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GENERALIZED FORM OF THE EQUATION OF STATE OF REAL GASES

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

UDC 536.71

A simple and reliable equation of state is proposed on the basis of an analysis of the geometric structure of the thermodynamic surface. A three-parameter procedure for generalizing the properties of a wide range of nonpolar gases is validated.

One of the most important conditions for the successful use of the theory of thermodynamic similarity to calculate properties of little-studied gases is the existence of a physically sound equation of state common to the materials being considered which has a form giving the correct configuration of thermodynamic surfaces in the range of parameters being investigated.

To construct the equation of state corresponding to the condition indicated above we investigated the thermodynamic surfaces of a large number of technically important gases. The equation of the state surface can be written in the general form

$$X = X_0(T) + \Delta X(T, \rho), \quad (1)$$

where $X_0(T)$ is the ideal-gas component of the property X and $\Delta X(T, \rho)$ is a function which takes account of the difference between the properties of the real and ideal gas. The latter can be written in the form of a virial series. Then when $X = \rho V$, Eq. (1) has the form

$$\rho V = RT + RTB\rho + RTC\rho^2 + \dots \quad (2)$$

Lines on the state surface along which the properties of a real gas coincide with those of an ideal gas at those same temperatures are called ideal curves. These include curves of minima on isotherms of various properties $(\partial \Delta X / \partial \rho)_T = 0$ (Boyle, inversion, Joule curves), ideal curves $\Delta X = 0$ (curves of an ideal gas, ideal enthalpy, ideal internal energy).

In spite of the different meaning which is commonly inserted into the definitions of these properties (thermal, caloric) they have a number of common, not always obvious, regularities which are manifested only in the combined processing of experimental data. We have noted [2] that the ideal curves $\Delta pV = 0$, $\Delta H = 0$, $\Delta U = 0$ in the coordinates (T, ρ) are isomorphic, i.e., they are characterized by the repetition of configurations; the same applies to the curves $(\partial \Delta pV / \partial \rho)_T = 0$, $(\partial \Delta H / \partial \rho)_T = 0$, and $(\partial \Delta U / \partial \rho)_T = 0$. In addition, ideal curves of various properties are connected by thermodynamic relations which result from the coincidence of the lines $\Delta pV = 0$ and $(\partial \Delta F / \partial \rho)_T = 0$, $(\partial \Delta pV / \partial T)_\rho = 0$ and $(\partial \Delta U / \partial \rho)_T = 0$, $(\partial \Delta H / \partial \rho)_T = 0$ and $(\partial \Delta pV / \partial T)_\rho = 0$. In addition, it should be noted that the ideal curves $\Delta X = 0$ are rectilinear in the coordinates T, ρ , and when extended to $T = 0$ intersect at the common density ρ_0 [1], which as shown by one of the authors [10] can be identified with the density of the ideal unstressed crystal at 0°K. And finally, the most important fact: the curves $\Delta pV = 0$, $\Delta H = 0$, $\Delta U = 0$ belong to the extensive family of curves which satisfy the condition [1]

$$\frac{\partial}{\partial T} [\Delta pV \cdot T^n]_\rho = 0, \quad (3)$$

or

$$\frac{1}{n} \left(\frac{\partial \Delta pV}{\partial T} \right)_\rho = - \frac{\Delta pV}{T}, \quad (4)$$

Physicochemical Institute, Academy of Sciences of the Ukrainian SSR. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 37, No. 4, pp. 699-704, October, 1979. Original article submitted February 20, 1979.

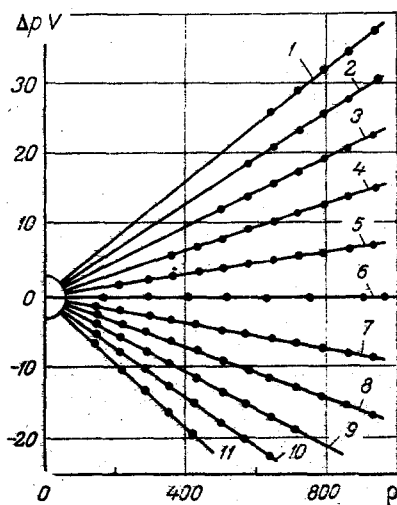


Fig. 1. Ideal curves $T_0(n) = \text{const}$ on the state surface of argon according to data of [9]: 1) $T = 602^\circ\text{C}$; 2) 564.6; 3) 526.1; 4) 490.6; 5) 445.8; 6) 407.8; 7) 367.6; 8) 326.7; 9) 285.4; 10) 243.1; 11) 201.8°K .

where n is a parameter which is constant for each curve. This is easy to see by using (2) and (4) to write

$$B = -\frac{T}{n+1} \frac{dB}{dT}, \quad (5)$$

from which it is clear that $n = \pm\infty$ corresponds to the curve for an ideal gas having the Boyle temperature ($B = 0$) at its origin, and $n = -2$ gives the condition for the temperature inversion $dB/dT = B/T$; similarly for $n = -1$ $dB/dT = 0$ ($\Delta U = 0$). For other values of n (both negative and positive) condition (4) corresponds to an ideal curve, as can be seen by rewriting Eq. (4) in the form

$$T \left(\frac{\partial P}{\partial T} \right)_\rho + nP = RT\rho + nRT\rho, \quad (6)$$

where $RT\rho$ is the pressure of an ideal gas. The above noted relations which are characteristic for the curves $\Delta X = 0$ are also valid for these curves [2]; i.e., the equation of curves (4) in the coordinates T, ρ has the form

$$T = T_0(n)(1 - \rho/\rho_0). \quad (7)$$

On the other hand, since there are no restrictions on the choice of the values of the variables T, ρ , and n , we can conclude that Eq. (4) is one of the forms representing a thermodynamic surface consisting of the family of ideal curves (4). In subsequent arguments instead of the parameter n we shall use the quantity $T_0 = T/(1 - \rho/\rho_0)$, which is constant along a line on the state surface characterized by Eqs. (4) and (6).

An analysis of experimental data on a large number of well-studied gases (the inert gases, $\text{CO}_2, \text{N}_2, \text{CH}_4, \text{C}_2\text{H}_6$, and many others) showed that the lines for a constant value of T_0 are rectilinear in the coordinates pV, ρ ($\Delta pV, \rho$) (Fig. 1). This fact permits a nontrivial conclusion to be drawn about the geometric structure of the thermodynamic surface.

Since the observed features are characteristic over the whole range of parameters of the gaseous phase, and the state surface of nonpolar gases can be represented as a family of ideal curves, i.e., each point of the surface lies on an ideal curve characterized by its values of T_0 and the density ρ_0 which is the same for all curves, the rectilinearity of the ideal curves shows that the thermodynamic surface in the coordinates $(\Delta pV, T, \rho)$ is a ruled surface. The equation of state of a real gas having such a ruled surface can be obtained from (2) by introducing into it Eqs. (3) and (7).

Omitting some simple transformations, we write finally

$$pV = RT \left[1 + B(T_0) \frac{\rho}{1 - \rho/\rho_0} \right] \quad (8)$$

or, introducing the dimensionless quantities $Z = pV/RT, \Theta = T_0/T_B, \omega = \rho/\rho_0, B^* = B\rho_0,$

$$Z = 1 + B^*(\Theta) \frac{\omega}{1 - \omega}. \quad (9)$$

As a result of choosing the reduced density ρ_0 as a parameter, all the ideal curves in the coordinates (T, ω) have their origin at the point $\omega = 1$.

As a consequence of this form of the equation of state stringent demands are imposed on the accuracy of B^* , yet the values of the second virial coefficient for a rarefied gas determined from Eq. (2) admit an appreciable arbitrariness as a result of the small value of the density, which is then compensated by the arbitrariness in the determination of the higher virial coefficients. Therefore, the problem of setting up the equation of state in the form (9) is reduced to that of determining B^* as a function of Θ with an error of 0.1-0.2%. For well-studied nitrogen an equation of state in the form (9) was set up with $T_B = 325.68^\circ\text{K}$, $\rho_0 = 1125.3 \text{ kg/m}^3$, and $B^*(\Theta) = 1431.2135 + 11.703751(1/\Theta) - 1956.5272(1/\Theta)^2 - 170.84099(1/\Theta)^3 + 1316.0277(1/\Theta)^4 - 808.62325(1/\Theta)^5 + 193.33084(1/\Theta)^6 - 16.396136(1/\Theta)^7$ describing the data of [3, 4] with an error, except for a rare exception, not exceeding 0.5% in the 100-1000°K range, and up to a density of the order of $2.0\rho_k$. Similar results obtained for Ar, CO_2 , and CH_4 lead to the conclusion that this form of the equation of state is universal for materials of simple molecular structure with a zero or small dipole moment.

In speaking of the similarity of a group of gases whose thermodynamic surfaces exhibit the above-mentioned regularities and are described by Eq. (9), it must be remembered that ruled surfaces are affine. The characteristic feature of such a surface is that for $\Theta, \omega = \text{idem}$, straight lines identified with the ideal curves (3) coincide for equal values of the coordinates of the origins and slopes. In the present case the coordinates of the origins are $\Delta pV = 0, \omega = 0$, and the slope is

$$\beta = R\Theta B^*(\Theta). \quad (10)$$

Thus, the problem is reduced to that of obtaining identical values of $B^*(\Theta)$ for the same values of Θ . By writing the second virial coefficient in terms of the notation introduced:

$$B^*(\Theta) = -\frac{2}{3}\pi N\rho_0 \int_0^\infty \left[\exp\left(-\frac{\mathcal{U}^*(r)}{\Theta}\right) - 1 \right] r^2 dr, \quad (11)$$

where $\mathcal{U}^* = \mathcal{U}/kT_B$, it follows that this is possible only if the intermolecular potentials of the interaction of the materials being compared are conformal with respect to the potential parameters which are uniquely related to the temperature T_B and the density ρ_0 .

It is appropriate to compare Eq. (8) with van der Waals equation, which gives qualitatively all the above noted characteristics of the ideal curves (3). From van der Waals equation in the form $pV = RT/(1 - bp) - ap$ for $T_0 = T/(1 - bp) = \text{const}$, we obtain

$$\left(\frac{\partial pV}{\partial p} \right)_{T_0} = -a, \quad (12)$$

i.e., the ideal curves (3) in the coordinates (pV, ρ) are parallel. Similarly from (8) we find

$$\left(\frac{\partial pV}{\partial p} \right)_{T_0} = RT_0 \left(B - \frac{1}{\rho_0} \right), \quad (13)$$

from which it follows that the difference between a real and a van der Waals gas can be reduced to the difference in slopes of their ideal curves in (pV, ρ) coordinates. In addition, by comparing Eqs. (12) and (13) and taking account of the physical meaning of the quantities appearing in them, it can be seen that the slope of the ideal curves is determined by the attractive part of the interaction potential. Hence it follows that the similarity of a broad range of real gases is related primarily to the conformity of the part of the potential describing the attraction between molecules. The arguments presented are additional evidence of the validity of the conclusions reached in [5].

On the basis of independent considerations it was shown in [6, 7] that in choosing T_B and ρ_0 as reference parameters the equations of state of the material being investigated (subscript i) and the reference material (subscript r) for Θ and $\omega = \text{idem}$, can be written in the form

$$\Delta Z_i = A\Delta Z_r, \quad (14)$$

where according to (9) the similarity parameter

TABLE 1. Value of Similarity Parameter A along Boyle Curves

$\tau^{B.c}$	Ar	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	iC ₄ H ₁₀	Air	N ₂ -C ₂ H ₆			CH ₄ -iC ₄ H ₁₀
									$x=0,2733$	$0,5244$	$0,7318$	$x=0,27703$
									$\rho_0, \text{ kg/m}^3$			
	1837	574,5	780	738,5	851	818	858,7	1208	846	921	959	826
	407,1	508,3	720,2	774,85	897,9	904,05	968,6	343,1	645,4	534,4	453,25	863,1
0,42	0,93	0,91	1,04	—	—	—	—	—	—	—	—	—
0,44	0,93	0,90	1,05	1,05	1,15	1,16	1,27	0,97	—	—	—	—
0,46	0,93	0,91	1,05	1,05	1,15	1,16	1,27	0,97	—	—	—	—
0,48	0,93	0,91	1,04	1,05	1,15	1,16	1,26	0,98	—	—	—	1,18
0,50	0,93	0,91	1,04	1,04	1,14	1,15	1,26	0,99	1,05	—	—	1,18
0,52	0,93	0,91	1,04	1,05	—	—	1,25	1,00	1,06	1,04	—	1,18
0,54	0,93	0,91	1,03	1,04	—	—	1,25	0,99	1,05	1,03	—	1,17
0,56	0,93	0,91	1,03	—	—	—	1,26	0,99	1,07	1,04	—	1,18
0,58	0,93	0,90	1,02	—	—	—	1,24	0,98	1,07	1,05	0,95	1,17
0,62	0,93	0,91	—	—	—	—	—	—	1,07	1,05	0,95	—
0,66	0,92	0,91	—	—	—	—	—	—	1,06	1,05	0,95	—
0,70	0,93	0,90	—	—	—	—	—	—	1,05	1,02	0,94	—
A	0,93	0,91	1,04	1,05	1,15	1,16	1,26	0,99	1,06	1,04	0,95	1,18

$$A = \frac{B_i^*(\theta)}{B_r^*(\theta)} \quad (15)$$

in general can depend on θ . However, in the theory of L. P. Filippov [5] based on calculations with an atom-atom potential model it is found that the parameter A, related to the nonconformality of attractive potentials, must be a constant characteristic of the molecular structure. In this case the relative value of A is considered for the materials under study; the parameter A is taken equal to 1 for the reference gas nitrogen. We investigate the character of the variation of the similarity parameter A along particular lines on the state surface. For a Boyle curve $(\partial \Delta Z / \partial \omega)_T = 0$ we find from Eq. (11)

$$\Delta Z^{B.c} = -\theta \frac{dB^*(\theta)}{d\theta} \cdot \frac{\omega^2}{1-\omega},$$

i.e.,

$$A = \frac{\Delta Z_i^{B.c}}{\Delta Z_0^{B.c}} = \frac{(dB^*/d\theta)_i}{(dB^*/d\theta)_r} \quad (16)$$

Similarly on an inversion curve $(\partial \Delta Z / \partial T)_P = 0$ and

$$\Delta Z^{I.c} = \left[\theta \frac{dB^*(\theta)}{d\theta} + \omega \theta^2 \frac{d^2 B^*(\theta)}{d\theta^2} \right] \frac{\omega}{1-\omega},$$

$$A = \frac{(dB^*/d\theta)_i + \omega \theta (d^2 B^*/d\theta^2)_i}{(dB^*/d\theta)_r + \omega \theta (d^2 B^*/d\theta^2)_r} \quad (17)$$

It follows from Eqs. (15), (16), and (17) that for $\theta, \omega = \text{idem}$ the parameter A is independent of θ and ω . This can also be deduced by investigating the equations for dimensionless values of the enthalpy and internal energy:

$$\frac{\Delta H}{RT_B} = \theta B^*(\theta) - 2\tau B^*(\theta) + \tau B^*(\theta)_{\theta=\tau}, \quad (18)$$

$$\frac{\Delta U}{RT_B} = \tau B^*(\theta) - B^*(\theta)_{\theta=\tau}. \quad (19)$$

We have calculated the values of A for a number of materials by using the data of [8] along Boyle curves (Table 1). Well-studied nitrogen was taken as a reference material. It is clear from Table 1 that the variation of A along Boyle curves is negligible; i.e., with the average values of this parameter listed in the last row the thermodynamic surfaces of the gases considered can be described to an acceptable accuracy.

In conclusion it should be noted that since the similarity parameter is independent of θ and ω it can be determined from limited information on the thermodynamic properties of simple nonpolar gases.

NOTATION

T, temperature; p, pressure; V, volume; ρ , density; R, gas constant; B, second virial coefficient; H, enthalpy; U, internal energy; r, intermolecular distance; \mathcal{U} , intermolecular potential function.

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TEMPERATURE DISTRIBUTION IN A ROTATING HOLLOW CYLINDER

I. A. Ignashov and V. A. Bystroumov

UDC 536.24.02

The temperature distribution in a hollow cylinder rotating with a given angular velocity is found for steady-state boundary conditions of the first kind.

We consider an infinitely long cylinder whose radial cross section is a doubly connected region S bounded on the outside by contour L (a circle of radius R) and on the inside by contour L_0 (a circle of radius R_0). A certain portion of the outer surface of the cylinder is in contact with a strip of hot metal translating with a velocity V. As a result of the contact with the moving strip the cylinder rotates about a fixed axis with an angular velocity $\omega = V/R$. The cylinder receives heat by contact, convective, and radiant heat transfer. At time $t = 0$ when the thermal process begins, a liquid enters the channel of the cylinder under turbulent conditions and maintains the temperature of the inner surface constant. The temperature on contour L at $t = 0$ is established instantaneously and does not change with time in the XOY system (Fig. 1); the initial temperature in the volume of the cylinder is assumed constant. It is required to find the temperature distribution in the cylinder at any time $t > 0$.

The temperature at the boundary is a continuous periodic function of points on contour L, and can be represented in the XOY system by a Fourier series:

$$\Theta(l, \varphi) = \bar{\Theta} + \sum_{n=1}^{\infty} [\beta_n \sin(n\varphi) + \gamma_n \cos(n\varphi)], \quad (1)$$

$$\Theta(\rho_0, \varphi) = \Theta_1; \quad \Theta(\rho, \varphi, Fo) \Big|_{Fo=0} = \Theta_2. \quad (2)$$

The required temperature which satisfies boundary condition (1) and the initial condition (2) is determined by solving the heat-conduction equation

$$\frac{\partial^2 \Theta}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial \Theta}{\partial \rho} + \frac{\partial^2 \Theta}{\partial \varphi^2} = Pd \frac{\partial \Theta}{\partial \varphi} + \frac{\partial \Theta}{\partial Fo}. \quad (3)$$