PROCEDURE FOR CONSTRUCTING AN EQUATION OF STATE FOR A LIQUID FROM EXPERIMENTAL p, v, T DATA WITH THE AID OF A COMPUTER

A. A. Vasserman and A. Ya. Kreizerova

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We propose a procedure for the construction of an equation of state of a liquid on a computer, based on the simultaneous determination of all the coefficients of the equation by the method of least squares. This enables one to describe experimental p, v, T data analytically, as represented for individual values of temperature and pressure for every experimental point. The procedure is tested on the basis of experimental data on liquid nitrogen, argon, and carbon dioxide.

Among semiempirical equations of state for liquids an equation of the form [1, 2]

$$p = A(T)\rho^n + B(T)\rho^{n+2} + C(T)\rho^{n+4} + \ldots \tag{1}$$

has proved to be promising.

This equation follows from an equation obtained by Ya. I. Frenkel' [3] on the basis of the self-consistent field method, if it is assumed that the parameters of the function of intermolecular interaction depend on the temperature. This assumption was successfully employed in [4, 5] in the calculation of thermophysical properties of gases. Equation (1) is valid for liquids and compressed gases at values of the reduced density $\omega > 1.8$ because at lower values representations of the self-consistent field, on which the derivation of the equation is based, begin to break down.

The graphical method developed earlier [1] for the construction of an equation of state of the form (1), based on a sequential determination of the temperature functions by means of the rectification of the isotherms, requires representations of experimental p, v, T data along the isotherms. The method of constructing the equation of state (1) on a computer, proposed in [6], realizes the procedure of [1] and imposes the same requirements on the form of the representation of the experimental data. Moreover, the program formulated in [6] stipulates certain restrictions on the form of the equation of state, namely that only three temperature functions appear in the equation and that the function C(T) be linear.

In view of these circumstances we have developed a new procedure for constructing an equation of state for a liquid, based on the simultaneous determination of the coefficients of the equation by the method of least squares.

The algorithm of the procedure provides for a preliminary determination of the weight of each experimental point, for which the quantity $1/\Delta p^2$ is taken, where Δp is the allowable error in the value of the pressure. In estimating the accuracy of the experimental data the authors have for the most part indicated the error by density, taking account of the reference error, so that Δp can be calculated by the simplified formula

$$\Delta p = \rho\delta\rho\,(\partial p / \partial\rho)_T \tag{2}$$

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In the determination of the quantities Δp from experimental data, represented on the isotherms, values of the derivative $(\partial p/\partial \rho)_T$ were found earlier by numerical methods [1, 6]. In order to employ data obtained for arbitrary values of the temperature, we now specify construction by the method of least squares at the initial stage of the calculations of an approximate equation of state with a prescribed number of coefficients and an exponent of degree $n = 1$, without taking account of the weight of the experimental points. The number of coefficients in this equation is usually chosen as intermediate between the initial and final numbers for the basic equations of state. The approximate equation is used for the calculation of the quantities Δp at each experimental point by Eq. (2).

After determination of the weight of the experimental points, two equations of state with the weight taken into account are constructed, having the same number of constants as the approximate equation and with values of the exponent of degrees $n = 1$ and $n = 2$. For subsequent calculations one chooses the value of n corresponding to the smaller sum of the squares of the deviations of the calculated values of the pressure from the experimental ones. In principle, the optimum value of n should depend both on the total number of constants in the equation and on the form of the analytical expressions for the temperature functions. However, numerous tests have indicated that this value usually lies within narrow limits (1-2) and that as a rule, for a definite group of p, v, T data and choice of the form of the temperature functions, it does not change with a subsequent increase in the number of constants in the equation of state. Therefore, to minimize the expenditure of machine time, we restricted ourselves to a single choice of one of the limiting integer values of n up to the start of the basic calculations.

The program provides for the use of various numbers of experimental points in the construction of the approximate equation of state, the choice of the optimum value of n, the construction of the basic equations, and the final comparison with the experimental data. One can construct the approximate equation from a limited number of experimental data, embracing the entire range of values of the parameters that is under study. For the choice of n and especially for the construction of the basic equations it is advisable to use the most reliable data. In the final comparison of calculated values of the density with experimental ones the data of all authors can be invoked.

After n has been chosen, a system of normal equations for the determination of the coefficients of the temperature functions of the desired equation of state is formed and solved. These coefficients are stored in the computer's memory bank. The values of the density at the experimental points are calculated according to the equation so constructed. The roots of Eq. (1) are determined by Newton's method [7], the experimental values of the density being used as the initial approximation.

After calculation of each value of the density, the relative deviation $\delta\rho$ from the experimental value is determined and registered in the operative memory of the computer. Then, on the basis of the values of $\delta\rho$ so obtained, points at which deviations exceed the prescribed allowable value are determined. The program provides for an automatic change in the weight of each of such aberrant points, namely a doubling of the weight of points at which deviations do not exceed twice the root-mean-square deviation $\langle\delta\rho\rangle$ for all data used in the construction of the equation or for appropriate groups of data and an assignation of zero weight to the remaining aberrant points. The procedure of assigning zero weight is fully justified [8]. After the weights have been changed, the equation of state is constructed once more, and calculated values of $\delta\rho$ are compared with those prescribed.

The performance of cycles of calculations relating to the change in weight of the experimental points and the construction of different variants of an equation of state with a prescribed number of coefficients makes it possible in many cases to reduce the number of points at which the deviations $\delta\rho$ exceed the prescribed limits, or to reduce the magnitude of the deviations at these points. The number of points with large deviations is one of the important criteria for the accuracy of an equation of state. As a rule a reduction in the number of such points favors a decrease in the root-mean-square deviation $\langle\delta\rho\rangle$ for the entire block of data used. Therefore the refinement cycles are repeated until the sum of the squares of the relative deviations $\Sigma\,\delta\rho^2$ for the aberrant points is minimized, and the variant of the equation corresponding to the minimum value of this sum is chosen as optimal.

For all variants of the equation of state the number of points used in its construction and the number of aberrant points, the values of $\Sigma\delta\rho^2$ and $\langle\delta\rho\rangle$ for both groups of points, and the coefficients of the temperature functions are printed. In addition, for the optimal variant, the total number of points, including points used only for comparison with the calculated values of the density, the corresponding values of $\Sigma\,\delta\rho^2$ and $\langle\delta\rho\rangle$, the deviations $\delta\rho$ at all points, and also data for the construction of histograms of the deviations are printed. These data are obtained by determining on the computer the number of points, lying within prescribed intervals, at which the deviations are of different sign. At the same time the possibility of grouping the absolute values of the deviations according to 11 intervals is provided for. The data can be obtained both for all experimental points and also for selected groups, with the possibility of choosing the size of the intervals for each group individually. The total number of points in a group and the corresponding values of $\Sigma \delta\rho^2$ and $\langle \delta\rho \rangle$ are also determined and printed.

The program for the "Minsk-22" computer provides for the possibility of constructing an equation of state with either three or four temperature functions and of increasing the number of coefficients of the analytic expressions of all or of certain functions within prescribed limits up to the point where the total number of coefficients of the equation does not exceed 28. For each set of coefficients in the equation of state all the operations described above are repeated.

TABLE 1. Coefficients of the Temperature Functions of Equations of State for Liquid Nitrogen, Argon, and Carbon Dioxide

$$p = \rho^n \sum_{i=0}^{k} a_i \theta^i + \rho^{n+2} \sum_{i=0}^{l} b_i \theta^i + \rho^{n+4} \sum_{i=0}^{r} c_i \theta^i + \rho^{n+6} \sum_{i=0}^{s} d_i \theta^i$$

$$(\theta = T/100)$$

Coefficient	N_2 ($n = 1$)	Ar ($n = 2$)	CO_2 ($n = 2$)
a_0	1924.335	—882.8232	—1758.230
a_1	—2095.639	794.3664	679.8640
a_2	680.8802	—19.13600	6.242337
a_3	—	37.19111	—
a_4	—	—78.41004	—
a_5	—	25.40086	—
b_0	—11565.26	—418.0970	—244.5904
b_1	9683.481	39.00315	—18.62383
b_2	—1887.699	—	—63.69379
c_0	8419.182	193.4893	—260.2792
c_1	—2695.553	69.36950	—201.2977
c_2	20.18040	—	192.1338
d_0	—	—	—188.4002
d_1	—	—	502.7981
d_2	—	—	—138.4705

The procedure discussed above has been applied to the construction of equations of state for liquid nitrogen, argon, and carbon dioxide. The density of these substances in the liquid state has been thoroughly investigated experimentally over a wide range of the parameters, and the employment here of data of certain authors, published only recently, has made it possible to construct equations of state that are more reliable than those obtained earlier [1, 9].

For nitrogen the following data were used: [10] on the coexistence curve, [11-13] on the saturation curve, and [13-15] in the single-phase region. In order to ensure good agreement of the equation with the coexistence curve and with data for the gas, smoothed values of the density [1] on several isotherms were also used. The data just enumerated cover a temperature range of 63.6-140°K and pressures up to 709 bar.

The equation of state for liquid argon was constructed on the basis of experimental data for the saturation curve [12, 16-18] and the single-phase region [17-20] and part of the data for the coexistence curve and the single-phase region of [21, 22]. The data used are represented in a temperature range of 85.7-173.2°K with pressures up to 1186 bar.

For carbon dioxide we used data on the coexistence curve,† on the saturation curve† [23], and in the single-phase region†,‡ [23-30]. The widest range of the parameters ($T = 219.2-329.4$°K, $p = 6-2493$ bar) is covered in the work referenced in the first footnote.

For each of the indicated substances several equations of state were obtained, describing experimental values of the density of the liquid (and of the compressed gas on the near-critical isotherms) for $\omega > 1.8$ within the limits of experimental error. The coefficients of the optimal variants of the equations are shown in Table 1. The root-mean-square deviations of data obtained through use of the equations of state from experimental data are as follows: for nitrogen 0.13% (according to the data of various authors 0.09%* [10-13], 0.10% [13], 0.13% [14], 0.19% [15], 0.15% [1]), for argon 0.13% (according to the data of various authors 0.09%* [12, 16-18, 21, 22], 0.16% [17], 0.08% [18], 0.13% [19, 20], 0.20% [21], 0.12% [22]), for carbon dioxide 0.08% (according to the data of various authors 0.15%* [23] and the work referenced in footnote 1, 0.05% [25] and the work referenced in footnote 1, 0.12% [23, 24], 0.11% [26, 27], 0.03% [28, 29], 0.09% [30] and the work referenced in footnote 2), where the asterisks distinguish data on the saturation and the coexistence curves. A further augmentation of the number of coefficients in the equations of state did not lead to an increase in accuracy of the description of the experimental data in view of the scatter and insufficient agreement of the latter.

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†E. A. Golovskii, Investigation of the Thermodynamic Properties of Liquid Carbon Dioxide at Pressures up to 2500 bar, Author's Abstract of Candidate's Dissertation, M. V. Lomonosov University, Dept. of Tech. Information (1969).

‡M. Kh. Sayapov, Experimental Investigation of the Thermal and Caloric Properties of Carbon Dioxide in the Liquid Phase [in Russian], Author's Abstract of Candidate's Dissertation, Moscow Power Engineering Institute (1970).

An investigation of the influence of the form of the analytic expressions for the temperature functions in Eq. (1) on the accuracy of the description of the data indicated that equations with a uniform distribution of the coefficients among the temperature functions and with a linear function C(T) (and also D(T) for CO_2), the total number of coefficients being fixed, satisfied the experimental data with the same degree of accuracy and that an equation with a linear function A(T) was less accurate. This was true both for nitrogen, for which most of the data lay in the range 0.6-0.9 g/cm^3, and for argon and carbon dioxide, for which the ranges were 1.1-1.4 g/cm^3 and 0.85-1.25 g/cm^3 respectively. When the temperature functions were determined sequentially by the method of rectification of isotherms, it was discovered [1] that the function A(T) has a more complicated form. From the calculations that have been carried out it can be concluded that such a form of the function A(T) is due not so much to the procedure by which it is determined as to the physical meaning of this function.

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