# FORM OF THE GENERALIZED THERMODYNAMIC SURFACE OF REAL GASES

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Features of the geometric structure of thermodynamic surfaces of nonpolar nonassociative gases and liquids are considered to produce an effective generalization.

Study of single-parameter families of isochoric ideal curves satisfying the condition

$$\left[\frac{\partial}{\partial T}(pv - RT)\,T^n\right]_\rho = 0, \tag{1}$$

where n is a parameter defining the concrete ideal curve, has shown [1, 2] the desirability of transition from representation of the thermodynamic surface in the space (P, v, T) to the space (pv, ρ, T), for in the latter case the form of the surface simplifies and approaches linearity. This is immediately evident in the case of an ideal gas, for which the thermodynamic surface becomes a plane perpendicular to the ρ axis.

A simple model for real materials is the van der Waals gas, the equation of state of which has the form

$$Z = 1 + \left(1 - \frac{1-\omega}{\tau}\right)\frac{\omega}{1-\omega}. \tag{2}$$

Here $\omega = \rho/\rho_0$, $\tau = T/T_B$ (where $T_B$ is the Boyle temperature, $\rho_0$ is the density corresponding to extrapolation of the line Z = 1, the ideal gas curve,* to T = 0, and for a van der Waals gas $T_B = a/Rb$ and $\rho_0 = 1/b$).

Transforming to the space (pv, ρ, T) in the reduced coordinates $\omega, \tau, \psi = pv/RT_B$, we obtain from Eq. (2)

$$\omega^2 + \psi\omega - \omega - \psi + \tau = 0. \tag{3}$$

As can easily be seen by finding the invariants of this system relative to rotation and parallel translation of the coordinate system, it is a hyperbolic paraboloid [3].

It should be noted immediately that because of the rectilinearity of the ideal gas curve intrinsic to the van der Waals model ($\tau = 1 - \omega$) Eq. (2) allows the single-parameter generalization

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*At present there is no unified opinion as to what this curve should be called. In Soviet literature one finds most often the term "ideal gas curve" (É. É. Shpil'rain and P. M. Kessel'man, Fundamentals of the Theory of Thermophysical Properties of Materials, Ya. Z. Kazavchinskii, Lectures on Thermodynamics, A. A. Vasserman, Ya. Z. Kazavchinskii, V. A. Rabinovich, Thermophysical Properties of Air and Its Components, L. P. Filippov, Similarity of Properties of Matter, etc. Occasionally one meets the term introduced by A. I. Bachinskii, "orthometric curve," as well as "ideal curve" (M. P. Vukalovich, I. I. Novikov, The Equation of State of a Real Gas).

In Western literature the curve is called the classical ideal curve (Morsey, Shtraub, Shoeber), the unitary compressibility curve (Holleran), the zeroth-order characteristic curve (Brown, Stefanson) and even, on one occasion, the Boyle curve (Pauls). This last term is erroneous, since it should be applied to the curve formed by minima of the compressibility isotherms.

We will use the term "ideal gas curve," because the equation of this line formally coincides with the equation of state of an ideal gas.

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$$Z=1+A\left(1-\frac{1-\omega}{\tau}\right)\frac{\omega}{1-\omega}, \tag{4}$$

where the individual parameter $A > 0$. To this equation there corresponds a continuous family of hyperbolic paraboloids which intersect along the ideal gas curve. Since the ideal gas curve is rectilinear for the entire class of nonpolar nonassociative substances and in the reduced coordinates is the line of intersection of their thermodynamic surfaces [4], Eq. (4) is an analytical expression of a single-parameter law of corresponding states, which has been established empirically for just this class of materials [5].

As is well known [3], the hyperbolic parabolid has two pairs of rectilinear directrices, described in the canonical variables (x, y, z) by the systems of equations

$$x-y=\mu \qquad x+y=\lambda$$

and

$$x+y=\frac{2z}{\mu} \qquad x-y=\frac{2z}{\lambda}. \tag{5}$$

It is important to clarify what real physical lines on the thermodynamic surface correspond to these directrices.

By performing parallel translation and rotations of the coordinate system after several simple but lengthy transformations, for the thermodynamic surface of a Van der Waals gas in the generalized form of Eq. (4) we obtain the following equations relating the canonical variables to $\omega$, $\psi$, and $\tau$:

$$\begin{aligned} x&=\left(A+\frac{1}{4}\right)(\omega-1)+\psi+(A-1)\tau,\\ y&=\left(A-\frac{1}{4}\right)(\omega-1)+\psi+(A-1)\tau,\\ z&=\frac{A}{2}(\omega-1)-\frac{A}{2}\tau. \end{aligned} \tag{6}$$

Then the first pair of directrices corresponds to linear isochors

$$\begin{aligned} \omega&=2\mu+1,\\ \psi&=-A\mu\left(2+\frac{1}{\mu}\right)-\left(A-1+\frac{A}{2\mu}\right)\tau. \end{aligned} \tag{7}$$

The second pair of directrices is described by the equtions

$$\begin{aligned} \tau&=\left(1+\frac{\lambda}{2A}\right)(1-\omega);\\ \psi&=\left(1+\frac{\lambda}{2A}\right)+\left[(A-1)\left(1+\frac{\lambda}{2A}\right)-A\right]\omega, \end{aligned} \tag{8}$$

which correspond to the equations of [1, 2] for the ideal curves of Eq. (1), obtained by processing of experimental thermal data, with each ideal curve characterized by a parametric temperature equal to $\Theta = 1 + \lambda/2A$.

Thus, the generalized van der Waals equation (4) in the space (pV, $\rho$, T) corresponds to thermodynamic surfaces in the form of a continuous family of hyperbolic paraboloids formed by either rectilinear isochors or rectilinear ideal curves, Eq. (1). If we assume that the ideal curves of real materials are rectilinear, then it is natural to replace the expression in brackets in Eq. (4), which is the second virial coefficient of the van der Waals gas as a function of parametric temperature $\Theta = \tau/(1 - \omega)$, by the real second virial coefficient $B(\Theta)$. This leads to the equation of state of [1], while the parameter A coincides with the Holleran parameter $k_B = \rho_0 V_B$ (where $V_B = (TdB/dT)T_B$ is the Boyle volume).

However, it should be considered that for real materials rectilinear isochors do not exist, and the ideal curves can only approximately be considered rectilinear. Then it is logical to assume that the value A is a function of temperature and density, and maintain the expression in brackets in Eq. (4) unchanged in order to agree with the reliably determined experimental fact of rectilinearity of the ideal gas curve. It should be noted that direct determination of the functional dependence $A = A(\tau, \omega)$ from p-, v-, T-data is in itself a complex problem, since solution of Eq. (4) for A is quite sensitive to the accuracy of the thermal data, especially at low densities and high temperatures. Thus, for example, for argon at 150°K and density $\omega = 0.05$ the uncertainty in calculation of A with thermal data defined to an accuracy of 0.1-0.3% comprises 2-3%, but at 300°K and the same density the uncertainty reaches 10%, with increase in density to $\omega = 0.2$ reducing this value only to ~6%. If we consider that values of A determined from thermal data at $T > (1.2\text{-}1.5)T_{cr}$ along isotherms vary within limits of +5%, it is evident that the general pattern of the dependence of A on $\omega$ is quite distorted.

This fact permits use of the assumption that A is a function of temperature only, and taking $A = \alpha\tau^{-1/8}$, from Eq. (4) we can obtain the equation of state of [6], which permits calculation of thermodynamic properties of gases at $T > (1.2\text{-}1.5)T_{cr}$ with high accuracy. However, at $T < 1.5T_{cr}$ the function $A = A(\omega)$ has been traced quite well, with A decreasing at low densities, reaching a minimum at $\omega \approx 0.25\text{-}0.35$, and then increasing somewhat, remaining practically constant at $0.4 < \omega < 0.6$. We note that at $0.95 < T/T_{cr} < 1.5$ the ideal gas curve experiences a "diffused" break and becomes straight only in the liquid region. This makes use of equations of the form of Eq. (4) in this temperature interval improper, since the equation describes a linear dependence of temperature upon density along the ideal gas curve.

Substituting Eq. (4) in Eq. (1) yields

$$\tau = \frac{nA + \tau(\partial A/\partial\tau)_\omega}{(n+1)A + \tau(\partial A/\partial\tau)_\omega}(1-\omega). \tag{9}$$

The factor before $(1-\omega)$ may be constant along the ideal curve, if A is a homogeneous function of temperature, i.e., $A = \alpha\tau^\beta$. This condition corresponds to rectilinear projections of the ideal curve on the plane $(T, \rho)$ while the parametric temperature for each ideal curve is defined by the relationship

$$\Theta = \frac{n+\beta}{n+\beta+1}. \tag{10}$$

Values of $\Theta$ calculated with this relationship for various values of n agree with results obtained using a high accuracy empirical equation of state from [7] for nitrogen within the limits of accuracy of their definition in the temperature interval $200 \le T \le 1000$°K.

However, in this case the projections of the ideal curve on the planes $(pV, \rho)$ and $(pV, T)$ are nonlinear. In fact, from Eq. (4), it follows that

$$\psi = \Theta + [\alpha\Theta^\beta(\Theta-1)(1-\omega)^\beta - \Theta]\,\omega. \tag{11}$$

From this it is evident that the slope of the projection of the ideal curve on the plane $(\psi, \omega)$ is a function of density, but in view of the smallness of $\beta$ in a limited region of states the curvature of the ideal curve is small, which permits assuming the thermodynamic surface linear at least within this region.

We note that according to [8] the internal pressure from Eq. (4) is defined as a quadratic function of density $\pi_i = A\omega^2$. This corresponds to assumption of an equiprobable distribution of molecules in space, the basis of the van der Waals theory, and thus has definite limitations. However, these limitations involve the low pressure range, and are obviously related to formation of molecular associations. In fact, because of formation of the latter, it becomes impossible to speak of an equiprobable distribution of molecules and the internal pressure will be determined by the number of associations; consequently, the value of A will depend on density. It is then natural to expect that the maximum number of associations will occur at densities close to critical, and since for nonpolar substances the latter is equal to $\omega_{cr} \approx 0.25\text{-}0.29$, it is in this region or somewhat further that minima are found in the curves $A = A(\tau, \omega)$ at $T < (1.2\text{-}1.5)\,T_{cr}$.

A second limitation is related to development of close order in the spatial distribution of molecules at high density, which also leads to change in the character of the dependence of internal pressure on density, which approaches a lattice dependence [8]. The corresponding transition is observed at densities $\omega \approx 0.5$-$0.6$ and it should be noted that curvature of the ideal gas curve takes place at just such densities. Nevertheless, on the whole this does not change the structure of Eq. (4) and substitution of the expression for A following from lattice internal pressure [8] leads to the equation of state of a liquid of [9], which can be written in the form

$$\pi = \tau\omega + \gamma(\tau)\omega^3(\omega + 1)(\tau + \omega - 1), \tag{12}$$

where $\pi = p/RT_B\rho_0$; $\gamma(\tau)$ is a function of temperature only.

If we take for $\gamma$ just as for A, a power dependence on temperature, then it follows from Eq. (12) that the ideal curves have linear projections on the plane (T, $\rho$), but their projections on the planes ($\rho$V, $\rho$) and (PV, T) will be nonlinear. Nevertheless, over a quite wide range of states the deviations from a linear dependence are small, which permits use of the approximation of a linear thermodynamic surface for the liquid state as well [10]. It should be noted that Eq. (12) is equally applicable to a liquid and a dense gas. The only differences are the parameters $\rho_0$ and $T_B$ and the coefficients $\alpha$ and $\beta$ for the power dependence of the function $\gamma = \gamma(\tau)$.

## NOTATION

P, pressure; v, specific volume; $\rho$, density; T, temperature; $Z = P/RT\rho$, compressibility coefficient; $\omega$, $\tau$, $\pi$, dimensionless density, temperature, and pressure; $a$ and b, constants in van der Waals equation; B, second virial coefficient.

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