THE "IDEAL CURVE" METHOD IN THE THERMODYNAMICS OF REAL GASES AND GAS MIXTURES

V. I. Nedostup and E. P. Gal'kevich

UDC 536.71

The possibility of using the "ideal curve" method for study of the properties of individual gases and gas mixtures is demonstrated.

The development of the theory of the equation of state of a real gas is often related to generalization of new experimental facts, including the detailed information which has appeared in recent years on so-called "ideal curves," which are lines on real surfaces of state along which conditions characteristic of an ideal gas are satisfied [1,2].

The ideal curves contain significant information on both the geometrical structure of the thermodynamic surface, and on peculiarities of a physical character — the radial distribution function and intermolecular potential [2-4]. On the basis of principles observed in the behavior of certain ideal curves [5-8], methods for generalizing and predicting the properties of various gases have been proposed. Subsequent development of this approach has permitted creation of an effective technique for comparison of the equation of state of gases and mixtures in a form which considers these principles.

For further development, it is important to note that any state of a real gas may be referred to some ideal curve. This is equivalent to saying that the huge (by definition) manifold of ideal curves encompasses all possible states of a real gas. This can be proven without difficulty if we consider a one-parameter family of so-called isochoric ideal curves, the definition of which was introduced in [1], and may be described by the expression

$$\left[\frac{\partial}{\partial T}(P-P_{\mathrm{id}})T^{n}\right]_{\rho}=0, \tag{1}$$

where $P_{\mathrm{id}} = RT\rho$ is the pressure of an ideal gas and n is a parameter which takes on arbitrary values. A special case of this family is the curve of an ideal gas $P = P_{\mathrm{id}}$, where n takes on the value $\pm\infty$. From Eq. (1) and the virial equation of state it follows that as $\rho \to 0$

$$\frac{B}{T}=-\frac{1}{(n+1)}\,\frac{dB}{dT}. \tag{2}$$

From Eq. (2) it is evident, e.g., that at $n = \pm\infty$ $B = 0$ and the corresponding isochoric curve, i.e., the ideal gas curve, commences at the Boyle temperature T_B; for $n = -2$ $B/T = dB/dT$ and the origin of the curve is the inversion temperature T_{in}; for $n = -1$ $dB/dT = 0$, i.e., the origin of the curve coincides with the Joule temperature T_J. In the region of existence of a real gas at temperatures below T_B n takes on positive values from $+\infty$ to ~ 0.7 at the triple point. Thus, the parameter n, maintaining a constant value along each ideal curve, uniquely defines a certain temperature on this curve upon extrapolation to the point $\rho = 0$. On this basis it can be concluded that over the entire range of existence of a real gas there are no limitations imposed on any of the variables appearing in Eq. (1), and the latter may be written in the form

$$f(T,\ P,\ \rho,\ n)=0,$$

i.e., it may be stated that the thermodynamic surface of a real gas is a family of isochoric ideal curves.

Analysis of experimental data on the properties of light hydrocarbons, inert gases, a number of Freons, and atmospheric gases has permitted two fundamental conclusions as to peculiarities in the behavior of the curves of Eq. (1):

1) in the coordinates (T, ρ) over a wide parameter range the curves are straight lines

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Physicochemical Institute, Academy of Sciences of the Ukrainian SSR, Odessa. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 38, No. 4, pp. 702-708, April, 1980. Original article submitted June 14, 1979.

0022-0841/80/3804-0424$07.50

TABLE 1. Coefficients a_i of Eq. (6) for Mixture CH_4—CF_4 (x, molar concentration of CH_4)

i	x				
	1,0	0,75	0,5	0,25	0,0
0	1,3321603	15,926629	40,163715	16,285395	18,356514
1	0,41457562	—41,007975	—202,87632	—71,250938	—73,738854
2	—3,7923209	—45,090779	412,77922	123,35871	103,66162
3	3,2545009	310,40104	—397,23036	—77,533021	—11,268841
4	—1,5587057	—500,73847	144,20723	—32,016560	—120,07436
5	0,40065466	384,53632	37,533249	70,637532	129,74675
6	—0,053677644	—146,12979	—43,969484	—35,586214	—55,431860
7	0,002999345	22,105769	9,3962177	6,1081123	8,7534320

with a common density ρ_0 at their extension to the point T = 0, i.e.,

$$T = T_0(1 - \rho/\rho_0),$$

where T_0 is the temperature value on each of the ideal curves upon extrapolation to the point $\rho = 0$, so that the condition n = const is equivalent to the condition T_0 = const;

2) in the coordinates (PV, ρ) over the same parameter range the curves are also straight lines, and their slope is determined by the value of the second virial coefficient at the temperature T_0, $B(T = T_0)$:

$$\left(\frac{dPV}{d\rho}\right)_{T_0=\text{const}} = \frac{RT_0}{\rho_0}\,[B(T = T_0)\,\rho_0 - 1].$$

This expression can be obtained easily from the virial equation of state with consideration of the indicated peculiarities of the ideal curves. Omitting simple transformations, we write the equation of the thermodynamic surface having the properties indicated above:

$$PV = RT + RTB(T = T_0)\frac{\rho}{1 - \rho/\rho_0}. \tag{3}$$

As an example, we will consider the well-studied gas methane, using the Lennard-Jones potential to calculate the values B and ρ_0 required by Eq. (3).

The density value ρ_0 may be found from the relationship of the slope of an ideal gas curve in (T, ρ) coordinates, represented in the form of a virial equation of state

$$\left(\frac{dT}{d\rho}\right)_{\substack{\rho\to 0\\ (T\to T_B)}} = -\left(\frac{C}{dB/dT}\right)_{T=T_B}.$$

Then, substituting the values of C* and T*dB*/dT* tabulated in [9] and considering the fact that the ideal gas curve is a straight line in these coordinates, we obtain:

$$\rho_0 = \left(\frac{T\dfrac{dB}{dT}}{C}\right)_{T=T_B} = \frac{2{,}398}{2/3\pi N\sigma^3}.$$

Considering that the Lennard-Jones potential is a model one, we introduce the dependence of its parameters upon the quantity T_0. As a result of processing experimental data on methane [10] the following expressions are obtained for $\sigma(T_0)$ and $\varepsilon(T_0)$:

$$\sigma(T_0) = 3.757276402 - 0.0269704398\left[\exp\left(-1.01312395\,\frac{T_0}{\varepsilon}\right) - 1\right], \tag{4}$$

$$\varepsilon(T_0) = 1.53269493\times 10^2 - 7.02553543\times 10^{-2}T_0 + 2.34039536\times \times 10^{-4}T_0^2 - 2.85274502\times 10^{-7}T_0^3 + 1.23368679\times 10^{-10}T_0^4. \tag{5}$$

The values of the methane ideal gas curve obtained with the aid of Eqs. (4), (5) (ρ_0 = 35.82 kmole/m^3, T_B = 508.63°K) agree well with those obtained directly from experimental data [10,11] (35.90 kmole/m^3 and 508.53°K, respectively) and substitution of these values together with the expression for the second virial coefficient of the Lennard-Jones potential [9] in Eq. (3) leads to a description of the experimental data [10] with a mean δ^{mean} = 0.07% and maximum δ^{max} = 0.3 % error.

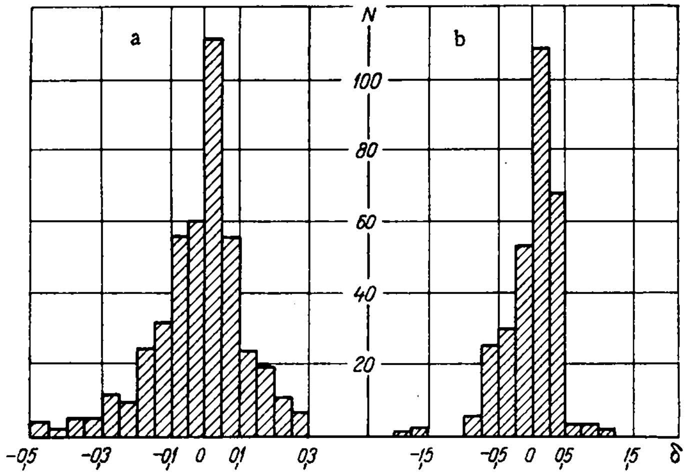

Fig. 1. Histograms of deviation (%) of experimental values of CH_4 [10,11] (a) and CF_4 [10] (b) compressibility coefficients from values calculated with Eq. (3).

An equation of state in the form of Eq. (3) can be produced directly from experimental PVT data without use of a model potential. Approximate equations obtained in this manner for the second virial coefficient can be written in the form

$$B^* = \sum_{i=0}^{7} a_i \theta^{-i}, \tag{6}$$

where $B^* = B\rho_0$; $\theta = T_0/T_B$. The coefficients of Eq. (6) presented in Table 1 as an example for Freon F-14 (ρ_0 = 27.54 kmole/m^3, T_B = 520.64°K) and methane (ρ_0 = 35.90 kmole/m^3, T_B = 508.53°K) describe the experimental data to the accuracy shown in Fig. 1.

Figure 2 presents data of various authors on the second virial coefficient of methane, obtained by the usual methods based on processing of PVT data for the rarefied gas, together with the curve of Eq. (6). It should be noted that the method proposed here provides much smaller tolerance in the values of the second virial coefficient as compared to traditional methods, since reliable data over a wide density interval are used. Moreover, due to the peculiarities of the thermodynamic surfaces mentioned above, the values of the second virial coefficient can be determined over a wider range of temperatures $T = T_0$ than by the classical methods along isotherms.

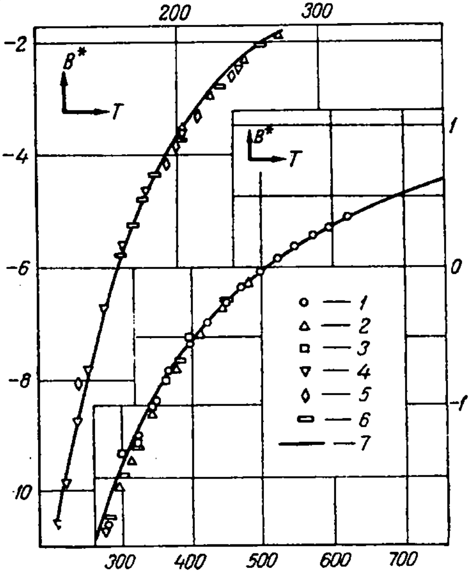

Fig. 2. Second virial coefficient $B^* = B\rho_0$ versus temperature, °K: 1) [10]; 2) [12]; 3) [13]; 4, 5, 6) data of Berne, Hoover, and Sengers et al., respectively, from [14]; 7) $B^*(T = T_0)$, Eq. (3).

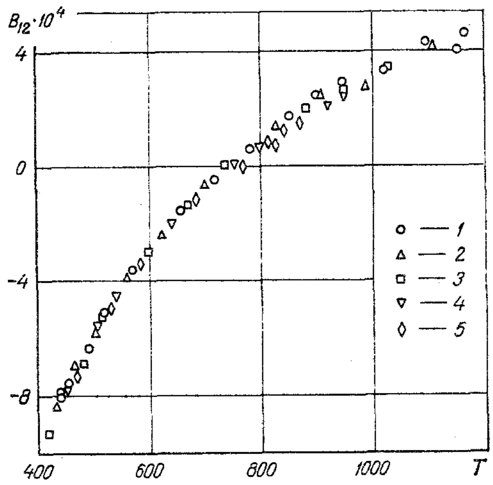

Fig. 3. Mixed second virial coefficient B_{12}, m^3/kg vs temperature $T = T_0$, °K, mixtures nC_4H_{10}—CO_2 [15]: 1) x = 0.16938; 2) 0.33335; 3) 0.49843; 4) 0.67396; 5) x = 0.82729 (where x is the molar fraction of nC_4H_{10}).

Together with indisputable advantages (quite high accuracy over a wide parameter range and simplicity of formulation and use), Eq. (3) has a shortcoming in that it reliably describes only that portion of the surface of state upon which the ideal curves of Eq. (1) are linear. Curvature of the latter in the region of low temperatures and high densities, or curvature produced by the presence of a high molecular dipole moment in the material under study leads to a sharp reduction in the accuracy of the description of properties.

A most important consequence of the proposed form of Eq. (3) is the capability of use for calculating gas mixtures. The problem of constructing an equation of state for dense gas mixtures, which require a large number of virial coefficients, has not yet been solved because of the impossibility of reliably determining the so-called cross virial coefficients of higher order than the second. Other theoretical methods, e.g., those based on perturbation theory, despite certain successes which have been achieved, have been used only in limited cases for very simple gases. The applicability of the equation of state in the form of Eq. (3) to description of gas mixtures is justified by the fact that the thermodynamic surfaces of the latter, given a constant composition, possess the same properties as the surfaces of pure substances.* The function $B_{mix}(T = T_0)$ considered here for the mixture CH_4—CF_4 [10] is similar in form to the function $B(T = T_0)$ of the pure components (Fig. 2). Calculations of the compressibility factor for three compositions of this mixture using the coefficients presented in Table 1 gave the following maximum and rms errors: for the composition 0.25 CH_4, $\delta^{max} = 0.8\%$, $\delta^{mean} = 0.3\%$; for the composition 0.5 CH_4, $\delta^{max} = 0.7\%$, $\delta^{mean} = 0.2\%$; for the composition 0.75 CH_4, $\delta^{max} = 0.8\%$, $\delta^{mean} = 0.2\%$; values of ρ_0 = 28.91, 30.77, 32.87 $kmole/m^3$ and T_B = 505, 493, 490°K were used.

The presence in Eq. (3) of only the second virial coefficient and its high accuracy in describing experimental data permits the conclusion that the problem of its composition reduces to the simple theoretical expression

$$B_{mix} = x_1^2 B_1 + x_2^2 B_2 + 2x_1 x_2 B_{12}. \qquad (7)$$

The values of $B_{12}(T = T_0)$ obtained from Eq. (7) for the mixtures CH_4—CF_4 and nC_4H_{10}—CO_2, shown in Fig. 3, as would be expected, show no composition dependence, while the approximate equation for the mixture CH_4—CF_4

$$B_{12} = 0.6134201 - 1.8497908(1/\theta) - 0.7767527(1/\theta)^2 + $$
$$+ 10.981797(1/\theta)^3 - 19.6017535(1/\theta)^4 + 16.0359707(1/\theta)^5 - 6.4222897(1/\theta)^6 + 1.0194078(1/\theta)^7, \qquad (8)$$

describes the experimental data on compressibility of all three compositions with an error

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*This is also the justification for use of the thermodynamic similarity method for gas mixtures.

not exceeding 1% as a rule. It should be considered that the equations of each of the components produce a contribution to the error in determining data for the mixture.

An interesting consequence of Eq. (3) becomes apparent when it is compared with theoretical equations written with use of the radial distribution function

$$PV = RT + RT\rho \int \frac{dU}{dr} g(r,\ T,\ \rho)\, r^3 dr. \tag{9}$$

At the same time, Eq. (3), which considered the dependence $B(T_0)$, may be written in the form

$$PV = RT + RT\rho \int \frac{dU}{dr} \exp\left[-\frac{U(r)}{kT}(1-\rho/\rho_0)\right] r^3 dr. \tag{10}$$

From this we see that the peculiarities of the thermodynamic surface which were noted above lead to a radial distribution function of the form

$$g(r,\ T,\ \rho) = \exp\left[-\frac{U(r)}{kT}(1-\rho/\rho_0)\right]. \tag{11}$$

The form obtained for g(r, T, ρ) does not contradict the universally known form in which decaying oscillations must appear. It should be noted that all studies concerning determination of the form of g(r) concern only liquids or very dense fluids. At the same time, in the range of gas existence the oscillations in g(r) need not exist, since thermal motion in a gas does not assume the presence of an ordered structure, as was noted in [4]. In connection with this Eq. (11) is then fully valid.

The presence of a simple relationship between g(r) and U(r) opens great possibilities for performing special calculations related to transfer properties, for calculation of higher virial coefficients [16], and for solving a most important applied problem — the determination of the true intermolecular interaction function from data on scattering and macromolecular properties.

In the latter case, known methods of potential inversion [17,18] find direct application. This is true because instead of partially missing and quite inaccurate values of the second virial coefficient, data on any thermodynamic properties, including caloric ones and phase transition curves, may now be used. Use of the entire complex of thermodynamic properties undoubtedly increases the accuracy of U(r) determination.

In conclusion, it should be noted that introduction into the thermodynamics of real gases of the concept of ideal curves is most useful from both practical and theoretical viewpoints.

NOTATION

P, pressure; T, temperature; ρ, density; B and C, second and third virial coefficients, respectively; R, universal gas constant; σ and ε, Lennard-Jones potential parameters; r, intermolecular distance; g, radial distribution function; U, intermolecular interaction energy; N, Avogadro's number; k, Boltzmann's constant.

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A METHOD OF STATISTICAL MODELING TO ESTIMATE THE ERROR IN DETERMINING THE COEFFICIENT OF MOISTURE DIFFUSION

N. I. Gamayunov, R. A. Ispiryan,
and A. A. Sheinman

UDC 536.2.083

A method is considered which connects errors in the measurement of moisture content with the determination of the diffusion coefficient.

The majority of known methods of experimental determination of the coefficient of moisture diffusion require, during their practical implementation, creation in test special conditions such as, e.g., constant moisture content or flux of moisture on the surface, semifiniteness of the medium, and uniformity of the initial distribution. In addition, as is mentioned in [1,2], during the solution of inverse problems insufficient attention is devoted to the error estimate. Often, incorrectly, the errors of direct and inverse problems are taken as identical.

Since existing methods of measurement of moisture fields give large errors, there arises need to work out methods of analysis of experimental data.

The essence of the method being proposed here consists of the following. Let there exist a testpiece of the material in which, as a result of external action, there is created a one-dimensional isothermal process of moisture transfer. We assume that at two points with the coordinates $x = 0$ and $x = l$ we know the dependence of moisture content on time $u(0, \tau) = f_1(\tau)$ and $u(l, \tau) = f_2(\tau)$, and also the distribution $u(x, 0) = g(x)$, referred to a time instant which conditionally is taken as the zero instant.

Usually in a real process the diffusion coefficient varies with time as a consequence of variation of the structure of the material. However, if we choose small time intervals and a thin layer l of the testpiece, then the moisture diffusion coefficient a within this layer can be considered as constant.

Kalinin Polytechnical Institute. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 38, No. 4, pp. 709-715, April, 1980. Original article submitted June 14, 1979.

0022-0841/80/3804-0429$07.50