PROCEDURE FOR SATISFYING MAXWELL'S RULE IN CONSTRUCTING UNIFIED THERMAL EQUATIONS OF STATE

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A procedure, which satisfies the conditions of the liquid–vapor phase equilibrium, for the construction of unified equations of state is proposed.

Unified equations of state (ES), which permit describing with high accuracy the thermal, caloric, and acoustic properties in the gaseous and liquid phases and on lines of phase equilibria are now increasingly used to construct tables of thermodynamic properties of substances. Here, if the equation satisfies Maxwell's rule, then additional information on the properties of a substance on the saturation line is not required [1]. In this case, the calculations in the gas and liquid phases are performed using a unified scheme [1-3], which significantly simplifies the algorithm and shortens the computational time. In addition, as shown in [4], this equation automatically satisfies the Planck–Gibbs rule also.

The question of the necessity of taking into account Maxwell's rule in the construction of ES is studied in a number of works [1-5] and methods for determining the coefficients in the equations under the condition that this rule is satisfied are proposed.

Thus it is proposed in [2, 3] that the coefficients in the equation be determined by minimizing by the method of least squares the functional

$$S=\sum_{i=1}^{N} w_i\left[(z''-z')_i^{\mathrm{exp}}-\int\limits_{\omega_i''}^{\omega_i'} z(\omega,\ \theta,\ b)\frac{d\omega}{\omega}\right]^2+\sum_{j=1}^{M} w_j\,[z_j^{\mathrm{exp}}-z(\omega,\ \theta,\ b)], \tag{1}$$

where the first term is introduced in order to satisfy Maxwell's rule.

A method of successive iterative improvement of the coefficients in the equation, which minimizes the deviations of the computed values of the isobaric–isothermal potential on the saturation line from the experimental values, is presented in [1].

As noted previously in [5] and as our analysis showed, the described methods have two important drawbacks: 1) the total number of coefficients is larger than for the equation obtained solely from P–v–T data and 2) the description of the starting P–v–T data is worse.

To eliminate the indicated drawbacks, we proposed the following procedure. In the gas and liquid phases all calculations are performed using a basic equation obtained by ignoring Maxwell's rule and describing with given accuracy the thermal properties on the phase-equilibrium lines. In the two-phase region the thermodynamic surface is represented in the form of a sum

$$z(\omega,\ \theta,\ b)=z_{\mathrm{fund}}(\omega,\ \theta,\ c)+z_{\mathrm{corr}}(\omega,\ \theta,\ a). \tag{2}$$

The correction z_{corr} is chosen so that its value and the values of the derivatives $\partial z_{\mathrm{corr}}/\partial\omega\cdot\partial z_{\mathrm{corr}}/\partial\theta$ on the boundary curves are equal to zero. The satisfaction of these conditions ensures that the main and corrected surfaces join along the bounding curves.

We shall show that aside from the indicated boundary conditions no other restrictions are imposed on the function $z_{\mathrm{corr}}(\omega,\ \theta,\ a)$, and if it is only necessary to satisfy Maxwell's rule, then the specific form of the dependence $z_{\mathrm{corr}}(\omega,\ \theta,\ a)$ is in general not necessary.

Since the correction equation is used to describe the thermodynamic surfaces only in the two-phase region and the conditions of joining at the boundary are satisfied, the calcu-

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lation of the thermal properties from the ES will be performed without using z_{corr}. To calculate the caloric and acoustic properties on the boundary curve of the liquid and in the liquid phase the values of $\int_{\omega''}^{\omega'} z_{\text{corr}}(\omega, \theta, a)\frac{d\omega}{\omega}$, $\int_{\omega''}^{\omega'} \partial z_{\text{corr}}(\omega, \theta, a)/\partial\theta \frac{d\omega}{\omega}$ and $\int_{\omega''}^{\omega'} \frac{\partial^2 z_{\text{corr}}(\omega, \theta, a)}{\partial\theta^2}\frac{d\omega}{\omega}$, which are functions only of the temperature, are required.

We denote

$$\int_{\omega''}^{\omega'} z_{\text{corr}}(\omega, \theta, a)\frac{d\omega}{\omega} = f(\theta), \tag{3}$$

$$\int_{\omega''}^{\omega'} \frac{\partial z_{\text{corr}}(\omega, \theta, a)}{\partial\theta}\frac{d\omega}{\omega} = \varphi(\theta), \tag{4}$$

$$\int_{\omega''}^{\omega'} \frac{\partial^2 z_{\text{corr}}(\omega, \theta, a)}{\partial\theta^2}\frac{d\omega}{\omega} = \psi(\theta). \tag{5}$$

If (3) is differentiated according to Leibnitz's rule, then we obtain

$$\frac{\partial}{\partial\theta}\int_{\omega''}^{\omega'} z_{\text{corr}}\frac{d\omega}{\omega} = \int_{\omega''}^{\omega'} \frac{\partial z_{\text{corr}}}{\partial\theta}\frac{d\omega}{\omega} + \frac{z'_{\text{corr}}}{\omega'}\frac{d\omega'}{d\theta} + \frac{z''_{\text{corr}}}{\omega''}\frac{d\omega''}{d\theta} = \int_{\omega''}^{\omega'} \frac{\partial z_{\text{corr}}}{\partial\theta}\frac{d\omega}{\omega}, \tag{6}$$

i.e.

$$\frac{\partial f(\theta)}{\partial\theta} = \varphi(\theta) \tag{7}$$

(based on the joining condition $z'_{\text{corr}} = z''_{\text{corr}} = 0$). It can be shown analogously that

$$\frac{\partial^2 f(\theta)}{\partial\theta^2} = \frac{\partial\varphi(\theta)}{\partial\theta} = \psi(\theta). \tag{8}$$

Thus, in order that the resulting equations satisfy Maxwell's rule, it is sufficient to determine the coefficients of the function f(θ), minimizing the functional

$$S = \sum_{k=1}^{K}(\Delta_k - f(\theta))^2, \tag{9}$$

where $\Delta_k = (z'' - z')_k - \int_{\omega''_k}^{\omega'_k} z_{\text{fund}}(\omega, \theta, c)\frac{d\omega}{\omega}$ is the "unbalance" according to Maxwell's rule for the main equation, and to use for the calculations in the liquid phase the corrections to the main equation calculated using (3)-(5).

The use of this method leads to a breakdown of the unified computational scheme based on the equation of state obtained. For $T > T_{\text{cr}}$ the calculation is performed without invoking the correction equation, and for $T < T_{\text{cr}}$ it is performed with the use of the correction. The total number of coefficients in the main and correction equations, however, is less than the number of coefficients in the equation obtained with the existing methods for satisfying Maxwell's rule, and the form of the correction equation is simple. The large increase in the computational time using the equation obtained will therefore not occur.

This procedure also has the advantages that the equations constructed ignoring Maxwell's rule can be corrected without changing their coefficients and it is possible to improve the description of the properties in the metastable region. The latter is achieved by including in the functional (9), when determining the coefficients of the correction equation, terms which take into account the unbalance with respect to the corresponding properties.

TABLE 1. Results of Calculations Based on the Starting and Corrected Equations

No. of coeffs. in starting Eq. (10)	Max. unbalance for starting Eq.	No. of coeffs. in correcting Eq. (11)	Residual unbalance		Deviations from data* [8], %			$\max\left(\frac{\Phi'-\Phi''}{\Phi''}\right)$, %	
			av $\cdot 10^2$	max $\cdot 10^2$	h'	c_p'	r	without correction	with correction
27	31,4	5	2,41	3,41	$\frac{12,4}{4,2}$	$\frac{12,0}{6,5}$	$\frac{9,2}{2,1}$	153,0	0,14
19	—1,02	5	0,17	0,46	$\frac{1,1}{0,6}$	$\frac{4,0}{1,8}$	$\frac{1,2}{0,8}$	5,0	0,14
17	—9,49	7	8,13	46,78	$\frac{8,4}{3,8}$	$\frac{15,0}{4,0}$	$\frac{5,0}{1,8}$	46,2	0,06
20	19,67	5	0,62	2,07	$\frac{2,0}{1,5}$	$\frac{5,0}{2,0}$	$\frac{1,8}{0,7}$	95,8	0,09
32	—60,17	4	0,74	2,02	$\frac{2,1}{1,4}$	$\frac{5,1}{1,8}$	$\frac{1,5}{0,6}$	290,0	0,25

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*The maximum deviations are given in the numerator and the average deviations are given in the denominator.

We checked the proposed procedure for the series of equations of state of n-hexane in the form [6, 7]

$$z = 1 + \sum_{i=1}^{R_1} \sum_{j=0}^{S_{1i}} c_{ij}\omega^i \theta^j + \sum_{i=1}^{R_2} \sum_{j=0}^{S_{2i}} c_{ij}^0 \omega^i \theta^{-j}, \tag{10}$$

whose coefficients were determined by different methods and with a different assignment of the weights for the starting data [7]. The conditions of phase equilibrium were ignored in the construction of these equations. For the same quality of description of the starting P—v—T data the equations differ significantly both by the magnitude and sign of the unbalance with respect to Maxwell's rule. The disagreement in the values of the isobaric—isothermal potential on the bounding curves of the liquid and vapor reached 290%. The parameters of the equations are presented in Table 1.

The equation for the corrections was constructed in the form

$$f(\theta) = \sum_{i=0}^{9} a_i \theta^i \tag{11}$$

by the method of step regression analysis. The values of P_s were chosen based on the data in [8]. The number of coefficients in the correction equations, the magnitudes of the residual unbalances, and the results of calculations based on the total equations are also presented in Table 1.

An analysis of the results shows that all equations obtained satisfy Maxwell's rule; in addition, the maximum deviation in the values of the isobaric—isothermal potential on the bounding curves of the liquid and vapor is equal to 0.25%. The deviations of the caloric properties calculated from the total equation from the data in [8] depend on the magnitude of the residual unbalance and for $\Delta_{res} < 2 \cdot 10^{-2}$ do not exceed the limits for the admissable values estimated in [8]. The possibility of describing the metastable state was not checked, since the equations obtained without the introduction of corrections satisfactorily describe the experimental data available for this region.

Thus, the proposed procedure permits smoothing the values of the isobaric—isothermal potential on the bounding curves of the liquid and vapor for any starting equation by introducing corrections with a relatively small number of coefficients. Here there is no need to correct the starting equation, and the accuracy of the description of the caloric properties on the saturation line and in the liquid phase is limited only by the quality of the approximation of the unbalance. With an appropriate choice of z_{corr}, together with the satisfaction of Maxwell's rule, it is possible to obtain a high-quality description of the metastable region.

NOTATION

S, functional being minimized; z, compressibility; $\omega = \rho/\rho_{cr}$, reduced density; ρ, density; $\theta = T_{cr}/T$, reduced temperature; T, absolute temperature; w, weight of an experimental point; z_{fund}, value of the compressibility calculated from the ES ignoring Maxwell's rule; z_{corr}, correction to the main equation; a_i, coefficients in the correction equation; Δ, the "unbalance" with respect to Maxwell's rule; ρ_{cr}, T_{cr}, critical parameters; c_{ij}, c_{ij}^{0}, coefficients of the main equation of state; R_2, R_1, S_1, S_2, parameters of the main equation of state; quantities marked with a single prime refer to the liquid in a saturated state; quantities with the index " correspond to the dry saturated vapor.

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