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

\[ X = X_0(T) + \Delta X(T, \rho), \]  

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

\[ \rho V = RT + RTB_0 + RTC_0 + \ldots. \]  

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 \( \Delta \rho V = 0, \Delta H = 0, \Delta U = 0 \) in the coordinates \((T, \rho)\) are isomorphic, i.e., they are characterized by the repetition of configurations; the same applies to the curves \((\partial \Delta \rho V/\partial \rho)_T = 0, (\partial \Delta H/\partial \rho)_T = 0, (\partial \Delta U/\partial \rho)_T = 0\). In addition, ideal curves of various properties are connected by thermodynamic relations which result from the coincidence of the lines \( \Delta \rho V = 0 \) and \((\partial \Delta F/\partial \rho)_T = 0, (\partial \Delta \rho V/\partial T)_\rho = 0 \) and \((\partial \Delta U/\partial \rho)_T = 0, (\partial \Delta H/\partial \rho)_T = 0 \). In addition, it should be noted that the ideal curves \( \Delta X = 0 \) are rectilinear in the coordinates \( T, \rho \), and when extended to \( T = 0 \) intersect at the common density \( \rho_0 \) [1], which is shown by one of the authors [10] can be identified with the density of the ideal unstressed crystal at \( 0^\circ K \). And finally, the most important fact: the curves \( \Delta \rho V = 0, \Delta H = 0, \Delta U = 0 \) belong to the extensive family of curves which satisfy the condition [1]

\[ \frac{\partial}{\partial T} \left[ \Delta \rho V \cdot T^n \right]_\rho = 0, \]  

or

\[ \frac{1}{n} \left( \frac{\partial \Delta \rho V}{\partial T} \right)_\rho = - \frac{\Delta \rho V}{T}. \]
Fig. 1. Ideal curves $T_0(n) = \text{const}$ on the state surface of argon according to data of [9]: 1) $T = 602.1$; 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°C.

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

$$B = -\frac{T}{n+1} \frac{dB}{dT},$$

from which it is clear that $n = \infty$ 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

$$T \left( \frac{\partial p}{\partial T} \right) + nP = RTp + nRTp,$$

where $RTp$ 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 $T, p$ has the form

$$T = T_0(n)(1 - p/p_0).$$

On the other hand, since there are no restrictions on the choice of the values of the variables $T, p$, 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 $T_0 = T/(1 - p/p_0)$, 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, CO$_2$, N$_2$, CH$_4$, C$_2$H$_6$, and many others) showed that the lines for a constant value of $T_0$ are rectilinear in the coordinates $pV, p (\Delta pV, \rho)$ (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 $\rho_0$ 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

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

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

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