METHOD OF EQUIVALENT EQUATIONS AND THE PARAMETERS OF MODEL INTERMOLECULAR POTENTIALS

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UDC 536.71:536.63:536.75

Using the method of equivalent equations we obtain improved ("true") values for the parameters of the spherical shell potential for n-pentane.

As is well known in the problem of extrapolating empirical equations of state beyond the limits of the original experimental data, which was used to determine the coefficients of the equation of state, the most effective method is the use of theoretically sound equations. These are equations which contain a minimum of adjustable parameters, where the parameters are constants of the model intermolecular potentials, and have definite physical interpretations.

Limiting our treatment to the first two terms of the virial expansion in the density (this can always be done by choosing the interval of approximation such that the contributions of the higher virial coefficients can be neglected) we have for the compressibility:

$$z = 1 + B^*(T^*)\, b_0\rho + c^*(T^*)\, b_0^2\rho^2, \tag{1}$$

where $z = P/\rho RT$; $B^* = B/b_0$; $C^* = C/b_0^2$ are the reduced virial coefficients; $b_0 = (2/3)\pi N_A \sigma^3$; $T^* = T/\varepsilon^*$; $\varepsilon^* = \varepsilon/k$, ε^*, σ are constants of the model intermolecular interaction potential.

Values of the reduced virial coefficients are tabulated for many of the model potential functions (see, for example, [7-9]). We chose the spherical shell potential. As shown in [10, 11] the spherical shell potential best reflects the nature of the interaction of many-atom molecules. In [4] the reduced virial coefficients for the spherical shell potential [8, 9] were approximated by the expressions

$$B^* = \sum_{i=1}^{7} a_i T^{*n_i}; \quad C^* = \sum_{i=1}^{7} c_i T^{*m_i}. \tag{2}$$

The values of a_i and c_i are given in [4].

From (1) and the differential relations of thermodynamics, we obtain for the heat capacity at constant volume

$$(C_v - C_{v_0})/R = -(2B_1^* + B_2^*)\, b_0\rho - 1/2\,(2C_1^* + C_2^*)\, b_0^2\rho^2, \tag{3}$$

where $B_1^* = T^*(\partial B^*/\partial T^*)$; $B_2^* = T^{*2}(\partial^2 B/\partial T^{*2})$; $C_1^* = T^*(\partial C^*/\partial T^*)$; $C_2^* = T^{*2}(\partial^2 C^*/\partial T^{*2})$. The quantities B_1^*, B_2^*, C_1^*, and C_2^* can be calculated by applying the relations (2).

Similarly, using the differential equations of thermodynamics, one can obtain the explicit dependence of the thermodynamic quantities on the parameters of the model interaction potential. The nonequilibrium properties, such as the viscosity and thermal conductivity, are also determined from the values of these parameters [2, 6].

For the spherical shell potential we have substituting the approximate reduced virial coefficients (2) into (1) and (3), expressions for the compressibility and heat capacity at constant volume, where the only unknown parameters are the spherical shell potential parameters ε^*, b_0. The effective values of these parameters are usually determined by the minimization of a quadratic functional for each property of the gas:

$$S(\varepsilon^*, b_0) = \sum_{j=1}^{N} \sum_{k=1}^{M} W_k^j [\gamma_{kj}^{\text{exp}}(T_k, \rho_k) - \gamma_{kj}^{\text{cal}}(\varepsilon^*, b_0, T_k, \rho_k)]^2, \tag{4}$$

M. D. Millionshchikov Groznensk Petroleum Institute. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 51, No. 4, pp. 629-633, October, 1986. Original article submitted August 20, 1985.

0022-0841/86/5104-1218$12.50

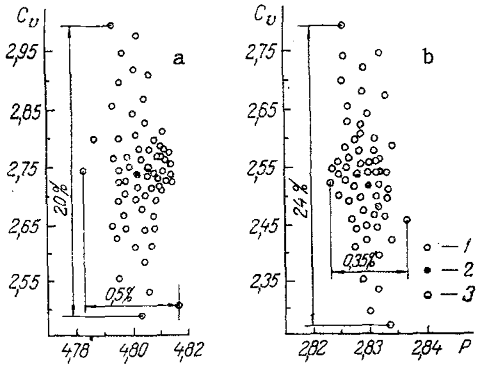

Fig. 1. Histograms showing the scatter of the calculated values of the heat capacity at constant volume and the pressure of n-pentane. a: T = 573.15°K, V = 10 cm³/g; b: T = 473.15°K, V = 12 cm³/g. 1) Values obtained from different equivalent equations; 2) values for the averaged potential parameters; 3) experimental values of [21]. C_V, kJ/kg·°K, P, MPa.

where $W_k{}^j$ is the weight of the k-th experimental point for the j-th property; $\gamma_{kj}^{\exp}$, $\gamma_{kj}^{\mathrm{cal}}$ are the experimental and calculated values of the j-th property for the k-th experimental point.

Hence, it follows from (4) that the effective values of the spherical shell potential constants can be obtained on the basis of different thermodynamic (z, C_V, C_p, δ_T, etc.) and transport (η, λ, D) properties by separate or joint analysis of all of these properties. For example, in [1] the parameters of the potential function were found from compressibility data, in [4, 5] data on the heat capacity at constant volume was used, and in [3] data on the isothermal Joule–Thomson effect was used. As shown by the analysis of different authors, the values ε^* and b_0 obtained from the analysis of different thermodynamic and transport properties may not be the same. Therefore, in [2, 6, 12] joint analysis methods were used to obtain unique values of the potential parameters, and hence also consistent equations of state, viscosity, thermal conductivity, and compressibility.

However, the method of joint analysis of different kinds of data may not always be effective. First of all, this method requires reliable and mutually consistent experimental data on all of the properties; secondly this data may not always be obtained for the same state variables (for the same interval of T and ρ), which is essential for the method.

In order to obtain unique parameters (the "true" values of ε^* and b_0) for n-pentane on the basis of compressibility data only, we used the method of equivalent equations, as developed in [13-15].

Because of the fact that the values of the parameters ε^* and b_0 are determined from a set of random quantities, these parameters themselves are random. Therefore, as in the case of the empirical equations of state of [13-15], for the same $P-\rho-T$ data it is possible to find a large number of model potential parameters ($\varepsilon_i{}^*$, b_{0i}) which will describe the original $P-\rho-T$ data with the same mean-square error, but will not be equivalent in the description of the caloric properties, in particular the $C_V-\rho-T$ properties. In the absence of reliable calorimetric measurements, the "true" values of the effective potential parameters can be found, according to [13-15], by averaging all of the obtained values of $\varepsilon_i{}^*$ and b_{0i}:

$$\varepsilon^* = \sum_{i=1}^{N} \varepsilon_i^*/N, \quad b_0 = \sum_{i=1}^{N} b_{0i}/N, \tag{5}$$

where $\varepsilon_i{}^*$ and b_{0i} are the effective values of the potential parameters corresponding to the i-th equivalent equation of state.

This method of finding the "true" values of the spherical shell potential parameters (ε^*, b_0) from $P-\rho-T$ data was applied to the case of n-pentane. On the basis of new experimental studies of the $P-\rho-T$ properties of n-pentane vapor in the temperature interval 378.15 to 658.15°K and in the density interval 4.6-116 kg/m³, and including about 120 points [6], we determined the parameters ε^* and b_0 of the spherical shell potential. The program FUMILI [17] was used to minimize (4) for the $P-\rho-T$ data in the interval mentioned above. The weight of the experimental points was specified according to the method of [18] with the formulas for the propagation of errors taken into account.

Our research, and also that of other authors [4, 19] shows that the density interval $0 \leq \rho \leq 116$ kg/m³ ($0.5\ \rho_k$) is reliable for the virial equation of state (1) with two virial coefficients.

A set of values of the spherical shell potential parameters ε_i^* and b_{0i} corresponding to different equivalent equations of state (1) was achieved by variation of the lower limit of the approximation interval in the density, variation of the weight of the experimental points, choice of the method of minimization of (4), variation of the number of coefficients in (2), the use of different forms of (2), etc. Equation (4) was minimized using various nonlinear least squares methods (the methods of Rosenbrok, Nelder–Mid, Newton, Hooke, Jivsa, etc.) [20]. N = 68 different equations of state were considered and therefore we obtained 68 different values of the spherical shell potential parameters ε^* and b_{0i} which is less than the experimental error. As evident from Fig. 1, the scatter of the C_V values for different values of the parameters ε_i^* and b_{0i} is about 20-25%, even though the scatter of the calculated values of the pressure does not exceed the experimental error.

The "true" values of the spherical shell potential parameters, which according to [13-15] correspond to the mean values of the set of N = 68 different values ε_i^* and b_{0i}, and which reproduce the mean values of the thermodynamic functions are:

$$\varepsilon^* = 717.38 \pm 0.12\ \text{K},\ b_0 = 3.635 \pm 0.0017\ \text{cm}^3/\text{g}. \tag{6}$$

The third spherical shell potential parameter $r_0^* = (d/\sigma) = 1.6$ (d is the diameter of the spherical shell) can be determined from structure data and the known length of the n-pentane molecule. We note that d can also be determined using the method of [10] through the similarity criterion A. The values of the potential parameters (6) can, within experimental error, be used to calculate the heat capacity at constant volume and the other caloric properties [21].

In [4, 5] the spherical shell potential parameters of n-pentane were calculated from $C_V-\rho-T$ measurements [21] in the vapor phase from the relations (2). These values are $\varepsilon^* = 661.9 \pm 0.14$°K, $b_0 = 4.04 \pm 0.0013$ cm^3/g and are close to the mean values (6) obtained with the method of equivalent equations. On the one hand, this indicates further that the average values of the potential parameters (5) obtained by the method of equivalent equations can be taken as estimates of the "true" values of the parameters obtained from the $P-\rho-T$ measurements. On the other hand, it indicates that the caloric measurements allow one to select in advance the optimum equivalent equation from the system of all possible equivalent equations with respect to the $P-\rho-T$ data.

The values of the potential parameters obtained in (6) for n-pentane can be used to calculate and extrapolate the thermodynamic properties of n-pentane in the vapor phase.

NOTATION

P, presure; ρ, density; T, temperature; z, coefficient of compressibility; B, C, second and third virial coefficients; N_A, Avogadro's number; R, the universal gas constant; K, the Boltzmann constant; ε, σ, the constants of the spherical shell potential; C_V, C_p, the heat capacities at constant volume and constant pressure; S, quadratic functional; W, weight of the experimental points; δ_T, isothermal compressibility; η, λ, D, coefficients of dynamical viscosity, thermal conductivity, and diffusion; N, number of equivalent equations; γ_{kj}^{exp}, γ_{kj}^{cal}, experimental and calculated values at the k-th point; d, diameter of the spherical shell.

LITERATURE CITED

1. V. N. Zubarev, A. D. Kozlov, and G. A. Spiridonov, Teplofiz. Vys. Temp., 9, No. 5, 943-947 (1971).
2. V. M. Kuznetsov, "Method of joint analysis of experimental data and its application to the obtaining of consistent equations of the equilibrium and nonequilibrium properties of moderately dense gases," Dissertation, Moscow (1980).
3. G. A. Spiridonov and L. R. Malov, Thermophysical Properties of Matter and Materials [in Russian], Issue 14, Moscow (1980), pp. 150-153.
4. I. M. Abdulagatov, B. G. Alibekov, and A. S. Aronson, Izv. Vyssh. Uchebn. Zaved., Neft. Gaz., No. 9, 55-59 (1982).
5. I. M. Abdulagatov and B. G. Alibekov, Zh. Fiz. Khim., 56, No. 5, 1162-1165 (1982).
6. Nitrogen. Second Virial Coefficient, Coefficients of Dynamical Viscosity, Thermal Conductivity, Self-Diffusion and Prandtl Number of the Dilute Gas Phase in the Temperature Region 65-2500°K [in Russian], (A. A. Vigasin, N. Kh. Zimina, V. E. Lyusternik, et al., Tables SSD, GSSD 49-83, Moscow (1961).
7. J. O. Hirschfelder, C. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids, Wiley, New York (1954).

8. T. S. Storvic, T. H. Spurling, and A. G. De Rocco, J. Chem. Phys., 46, No. 4, 1498-1506 (1967).
9. A. G. De Rocco and W. G. Hoover, J. Chem. Phys., 36, No. 4, 916-926 (1962).
10. L. P. Filippov and D. A. Tolstunov, Thermophysical Properties of Matter and Materials [in Russian], Issue 16, Moscow (1982), pp. 89-100.
11. D. A. Tolstunov and L. P. Filippov, Zh. Fiz. Khim., 56, No. 1, 129-132 (1982).
12. V. N. Zubarev and V. M. Kuznetsov, Teplofiz. Vys. Temp., 15, No. 5, 977-982 (1977).
13. G. A. Spiridonov, A. D. Kozlov, and V. V. Sychev, Thermophysical Properties of Matter and Materials [in Russian], Issue 10 (1976), pp. 35-53.
14. V. V. Sychev and G. A. Spiridonov, Dokl. Akad. Nauk, 241, No. 4, 808-811 (1978).
15. V. V. Sychev, Vestn. Akad. Nauk, No. 2, 24-32 (1980).
16. B. A. Grigor'ev, D. S. Kurumov, and Yu. L. Vasil'ev, Zh. Fiz. Khim., No. 2, 286-288 (1986).
17. I. N. Silin, "Standard program for the solution of problems by the method of least squares," JINR, 11-3362, Dubna (1967).
18. A. A. Vasserman, Teplofiz. Vys. Temp., 19, No. 5, 1103-1105 (1981).
19. W. Wagner, J. Ewers, and R. Schmidt, Cryogenics, No. 1, 37-43 (1984).
20. V. V. Sychev, G. A. Spiridonov, and Yu. I. Kas'yanov, Inzh.-Fiz. Zh., 45, No. 5, 855-860 (1983).
21. Kh. I. Amirkhanov, B. G. Alibekov, D. I. Vikhrov, and V. A. Mirskaya, Heat Capacity at Constant Volume and Other Caloric Properties of Hydrocarbons of the Methane Series [in Russian], Makhachkala (1981).

RADIATION TRANSPORT IN A SCATTERING MATERIAL EXPOSED TO A DIFFUSE FLUX OR ONE DIRECTED AT A CERTAIN ANGLE

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UDC 536.3

Absorbed flux densities have been calculated for a scattering material irradiated from one or both sides by a diffuse flux or a flux directed at a certain angle.

Considerable importance attaches to radiation transport in scattering material (polymer films, paint coating, textiles, paper, plant materials, etc.) on account of the need to describe heat and mass transfer during heat treatment and drying produced by diffuse or directed radiation fluxes [1-4].

To calculate the energy transport in a scattering material as affected by irradiation conditions, it is necessary to have data on the following major characteristics [1]: in diffuse irradiation, on the averaged absorption coefficients $\bar{k}_\lambda$, the effective attenuation L_λ and the two-hemisphere reflectivity of an infinitely thick layer $R_{\lambda\infty}$; with collimated radiation, one needs information on $\bar{k}_\lambda$, L_λ, $R_{\lambda\infty}$, as well as on the absorption coefficient k_λ, the extinction coefficient ε_λ, and the Dantley parameters C_1 and C_2, which incorporate the angle of incidence Θ for the collimated flux, the optimal characteristics, and the scattering indicatrix $\chi_\lambda(\gamma)$.

We have examined the scattering indicatrices of plant materials for this purpose. A scattering material has an indicatrix elongated in the forward direction [1], such as that shown in Fig. 1 for plant materials. The shape of the indicatrix can be incorporated by means of the coefficients δ_s and δ_f, which are numerically equal to the proportions of the flux scattered backwards and forwards by an elementary volume or layer on exposure to a flux in the solid angle $\omega' \leq 2\pi$ having an angular intensity distribution $B_\lambda(\Theta, \omega')$; δ_s and δ_f vary over the ranges $0 < \delta_s < 1$ and $0 < \delta_f < 1$, but the sum is always one: $\delta_s + \delta_f = 1$.

Moscow Food-Industry Technology Institute. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 51, No. 4, pp. 633-638, October, 1986. Original article submitted May 27, 1985.

0022-0841/86/5104-1221$12.50