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CONSTRUCTING A SINGLE EQUATION OF STATE FOR GAS AND LIQUID BY THE METHOD OF MINIMIZING THE SUM OF SQUARES OF THE RELATIVE DEVIATIONS

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The use of the sum of squares of the relative deviations as the minimization criterion in the scheme of the least-squares method is proposed for the construction of a single thermal equation of state.

A typological scheme for the comparison of tables of thermodynamical properties from experimental data must precede the stage of constructing the thermal equation of state on the basis of statistical treatment of compatible measurements and the subsequent calculation of thermodynamic functions from the resulting equation. Two approaches are possible [1]:

1. Only experimental P, v, T data are used to determine the constants of the thermal equation of state. Information on the other properties is taken into account indirectly in choosing the version of the equation of state optimal from the viewpoint of the simultaneous description of the thermal, caloric, and acoustic properties.

2. The empirical constants of the equation are determined on the basis of combined analysis of the various kinds of experimental data.

In both cases, the problem of determining the constants of the empirical equation of state reduces to the application of the generalized least-squares method. From a mathematical viewpoint, the problem consists in minimization of the quadratic functional

$$S=\sum_{q=1}^{Q}\sum_{k=1}^{n_q} w_k\left(x_{qk}-x_q(\omega_k,\ \theta_k,\ \bar{b})\right)^2. \tag{1}$$

In the first case, Q = 1, x = z. In the second, $x_q=\{z,\ h,\ c_v,\ \ldots\}$.

The least-squares method (LSM) in Eq. (1) consists in minimizing the sum of squares of the absolute deviations. In general form, for

$$\bar{Y}=X\bar{b}+\bar{\varepsilon} \tag{2}$$

the problem reduces to minimization of the quantity

$$\bar{\varepsilon}'\bar{\varepsilon}=(\bar{Y}-X\bar{b})'(\bar{Y}-X\bar{b}). \tag{3}$$

However, the quality criterion of the equation obtained by the method is not absolute, as a rule, but the relative mean-square deviation

$$\delta_{\mathrm{m.sq}}=\sqrt{\sum_{i=1}^{N}\left((y_{\mathrm{exp}_i}-y_{\mathrm{calc}_i})/y_{\mathrm{exp}_i}\right)^2/(N-M-1)}. \tag{4}$$

The values of the coefficients giving a minimum of the functional of the absolute and relative deviations do not necessarily coincide here [2]. In connection with this, the possibility of using the sum of squares of the relative deviations as the minimization criteria in the LSM scheme is investigated in the present work. In matrix form, the relative-devia-

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TABLE 1. Parameter Values of Eqs. (10)-(12)

Equation	Parameters
(10)	$r=9,\ s_i=\{6, 5, 5, 5, 5, 4, 3, 3, 2, 2\},$ $\rho_0=\rho_{cr}$
(11)	$r=8,\ s_i=\{8, 8, 8, 8, 8, 8, 8, 8\}$
(12)	$r_1=8,\ r_2=2,$ $s_{1i}=\{8, 8, 8, 8, 8, 8, 8, 8\},$ $s_{2i}=\{2, 2, 2, 2, 2, 2, 2, 2\},$ $s_{3i}=\{8, 8\},\ s_{4i}=\{2, 2\},$ $C_\omega=0,\ C_\omega^0=0,\ C_\theta=0,\ C_\theta^0=0$

tion vector is written in the form

$$\bar{\delta}=V\bar{\varepsilon}, \tag{5}$$

where $V=\mathrm{diag}(y_1^{-1}, y_2^{-1}, y_3^{-1}, \ldots, y_N^{-1})$.

Then the problem reduces to minimization of the quantity

$$\bar{\delta}'\,\bar{\delta}=(V\bar{\varepsilon})'(V\bar{\varepsilon})=\bar{\varepsilon}'V'V\bar{\varepsilon}=\bar{\varepsilon}'W\bar{\varepsilon}, \tag{6}$$

where $W=\mathrm{diag}(y_1^{-2}, y_2^{-2}, y_3^{-2}, \ldots, y_N^{-2})$.

According to [2-4], this expression leads to a weighted LSM, the weights being determined from the formula

$$w_i=y_i^{-2}. \tag{7}$$

For Eq. (1), with measurements of equal accuracy, the weights are

$$w_k=x_{qk}^{-2}, \tag{8}$$

while for measurements of unequal accuracy

$$w_k=(x_{qk}\Delta x_{qk})^{-2}. \tag{9}$$

In addition to the direct inclusion of the relative deviations in the minimization criterion, the proposed method has the following important advantage in constructing a single thermal equation of state for gas and liquid phases from experimental P, v, T data.

As shown by our analysis of the deviation of calculated values for the compressibility from the experimental results, the greatest deviation is observed close to the phase-transition curves (the melting and boiling curves and the triple point). In these regions of the parameters of state, the value of z is a minimum and, according to Eqs. (8) and (9), it is assigned a large weight. Therefore, in the case when a quadratic functional of the relative deviations is used as the minimization criterion, the quality of description of the thermodynamic surface close to these phase-transition curves should be improved.

To verify the proposed method, single equations of state of carbon dioxide (from the data of [5]) and ammonia (from the data of [6]) were constructed using the quadratic functional of the absolute and relative deviations as the minimization criterion. The equation used for carbon dioxide is

$$z=1+\rho\sum_{i=0}^{r}\sum_{j=0}^{s_i}b_{ij}(\rho-\rho_0)^i(\theta-1)^j \tag{10}$$

while for ammonia

$$z=1+\sum_{i=1}^{r}\sum_{j=0}^{s_i}b_{ij}\rho^i\theta^j; \tag{11}$$

these equations are constructed under the assumption that the measurements of the initial P, v, T data are of equal accuracy. In addition, for both groups of data, the equation

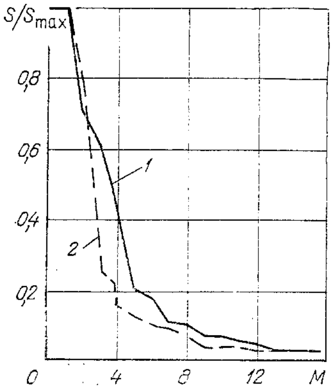

Fig. 1. Dependence of the value of the minimizing functional on the number of terms for Eq. (10): 1) absolute; 2) relative deviation.

TABLE 2. Comparative Data on the Errors of Calculating the Compressibility Coefficients from Eqs. (10)-(12) for Various Methods of Determining the Coefficients

Equation	Method of determining the coefficients	Minimization of the deviations									
		absolute					relative				
		1	2	3	4	5	1	2	3	4	5
(10)	I	50	0,732	1,323	0,213	0,056	50	0,687	0,840	0,325	0,079
	II	32	0,797	1,101	0,236	0,109	35	0,694	0,888	0,375	0,131
	III	26	0,861	2,057	0,182	0,119	29	0,720	0,910	0,251	0,109
(11)	I	72	2,637	3,020	0,590	0,180	72	2,081	2,500	1,270	0,330
	II	25	1,275	3,371	0,532	0,245	15	1,242	2,463	1,197	0,180
	III	21	1,708	2,849	0,487	0,194	14	1,189	1,357	1,323	0,171
(12)	I	—	—	—	—	—	—	—	—	—	—
	II	—	0,793	—	—	—	—	0,770	—	—	—
	III	—	0,981	—	—	—	—	0,883	—	—	—

Note. I) Complete-model method; II) successive inclusion of variables; III) stepwise regression analysis; 1) number of coefficients in the equation; 2) mean-square error over the whole mass of data; 3) mean-square error for the range $z < 0.2$; 4) for $z > 2.5$; 5) for $z \approx 1$.

$$\begin{aligned} z = 1 &+ \sum_{i=1}^{r_1} \sum_{j=0}^{s_{1i}} b_{ij} (\omega + C_\omega)^i (\theta + C_\theta)^j + \sum_{i=1}^{r_1} \sum_{j=1}^{s_{2i}} c_{ij} (\omega + C_\omega)^i \times \\ &\times (\theta + C_\theta^0)^{-j} + \sum_{i=1}^{r_2} \sum_{j=0}^{s_{3i}} d_{ij} (\omega + C_\omega^0)^{-i} (\theta + C_\theta)^j + \sum_{i=1}^{r_2} \sum_{j=1}^{s_{4i}} e_{ij} (\omega + C_\omega^0)^{-i} (\theta + C_\theta^0)^{-j} \end{aligned} \qquad (12)$$

is constructed, taking the unequal accuracy of the measurements into account.

To determine the unknown coefficients, the following methods of regression analysis are used: 1) construction of a complete model; 2) the method of successive inclusion of variables; 3) stepwise regression analysis. Numerical values of the parameters of the complete models are shown in Table 1.

Table 2 gives final data on the errors of calculating the compressibility coefficients from Eqs. (10)-(12) for different methods of construction. Analysis of the results shows that in all cases when the proposed method is used, the total mean-square deviation with respect to compressibility is reduced by an average of 1.2 times. This improvement is achieved mainly as a result of the reduction in deviation at small values of z (close to the phase-transition curves), where the deviation is reduced by an average of 1.6 times. The deviation at large z is increased here, but it does not pass beyond the permissible limits; in addition, this region of the state parameters corresponds to liquid at high pressure, where the error of calculating the density from the equation is much less than the error of the compressibility calculation.

The dependence of the residual value of the functional on the number of terms in the equation is shown in Fig. 1. Analysis of this graph shows that with minimization of the relative deviations of the velocity, the decrease in residual value of the error is increased, i.e., with the given value of the total error, the equation will contain a smaller number of terms.

On the basis of the foregoing, it may be concluded that the proposed method allows: improvement in the description of the total mass of P, v, T data as a whole; improvement in the reproducibility of the P, v, T surface in the vicinity of the triple point and the saturation curve; and reduction in the number of terms in the equation of state with a specified level of error.

NOTATION

w_i, weight of the i-th experimental point; $\bar{Y}$, dependent-variable vector; X, matrix of the dependent-variable values; $\bar{\varepsilon}$, absolute-deviation vector; $\bar{\delta}$, relative-deviation vector; Y_i, value of the dependent variable at point i; x_{qk}, value of the q-th independent variable at point k; z, compressibility; ρ, density; $\omega = \rho/\rho_{cr}$, reduced density; $\theta = T_{cr}/T$, reduced temperature; T, temperature; T_{cr}, critical temperature; $b_{ij}, c_{ij}, d_{ij}, e_{ij}$ —, parameters of the equation of state; h, enthalpy; c_v, isochoric specific heat; $\bar{b}$, vector of unknown coefficients of the equation; N, number of experimental points; M, number of coefficients of the equation; $\bar{\varepsilon}', \bar{\delta}', V'$, transposed matrices.

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GENERALIZED INTEGRAL VARIATIONAL PRINCIPLES OF PHENOMENOLOGICAL THERMODYNAMICS OF IRREVERSIBLE PROCESSES, AND THE NATURE OF VARIATION OF THERMODYNAMIC ACTION

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Generalized integral variational principles of phenomenological thermodynamics of irreversible processes (PTIP), as formulated by the present author, are stated.

1. Previous History of Integral Variational Principles. The first attempts of applying the apparatus of ordinary phenomenological thermodynamics (OPT) to dynamic systems [1] peaked in the construction of a linear formalism in Onsager's work [2]. The further development of dynamic methods of describing nonequilibrium systems [3-6] acquired global character, but Truesdell [6] provided a quite negative and nonobjective [7] estimate of the linear PTIP [2, 8]. A whole series of fundamental laws, reflecting the evolution of nonequilibrium thermodynamic systems, was established by means of the linear PTIP: the I. Prigogine minimum principle of entropy production [8], and the Onsager minimum principle of energy dissipation [2]. A generalized minimum principle of entropy production [9], following from the more general extremum integral variational principle in the entropy representation [10], was formulated for nonlinear Onsager systems.

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