METHOD OF CONSTRUCTING EMPIRICAL EQUATIONS OF STATE

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A method is described for approximation of the equation of state $p = p(\rho, T)$ in the form of a double polynomial by the method of least squares.

We understand a relationship between three thermodynamic quantities, $p = p(\rho, T)$, say, to be the equation of state of a homogeneous substance. Two methods exist for setting up this relationship.

1. A theoretical method permitting a deduction to be made about the behavior of the substance on the basis of the behavior of the separate atoms or molecules by using statistical mechanics.

2. An empirical method permitting a mathematical relationship to be obtained by using thermodynamic experimental results.

We obtain more exact results by using the second method in the presence of appropriate thermodynamic data.

It has been established by a careful analysis of available mathematical forms of the equations that the form

$$\frac{p}{\rho RT} = z = 1 + \rho \sum_{i=1}^{I_{\max}} \sum_{j=1}^{J_{\max}(i)} \tilde{\alpha}_{ij} \left(\frac{1}{T_c} - \frac{1}{T} \right)^{j-1} (\rho - \rho_c)^{i-1}, \tag{1a}$$

is most suitable for the solution of the problem on an electronic digital computer, where $\tilde{\alpha}_{ij}$ are coefficients. The subscript c denotes the critical state.

The dimensionless form is

$$\frac{\beta}{\omega I \vartheta} = 1 + \omega \sum_{i=1}^{I_{\max}} \sum_{j=1}^{J_{\max}(i)} \alpha_{ij} \tau^{j-1} \xi^{i-1}, \tag{1b}$$

where $\beta = p/p_c$; $\omega = \rho/\rho_c$; $\vartheta = T/T_c$; $I = RT_c\rho_c/p_c$; $\tau = 1 - 1/\vartheta$; $\xi = \omega - 1$.

This form of the equation is none other than a modification of the virial form with a finite number of terms

$$z = 1 + B(T)\rho + C(T)\rho^2 + \cdots, \tag{2}$$

where $B(T)$, $C(T)$ . . . are virial coefficients.

Stein [1] used the form (1b) in 1965. However, he did not succeed in extending the result to the liquid phase domain. Moreover, the Maxwell criterion was not satisfied.

Introduction of the variables ξ and τ facilitates compliance with the critical conditions since they become zero at the critical point and the majority of terms of the function hence drop out.

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The standard critical conditions are the following:

$$\left(\frac{\partial\beta}{\partial\omega}\right)_{\substack{v=1\\ \omega=1}} = 0; \qquad \left(\frac{\partial^2\beta}{\partial\omega^2}\right)_{\substack{v=1\\ \omega=1}} = 0;$$

$$(\beta)_{\substack{v=1\\ \omega=1}} = 1; \qquad \left(\frac{\partial\beta_s}{\partial\vartheta}\right)_{\substack{v=1\\ \omega=1}} = a_c,$$

where β_s is the saturation pressure. Application of these conditions to (1b) permits determination of the following coefficients

$$\alpha_{1,1} = (1 - I)/I; \ \alpha_{2,1} = (I - 2)/I; \ \alpha_{3,1} = (3 - I)/I; \ \alpha_{1,2} = (a_c - 1)/I.$$

By using known thermodynamic laws an equation of state for all the other state parameters can be derived from the determined equation of state, $\beta = \beta(\omega, \vartheta)$, say. If some equation exists in an appropriate potential form, then all the subsequent state parameters can be calculated therefrom by ordinary differentiation. Hence, it is recommended to reduce the initial equation to an appropriate potential form, called the canonical equation. The Helmholtz potential form (the specific free energy) f is applicable for the independent variables v and T. This potential is obtained from the equation $\beta = \beta(\omega, \vartheta)$ by means of the following transformation:

$$\varphi = f\rho_c/p_c = \int\limits_{\omega=0}^{\omega=\omega} \frac{\beta(\omega, \vartheta)}{\omega^2}\, d\omega + \varphi_{\mathrm{id}}^{1\mathrm{atm}}(\vartheta) + I\vartheta\left[\ln \frac{Ip_c\vartheta\omega}{1\ \mathrm{atm}} - [\ln \omega]_0^{\omega}\right], \tag{3}$$

where $\varphi_{\mathrm{id}}^{1\mathrm{atm}}(\vartheta)$ is the dimensionless form of the Helmholtz potential in the ideal gas state at a 1 atm pressure, and this potential is a pure function of the temperature and should be known. Application of the transformation (3) for equation (1b) leads to the expression

$$\varphi = \varphi_{\mathrm{id}}^{1\mathrm{atm}}(\vartheta) + I\vartheta\left[\sum_{i=1}^{I_{\max}}\left(\sum_{j=1}^{J_{\max}(i)} \alpha_{ij}\tau^{j-1}\right)\frac{1}{i}\,[\xi^i - (-1)^i] + \ln \frac{Ip_c\vartheta\omega}{1\ \mathrm{atm}}\right]. \tag{4}$$

Hence, all the state parameters are easily computed by means of appropriate differentiation:

the pressure p (equation (5) corresponds to (1b)):

$$\beta = p/p_c = \omega^2\left(\frac{\partial\varphi}{\partial\omega}\right)_v = \omega^2\vartheta I\left[\sum_{i=1}^{I_{\max}}\left(\sum_{j=1}^{J_{\max}(i)} \alpha_{ij}\tau^{j-1}\right)\xi^{i-1} + 1/\omega\right], \tag{5}$$

the specific entropy s:

$$\sigma = s\rho_c T_c/p_c = -\left(\frac{\partial\varphi}{\partial\vartheta}\right)_\omega = -\frac{\partial\varphi_{\mathrm{id}}^{1\mathrm{atm}}}{\partial\vartheta} - I\left[\sum_i\left(\sum_j \alpha_{ij}\tau^{j-1}\right)\frac{1}{i}\right.$$
$$\left.\times [\xi^i - (1)^i] + \ln \frac{Ip_c\vartheta\omega}{1\ \mathrm{atm}}\right] - I\vartheta\left[\frac{1}{\vartheta^2}\sum_i\left[\sum_j \alpha_{ij}(j-1)\tau^{j-2}\right]\frac{1}{i}\,[\xi^i - (-1)^i] + \frac{1}{\vartheta}\right], \tag{6}$$

the specific enthalpy h:

$$\varepsilon = hp_c/p_c = \varphi + \beta/\omega + \vartheta\sigma, \tag{7}$$

the isochoric specific heat c_v:

$$c_c T_c \rho_c/p_c = -\vartheta\left(\frac{\partial^2\varphi}{\partial\vartheta^2}\right)_\omega = \vartheta\left(\frac{\partial\sigma}{\partial\vartheta}\right)_\omega$$
$$= -\vartheta\,\frac{\partial^2\varphi_{\mathrm{id}}^{1\ \mathrm{atm}}}{\partial\vartheta^2} - I - \frac{I}{\vartheta^2}\left[\sum_i\left[\sum_j \alpha_{ij}(j-1)(j-2)\tau^{j-3}\right]\frac{1}{i}\,[\xi^i - (-1)^i]\right], \tag{8}$$

the Gibbs potential (the specific free enthalpy) g:

$$g\rho_c/p_c = \varphi + \beta/\omega. \tag{9}$$

Let us present a brief description of the approximation method to determine the coefficients α_{ij}.

It is a question of the general problem of mathematically determining a surface $F = F(x, y)$ in space, which is given by a set of experimental points x_1, y_1, f_1 and the weight w_1. The surface should be determined by the sum:

$$F(x,\ y)=\sum_{i=1}^{I_{\max}}\ \sum_{j=J_{\min}^{(i)}}^{J_{\max}^{(i)}}\alpha_{ij}q_{ij}(x,\ y). \tag{10}$$

The forms of the functions q_{ij} should be given for each i and j. The coefficients α_{ij} are determined by least squares

$$s=\sum_{l=1}^{L}w_l\Big[\sum_i\sum_j\alpha_{ij}q_{ij}(x_l,\ y_l)-f_l\Big]^2=MIN!, \tag{11}$$

where L is the number of experimental points. On the basis of the usual conditions for determining the minimum from (11) by partial differentiation with respect to each coefficient α_{ij}, whose subscript is denoted for distinction by $\mu\nu$, and equating this relationship to zero, we obtain

$$\sum_{l=1}^{L}w_lq_{\mu\nu}(x_l,\ y_l)\ \Big[\sum_i\sum_j\alpha_{ij}q_{ij}(x_l,\ y_l)-f_l\Big]=0. \tag{12}$$

We obtain such an expression for each coefficient $\alpha_{\mu\nu}$. By commutating the summation signs, (12) can be written as

$$\sum_i\sum_j\alpha_{ij}\Big[\sum_{l=1}^{L}w_lq_{\mu\nu}(x_l,\ y_l)\,q_{ij}(x_l,\ y_l)\Big]=\sum_{l=1}^{L}w_lq_{\mu\nu}(x_l,\ y_l)\,f_l. \tag{13}$$

For convenience in the exposition, we replace the subscripts ij by k and $\mu\nu$ by $\varkappa$, after which we obtain from (13)

$$\sum_{k=1}^{K_{\max}}\alpha_k\Big[\sum_{l=1}^{L}w_lq_{\varkappa}(x_l,\ y_l)\,q_k(x_l,\ y_l)\Big]=\sum_{l=1}^{L}w_lq_{\varkappa}(x_l,\ y_l)\,f_l, \tag{14}$$

where $K_{\max}$ is the total number of coefficients. The subscript $\varkappa$ also varies between 1 and $K_{\max}$, so that all the equations (14) can be written as one matrix equation. Using the notation

$$A_{\varkappa,k}=\sum_{l=1}^{L}w_lq_{\varkappa}(x_l,\ y_l)\,q_k(x_l,\ y_l);\quad B_{\varkappa}=\sum_{l=1}^{L}w_lq_{\varkappa}(x_l,\ y_l)\,f_l, \tag{15}$$

we obtain

$$\left|\begin{array}{llll}A_{1,1} & A_{1,2} & A_{1,3}\cdots A_{1,K_{\max}} & \\ A_{2,1} & & & \\ A_{3,1} & & & \\ \vdots & & & \\ A_{K_{\max},1} & & & A_{K_{\max},K_{\max}}\end{array}\right|\cdot\left|\begin{array}{l}\alpha_1\\ \vdots\\ \\ \\ \alpha_{K_{\max}}\end{array}\right|=\left|\begin{array}{l}B_1\\ \vdots\\ \\ \\ B_{K_{\max}}\end{array}\right|. \tag{16}$$

The matrix $\|A\|$ is symmetric.

Such a linear system of equations can be solved by the usual methods. We used the Gauss method with a subsequent correction.

The approximation method described permits simultaneous approximation of diverse data, i.e., distinct surfaces $F_1(x, y)$, $F_2(x, y)$ . . . , in the space, which are interrelated by mathematical relationships (thermodynamic rules). An appropriate matrix equation is derived for each kind of data by adding the individual matrices while taking account of the estimation factors, and then the system of equations obtained as a result of the addition is solved. Hust and McCarty [2], as well as Vukalovich, et al. [3] indicated the possibility of a simultaneous approximation of diverse data by the addition of the matrix equations. The fundamental advantages of this method over the usual approximation used up to now for data of one species (as a rule, approximations of the p–v–T values) are the possibility of processing a large number of data, and therefore, a large quantity of information; better correlation of the data; the possibility of deriving an equation of state for substances about which there are diverse data, but in a small quantity; improvement of the accuracy of the computed values because of strict conservation of the thermodynamic consistency in deriving the equation of state; improvement of the extrapolation in the equation of state; the possibility of approximate compliance with the singular conditions (the Maxwell criterion, for example).

The first attempts at taking account of diverse initial data in deriving the equation of state were made by Keyes, et al. [4] and Bender [5]. In the first case, values of the isobaric specific heat in an ideal gaseous state c_{p_0} and the saturation enthalpies h' and h" were approximated in addition to the p–v–T values in their equations, and the condition g'(T) = g"(T) in the second case. Recently, the equation of Altunin and Gadetskii [6] became known, in whose approximation the values of c_p and the condition g'(T) = g"(T) were used in addition to the p–v–T values.

The expressions needed in (10)-(16) for data of diverse species are

$$x_l = \tau_l = 1 - 1/\vartheta_l; \quad y_l = \xi_l = \omega_l - 1,$$

for the p–v–T data:

$$f_l = \beta_l/(\omega_l^2 \vartheta_l I) - 1/\omega_l; \quad q_{ij}(\tau, \xi) = \tau^{j-1}\xi^{i-1},$$

for the enthalpy data:

$$f_l = \left[\varepsilon_l - \varphi_{\text{id}}^{\text{1atm}}(\vartheta_l) + \vartheta_l \left(\frac{\partial \varphi_{\text{id}}^{\text{1atm}}}{\partial \vartheta} \right]_{v=v_l} \right] /(I\vartheta_l);$$

$$q_{ij}(\tau, \xi) = \tau^{j-1}\xi^{i-1}(\xi + 1) - (1 - \tau)(j - 1)\tau^{j-2}[\xi^i - (-1)^i]/i,$$

for data of the isochoric specific heat:

$$f_l = -\left[c_{v_l} I_c \rho_c / p_c + \vartheta_l \left(\frac{\partial^2 \varphi_{\text{id}}^{\text{1atm}}}{\partial \vartheta^2} \right)_{v=v_l} + I \right] \vartheta_l^2 / I;$$

$$q_{ij}(\tau, \xi) = (j - 1)(j - 2)\tau^{j-3}[\xi^i (-(-1)^i]/i,$$

for the condition g'(T)–g"(T):

$$f_l = \ln \frac{\omega''(\vartheta_s)}{\omega'(\vartheta_s)} + \frac{\beta_s}{I\vartheta_s} \left[\frac{1}{\omega''(\vartheta_s)} - \frac{1}{\omega'(\vartheta_s)} \right]; \quad q_{ij} = \tau_s^{j-1}(\xi'^i - \xi''^i)/i.$$

The subscript s is the saturation state.

The expressions presented above are deduced from (4) by using the relations (5), (7), (8), and (9).

The method described was used to derive a new equation of state for carbon dioxide.

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