). Moreover, it may be confirmed that in the case of helium deviations observed are caused by distortion effect which has significantly larger absolute value and opposite sign of system response in comparison with adsorption perturbation.

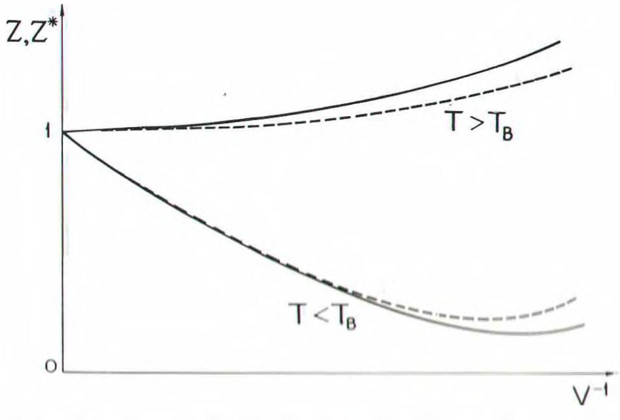

Figure 1. Influence of the adsorption perturbation upon pure gas isotherms at temperatures above and below Boyle temperature T_B. z is the compressibility factor, V is the molar volume. The solid lines: unperturbed system, the dashed lines: perturbed system.

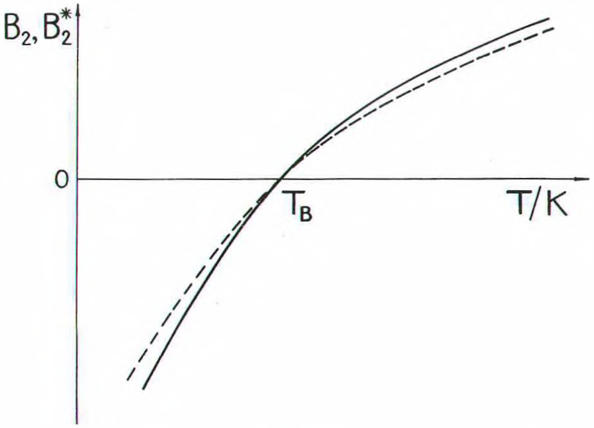

Figure 2. Influence of the adsorption perturbation upon temperature dependence of the second virial coefficient of pure gas. Key as for figure 1.

Further we consider a gaseous system which contains not only a pure component but also some impurities. A number of molecules adsorbed N_{am} may be given, like expression (5), by the equation

$$N_{\mathrm{am}} = \sum_{i=1}^{k} \bar{n}_i \tau_i , \tag{13}$$

where $\bar{n}$ and τ have been defined above in equations (3) and (4), the subscript i denotes a component in the k-component mixture, m designates the mixture. Following the above approximation such as slight nonideality of the system and weakly developed adsorption we can show that a number of molecules of the component i adsorbed may be represented by

$$N_{\mathrm{a}i} = A x_i^* T^{1/2} V_0^{2/3} \exp\,(Q_{\mathrm{a}i}/RT)/V_m M_i^{1/2}. \tag{14}$$

The last equation was obtained assuming that the system being studied obeys Dalton's law. Here x_i^* is the mixture composition (in mole fraction of the component i) perturbed by selective adsorption of components

$$x_i^* = (N_i - N_{\mathrm{a}i}) \Big/ \sum_{i=1}^{k} (N_i - N_{\mathrm{a}i}), \tag{15}$$

and it has been determined in an iterative procedure by substituting (14) in (15) with a first approximation

$$x_i = N_i \Big/ \sum_{i=1}^{k} N_i \tag{15'}$$

which is the initial mixture composition.

In the case of mixture adsorption–impurity perturbation parameter has the form analogous to (8)

$$t_m = \sum_{i=1}^{k} x_i^* t_i = A T^{1/2} V_0^{-1/3} \sum_{i=1}^{k} x_i^* \exp\,(Q_{\mathrm{a}i}/RT)/M_i^{1/2}. \tag{16}$$

Analysis of (16) reveals that impurity may increase or decrease the effects caused by adsorption of the major component. For example, for a binary gaseous mixture (the subscripts 1 and 2 designate the solvent and the impurity, respectively) $t_{1,2} > t_1$ when

$$\exp(Q_{a2}/RT)/M_2^{1/2} > \exp(Q_{a1}/RT)/M_1^{1/2},$$

that is equivalent to

$$Q_{a2} - Q_{a1} > RT \ln(M_2/M_1)/2.$$

Thus, the presence of impurity does not change, in principle, the picture of adsorption perturbation, in other words the relationship between the virial coefficients may be written like (11). However, the correlation between the theoretical second virial coefficients of the solvent $B_2^{(11)}(T)$ and that of the experimental perturbed by impurity $B_2^{(\exp)}(T)$ takes the following form

$$B_2^{(11)}(T) = x_1^{*-2}[(1 + t_m)B_2^{(\exp)}(T) - 2x_1^* x_2^* B_2^{(12)}(T) - x_2^{*2} B_2^{(22)}(T)]. \quad (17)$$

In the above $B_2^{(12)}(T)$ and $B_2^{(22)}(T)$ are the solvent–impurity cross second virial coefficient, and that of impurity, respectively. In this case the sign and the magnitude of the second virial coefficient response to adsorption and impurity perturbation should depend on such competing factors as adsorption–impurity perturbation parameter t_m, mixture composition x_i^* which has been corrected taking into account this perturbation, and the nature of the mixture expressed in terms of the second virial coefficients $B_2^{(12)}(T)$ and $B_2^{(22)}(T)$.

3. Results

Now we consider some numerical estimations of both adsorption and adsorption–impurity effects for helium, nitrogen, xenon, and their binary mixtures. Calculations were completed assuming that molecules have been adsorbed in a monomolecular layer manner because of relatively slight nonideality of the system (sufficiently low pressures and relatively high temperatures). This assumption also rests on the condition that the value of adsorption heat decreases sharply with layer number increasing [16]. For gases adsorbed on different metallic surfaces experimental heat of adsorption data are insufficient and are not in a good agreement. However, for the purpose of our estimations it is sufficient to know only an order of adsorption heat value. Heats of adsorption of xenon on nickel [17] and palladium [18] are equal to 29·3 and 42·7 kJ mol^{-1}, respectively. These values are about three times greater than that of xenon enthalpy of evaporation under normal pressure (12·6 kJ mol^{-1} [19]). The values of helium and nitrogen enthalpy of evaporation [19] were increased on the same scale to obtain necessary heats of adsorption of these gases.

Characteristic values of adsorption perturbation parameter $t_{r=0\cdot01}$ are listed in table 1. The estimations were made for the spherical vessel with radius 0·01 m. It can be seen that magnitude of perturbation effect is significantly dependent on heat of adsorption and temperature, and may reach considerable value even at relatively high temperature: for xenon 1·3 per cent at $T = 200$ K.

The results of the calculation of adsorption–impurity perturbation parameter t_m are summarized in table 2 and show that t_m value is strongly sensitive to the presence of impurity: addition of 0·01 per cent of xenon to pure helium leads to 300 times increase for t_m at $T = 200$ K.

Table 1. The adsorption perturbation parameters for pure gases. Q_a is heat of adsorption. $tV_0^{1/3}$ is some effective adsorption perturbation parameter for a vessel of arbitrary volume V_0. $t_{r=0\cdot01}$ is the adsorption perturbation parameter for the spherical vessel with radius 0·01 m.

	$Q_a^{(He)} = 1\cdot7\,kJ\,mol^{-1}$		$Q_a^{(N_2)} = 17\,kJ\,mol^{-1}$		$Q_a^{(Xe)} = 29\,kJ\,mol^{-1}$	
T/K	$tV_0^{1/3}/m$	$t_{r=0\cdot01}$	$tV_0^{1/3}/m$	$t_{r=0\cdot01}$	$tV_0^{1/3}/m$	$t_{r=0\cdot01}$
200	$7\cdot1 \times 10^{-11}$	$4\cdot4 \times 10^{-9}$	$3\cdot2 \times 10^{-7}$	$2\cdot0 \times 10^{-5}$	$2\cdot0 \times 10^{-4}$	$1\cdot3 \times 10^{-2}$
250	$6\cdot5 \times 10^{-11}$	$4\cdot0 \times 10^{-9}$	$4\cdot3 \times 10^{-8}$	$3\cdot0 \times 10^{-6}$	$3\cdot0 \times 10^{-5}$	$1\cdot9 \times 10^{-3}$
300	$6\cdot2 \times 10^{-11}$	$3\cdot9 \times 10^{-9}$	$1\cdot4 \times 10^{-8}$	$0\cdot9 \times 10^{-6}$	$7\cdot5 \times 10^{-7}$	$4\cdot7 \times 10^{-5}$
350	$6\cdot0 \times 10^{-11}$	$3\cdot8 \times 10^{-9}$	$5\cdot7 \times 10^{-9}$	$3\cdot6 \times 10^{-7}$	$1\cdot0 \times 10^{-7}$	$0\cdot6 \times 10^{-5}$

Possible influence of the adsorption–impurity effects upon the experimental values of second virial coefficients has been illustrated on data for gaseous Kr–SF_6 system. The second virial coefficients $B_2^{(exp)}(T)$ of a Kr–SF_6 mixture were measured recently [20] at different temperatures and mixture composition, and the cross second virial coefficients $B_2^{(Kr-SF_6)}(T)$ were calculated with the help of equation analogous to (17). In particular at $T = 273$ K $B_2^{(Kr-SF_6)} = -130\,cm^3\,mol^{-1}$ [20]. We have made the estimations of the possible uncertainties of this value for a wide range of t_m and $\Delta x = x^* - x$ according to

$$B_2^{(exp)}(1 + t_m) = x_e^{*2} B_2^{(Kr-Kr)} + 2x_e^*(1 - x_e)B_2^{(Kr-SF_6)} + (1 - x_e^*)^2 B_2^{(SF_6-SF_6)}, \quad (18)$$

where x_e^* is the perturbed composition of the equimolar mixture, $B_2^{(exp)}$ is the experimental second virial coefficient of the Kr–SF_6 mixture at $x = 0\cdot5$ and is equal to $-165\cdot7\,cm^3.mol^{-1}$ [20], $B_2^{(Kr-Kr)}$ and $B_2^{(SF_6-SF_6)}$ are the second virial coefficients of the pure components that were taken from [20]. The results of the calculations are presented in table 3. The upper values in the table represent the cross second virial coefficients $B_2^{(Kr-SF_6)}$ which have been corrected taking into account the possible adsorption–impurity effects, the lower ones correspond to the possible errors in measured second virial coefficient (in per cent).

It seems interesting to examine the influence of the distortion, introduced by the adsorption–impurity effects into measured second virial coefficients, on the intermolecular potential function parameters which are extracted from the experimental second virial coefficient data.

The second virial coefficient as a function of temperature may be used to define the potential energy function by employing an inversion technique developed by Smith and co-workers [3, 4]. From the second virial coefficient data we

Table 2. The adsorption–impurity perturbation parameters for helium–xenon mixtures. x is the mole fraction of component. $t_mV_0^{1/3}$ is some effective adsorption–impurity perturbation parameter for a vessel of arbitrary volume V_0.

		$t_mV_0^{1/3}/m$	
$x^{(He)}$	$x^{(Xe)}$	$T = 200$ K	$T = 300$ K
1·0000	0·0000	$7\cdot1 \times 10^{-11}$	$6\cdot2 \times 10^{-11}$
0·9999	0·0001	$2\cdot0 \times 10^{-8}$	$1\cdot4 \times 10^{-10}$
0·999	0·001	$2\cdot0 \times 10^{-7}$	$8\cdot0 \times 10^{-10}$
0·99	0·01	$2\cdot0 \times 10^{-6}$	$7\cdot5 \times 10^{-9}$
0·9	0·1	$2\cdot0 \times 10^{-5}$	$7\cdot4 \times 10^{-8}$

Table 3. The surface of the cross second virial coefficient $B_2^{(\mathrm{Kr-SF_6})}$ response to adsorption–impurity perturbation at $T = 273$ K. t_m is adsorption–impurity perturbation parameter. $\Delta x = x_e^* - x_e$, where x_e^* and x_e are perturbed and unperturbed compositions of the equimolar mixture Kr–SF$_6$ respectively. The upper values in the table represent the cross second virial coefficients $B_2^{(\mathrm{Kr-SF_6})}$ corrected taking into account the possible adsorption–impurity perturbation, in cm^3 mol^{-1}, the lower ones are the possible errors in measured $B_2^{(\mathrm{Kr-SF_6})}$, in per cent.

	Δx				
t_m	10^{-1}	10^{-2}	10^{-3}	10^{-4}	$10^{-\infty}$
10^{-1}	−219·3	−168·7	−163·7	−163·2	−163·1
	40·72	22·93	20·58	20·34	20·31
10^{-2}	−188·2	−138·8	−133·9	−133·4	−133·3
	30·93	6·36	2·89	2·53	2·48
10^{-3}	−185·1	−135·8	−130·9	−130·4	−130·3
	29·77	4·31	0·68	0·30	0·25
10^{-4}	−184·8	−135·6	−130·6	−130·1	−130·0
	29·66	4·09	0·45	0·07	0·03
$10^{-\infty}$	−184·8	−135·5	−130·6	−130·1	−130·0
	29·64	4·07	0·42	0·04	0·00

oped by Smith and coworkers [3, 4]. From the second virial coefficient data we

$$\tilde{r} = \left(\frac{B + T(dB/dT)}{2\pi N_A/3}\right)^{1/3}. \tag{19}$$

The intermolecular potential energy $U^{(1)}(\tilde{r})$ is then represented by

$$U^{(1)}(\tilde{r}) = G^{(0)}(T^*)kT, \tag{20}$$

where T^* is the reduced temperature, $G^{(0)}(T^*)$ is a slowly varying, temperature dependent inversion function which is not sensitive to the detailed form of the potential and hence may be calculated from some model potential function. Using such approximate values of $G^{(0)}(T^*)$ in (20) allows an estimate of energy $U^{(1)}(\tilde{r})$ appropriate to the separation $\tilde{r}$. The potential $U^{(1)}(\tilde{r})$ thus obtained allows a new inversion function to be calculated forming the basis for an iterative procedure as indicated by the general equation

$$U^{(n+1)}(\tilde{r}) = G^{(n)}(T^*)kT. \tag{21}$$

For a gaseous system perturbed by adsorption–impurity effects the second virial coefficient, as we showed above, is expressed by (11). We use (8) and (11) to obtain the expression for the temperature derivative of the second virial coefficient in perturbed system

$$\frac{dB^*}{dT} = \frac{dB}{dT}(1+t)^{-1} + \frac{Bt}{2T}\left(\frac{2Q_a}{RT} - 1\right)(1+t)^{-2}. \tag{22}$$

Substituting (11) and (22) into (19) yields perturbed characteristic distance

$$\tilde{r}^* = \left\{\frac{[B + T(dB/dT)](1+t)^{-1} - (Bt/2)[1 - (2Q_a/RT)](1+t)^{-2}}{2\pi N_A/3}\right\}^{1/3}. \tag{23}$$

For nonrigid conditions $2Q_a/RT \gg 1$ and $V_0^{1/3} \ll AQ_a \exp(Q_a/RT)/R(MT)^{1/2}$ the ratio $\tilde{r}^*/\tilde{r}$ is approximately

$$\tilde{r}^*/\tilde{r} \simeq (1+t)^{-1/3}. \tag{24}$$

Below we give some illustrative examples of calculations of the intermolecular parameters σ and ε/k perturbed by the adsorption–impurity effects. Argon and xenon were chosen as model systems. The Lennard-Jones 12-6 potential energy function parameters for argon are well established and equal [21]: $\varepsilon/k = 142{\cdot}5$ K, $\sigma = 0{\cdot}335$ nm. These values in conjunction with the values of $B^{\star}(T^*)$ and $T^*(dB^{\star}/dT^*)$ for the LJ 12-6 potential [22] were employed to generate the corresponding pseudoexperimental second virial coefficient and its temperature derivative data at $T = 114$ K. These data were then perturbed (see (11)) in accordance with the magnitude of the perturbation introduced into the system by the adsorption–impurity parameter t_m, which was taken equal to 10^{-3}, 5×10^{-3}, 10^{-2} and 5×10^{-2} (it can be seen from table 3 that such values of t_m may lead, respectively, to uncertainties in the measured second virial coefficient varying from about tenth parts of per cent to a few per cent). The perturbed pseudo-experimental values of B^* and dB^*/dT so obtained were inverted to determine the parameters of the LJ 12-6 potential. The inversion procedure used was similar in that proposed by Smith and coworkers [3, 4]. The results of the inversions are the following: $\sigma = 0{\cdot}3349$ nm at $t_m = 10^{-3}$, $0{\cdot}3344$ nm at 5×10^{-3}, $0{\cdot}3339$ nm at 10^{-2} and $0{\cdot}3296$ nm at 5×10^{-2} (see figure 3); $\varepsilon/k = 142{\cdot}5$ K for all the values of t_m. Figure 3 shows the LJ 12-6 potential energy function for argon calculated by use of the unperturbed and of the perturbed function parameters. It is seen from figure 3 that for the repulsive branch of the potential the adsorption–impurity effects can introduce significant uncertainties into intermolecular potential energy derived from the experimental second virial coefficient data.

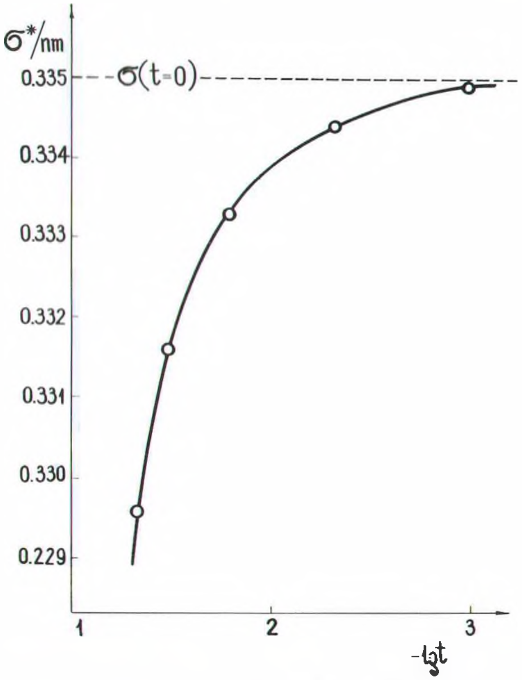

Figure 3. The adsorption perturbation of the collision diameter σ for argon molecules at various values of the adsorption perturbation parameter t. The points represent the results of the iterative procedure. The line is the results obtained using equation (24).

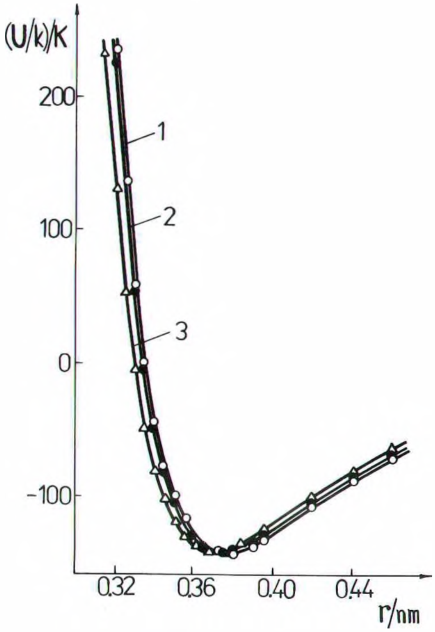

Figure 4. The LJ 12-6 potential function response to the adsorption–impurity perturbation for argon. 1 — $t_m = 0$; 2 — $t_m = 5 \times 10^{-3}$, 3 — $t_m = 5 \times 10^{-2}$.

To obtain the well depth parameter ε/k of the potential function of any form Nedostup [23] proposed transcendental relationship

$$\varphi(\varepsilon, T) = \frac{1 - \exp(-\beta\varepsilon)}{\varepsilon/k} \sqrt{\left[\frac{(1 + \beta\varepsilon)(1 - \exp(-\beta\varepsilon))}{\beta\varepsilon}\right]} = \frac{B(T - T_B)}{T^2[B - (dB/dT)(T - T_B)]}, \tag{25}$$

where $\beta = (kT)^{-1}$, T_B is the Boyle temperature. Unfortunately, the method proposed in [23] may serve for estimating an initial approximation to the true value of ε/k only: the variation in values of ε/k is about 20 per cent over the temperature range $1 \leqslant T^* \leqslant 4$.

We may show that for a gaseous system distorted by adsorption effects the above relationship can be rewritten as

$$\varphi^*(\varepsilon^*, T) - \frac{B(T - T_B)}{T^2[\alpha B - (dB/dT)(T - T_B)]} = 0, \tag{26}$$

with

$$\alpha = 1 - \frac{t(T - T_B)}{2T(1 + t)}\left(\frac{2Q_a}{RT} - 1\right) \simeq 1 - \frac{Q_a t(T - T_B)}{RT^2}. \tag{27}$$

From (26) we may calculate perturbed well depth parameter ε^*/k by using a method of dichotomy. Calculations of ε^*/k were carried out for argon and xenon by employing the second virial coefficient data for these substances from [24]. The function $\varphi^*(\varepsilon^*, T)$ response to adsorption perturbation for xenon is shown in figure 5.

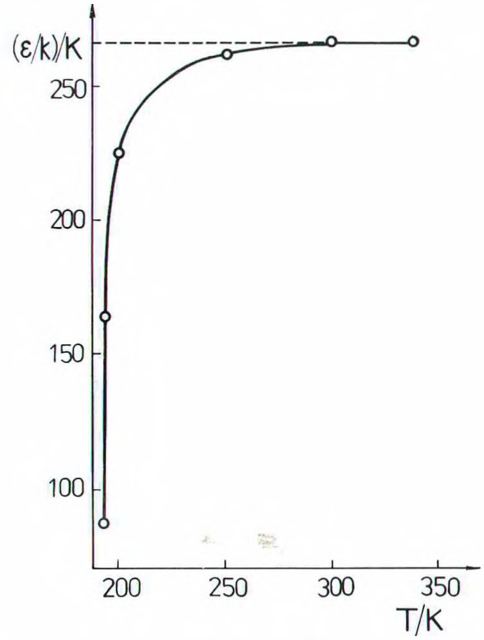

Figure 5. The adsorption perturbation of the well depth parameter ε/k defined by equations (26) and (27) for xenon molecules. A volume of the vessel V_0 is assumed equal to $15 \times 10^{-6}\,\mathrm{m}^3$. Solid line: a value of the temperature-dependent adsorption perturbation parameter t covers the range $t = 2{\cdot}6 \times 10^{-2}$ at $T = 185\,\mathrm{K}$ to $t = 10^{-5}$ at $T = 350\,\mathrm{K}$. Dashed line: $t = 0$. A value for ε/k of 267 K for xenon at $t = 0$ used in the calculations was taken from [25].

4. CONCLUSIONS

The above qualitative results allow us to make a conclusion as to the practical importance of estimations of uncertainties introduced by adsorption and adsorption–impurity effects into experimental measurements of P, V, T-data and virial coefficients. In particular, these estimations are important in connection with the development of methods for the direct inversion of second virial coefficient data to obtain the information about the intermolecular potential energy function [3]. Model intermolecular potentials are widely used to evaluate thermophysical properties such as enthalpy of dimerization [26], etc. If measurements and calculations are carried out in a range of state parameters for which perturbation effects are significant, the information about the intermolecular potential parameters may contain systematic errors. Unfortunately, they are not taken into consideration in the corresponding studies. To this aim special experimental studies for the investigation of the role of external effects in the intermolecular parameters determination from virial coefficient data are also necessary.

The method proposed here allows some observations to be made, that may be important in practice when the reverse problems of thermophysics of gaseous state are examined. Firstly, we require knowledge of the nature and the mole fraction of impurities in the gas being studied; secondly, it is necessary to make evaluation of the adsorption and the adsorption–impurity perturbations; and thirdly, if parameters of the model intermolecular potential function are determined from measurements of different thermophysical properties, e.g. the second virial coefficient in conjunction with the coefficients of the transport properties, they must be weighted with factors reversely proportional to their response to external perturbations.

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