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SELECTION OF THE OPTIMAL QUANTITY OF INITIAL DATA AND THE NUMBER OF COEFFICIENTS IN COMPILING EQUATIONS TO COMPUTE THE THERMOPHYSICAL PROPERTIES OF SUBSTANCES

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The question of limiting the quantity of data used in compiling the equations to compute the thermophysical properties of substances is investigated, and a method to optimize the number of coefficients therein is developed.

The use of an electronic computer permits compilation of multiconstant equations of state and equations of the transport properties by numerous experimental data. However, an increase in the volume of the data being used and in the number of coefficients does not always by far contribute to a rise in the accuracy of the equations. This is explained by calculational instabilities which occur in the solution of the appropriate system of high-order normal equations. The use of duplicate data in the formation of such a system can degrade its specificity. It is hence expedient to consider the question of a logical constraint on the volume of test data and the number of coefficients of the empirical equations.

Finding the optimal number of test points needed for a reliable description of a surface, and the density of their distribution on this surface requires the solution, in principle, of a very complex problem of the calculus of variations. Sufficiently general results can also be obtained by performing computations on reliable data for a well-studied substance, by using an electronic computer.

Initially, the possibility of limiting the number of p, v, T data in the compilation of the equation of state of a fluid whose thermodynamic surface is sufficiently simple was investigated [1]. To do this, a number of equations of state of water were compiled on the basis of a different number of tabulated data [2]. The array of initial data was separated into a number of groups, each of which included practically the whole surface being described. The number of groups being used was successively reduced in compiling the different equations of state, but a comparison was performed for the total array. A reduction in the number of points taking part in compilation of the equation from 882 to 55 contributed to a twofold reduction in the rms error of the description of the whole array.

The results in [1] were confirmed in a compilation of a single equation of state for water and steam for the 273-1073°K temperature range and pressures to 100 MPa. To approximate actual conditions in the machine experiment, random errors, normally distributed within ±0.10% limits, were inserted in the tabulated values of the specific volume at this stage of the investigation.

Besides the comparison with thermal data, the influence of curtailing the number of p, v, T data being used on the accuracy of describing the derivatives $(\partial p/\partial v)_T$, $(\partial p/\partial T)_v$ and the specific heat C_v was estimated by comparing the appropriate computed values and the data in [3, 4]. As in computations with the tabulated data, cutting down the number of "test" points used contributes to a rise in the accuracy of describing the initial data array (Fig. 1). The optimal accuracy is achieved in compiling equations on the basis of 816

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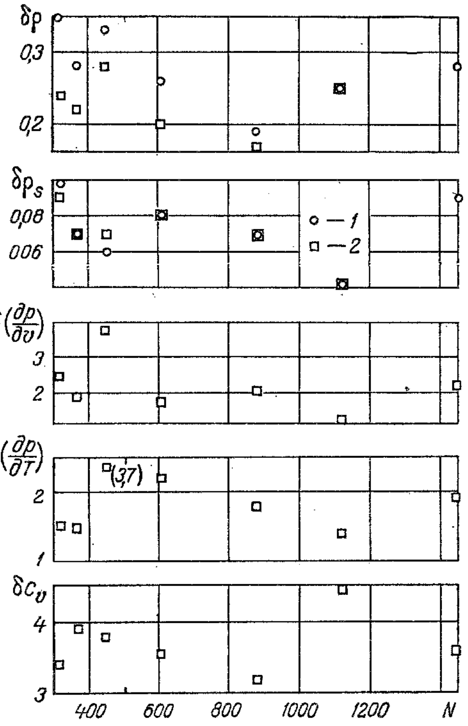

Fig. 1

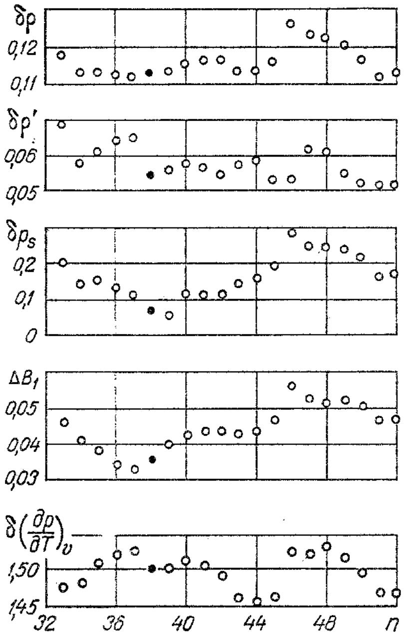

Fig. 2

Fig. 1. Dependence of the rms deviations of the thermal and caloric properties of water and steam on the number of test points N used in compiling a single equation of state: 1) for data used in compiling the equation; 2) for results used in compiling δp, δp_s, $\delta(\partial p/\partial v)$, $\delta(\partial p/\partial T)$, δC_v, %.

Fig. 2. Dependence of the rms deviations of the thermal properties of ethylene on the number of coefficients n of a single equation of state. Blackened points are deviations for an equation with an optimal number of instruments.

points for a single-phase domain on 33 isotherms arranged with a 20-30°K spacing, and 62 points for the saturation line. The equation mentioned satisfies the Maxwell rule and the checking array of caloric data well.

Computations performed showed that in composing an analytic equation of state that is valid in a broad range of temperatures and pressures with the exception of the critical domain, by using reliable experimental data, a substantial reduction in their number will contribute to raising the accuracy of the equation. This permits recommending the following scheme for planning and conducting experimental investigations of the thermal properties of substances.

Taking into account that the coefficients of the equation of state that are used to describe the experimental data are determined empirically, it is expedient to obtain first a limited number of test points, exceeding the quantity of desired coefficients of the equation (usually 10-15 for the equation of state of a fluid and 40-50 for a single equation) by 6-8 times. The test points should include the whole range of parameters of interest to us. For a reliable description of the saturation curve and the satisfaction of the Maxwell rule, 5-10% of the points should refer to the saturation curve when composing the equations.

An equation is composed on the basis of 2/3 of the obtained minimum number of points, and the rest of the points are used for a check. If the values of the rms errors of the approximations for both groups of points are substantially different, a new equation is composed by using all available data, additional checking points are obtained experimentally for intermediate values of the state parameters, and test and computed results are again compared. As soon as the values of the rms errors turn out to be statistically equivalent for the used and checking points, the experiment is terminated.

TABLE 1. Coefficients of a Single Equation of State for Ethylene*

i	j	a_{ij}	i	j	a_{ij}	i	j	a_{ij}
1	0	$0,2178270\cdot10^{1}$	3	0	$0,2451204\cdot10^{1}$	6	2	$0,7796775\cdot10^{0}$
	1	$-0,6821157\cdot10^{1}$		1	$-0,5898240\cdot10^{1}$		3	$0,2944196\cdot10^{0}$
	2	$0,6777108\cdot10^{1}$		2	$0,1780145\cdot10^{1}$		4	$0,3354969\cdot10^{0}$
	3	$-0,5711838\cdot10^{1}$		3	$-0,2412249\cdot10^{1}$		5	$0,2871860\cdot10^{-1}$
	4	$0,3670388\cdot10^{1}$		4	$0,1207102\cdot10^{1}$	7	0	$0,4419644\cdot10^{-1}$
	5	$-0,1385085\cdot10^{1}$		5	$0,1522029\cdot10^{1}$		1	$-0,4411061\cdot10^{-1}$
	7	$0,8122023\cdot10^{-1}$	4	0	$-0,7402457\cdot10^{0}$		2	$-0,1994349\cdot10^{0}$
	8	$-0,5478113\cdot10^{-2}$		1	$0,1760218\cdot10^{1}$		3	$-0,9131426\cdot10^{-1}$
2	0	$-0,2756311\cdot10^{1}$		2	$0,1731742\cdot10^{1}$		4	$-0,5642775\cdot10^{-1}$
	1	$0,7389625\cdot10^{1}$		3	$0,2142207\cdot10^{1}$	8	0	$-0,1787565\cdot10^{-1}$
	2	$-0,3513898\cdot10^{1}$		4	$-0,2073583\cdot10^{1}$		1	$0,3448953\cdot10^{-1}$
	6	$-0,3608164\cdot10^{0}$	5	2	$-0,2333161\cdot10^{1}$		3	$0,1604210\cdot10^{-1}$
				4	$-0,3837962\cdot10^{0}$			
				5	$-0,1379883\cdot10^{0}$			

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*The following values of the critical parameters and the gas constant are taken in the computations for the equation; T_{cr} = 282.35°K; $p_{cr} = 5.042$ MPa; $\rho_{cr} = 214.2$ kg/m³, and R = 296.376 J/kg·deg.

In connection with the fact that the surfaces of the transport coefficients are less complex, on the whole, than the thermodynamic surface, the deductions obtained are also applicable for the composition of equations for the transport properties. The scheme proposed can assure a substantial economy in the expenditure of time and labor in performing a complex and costly thermophysical experiment.

Considering another aspect of the problem of compiling optimized equations to describe the thermophysical properties of a gas and liquid, it should be emphasized that the number of coefficients should be minimal in the equations assuring the most confident behavior of the derivatives of the approximating functions and reliable extrapolation for accuracy of the description limited by access to the array of test data to be used.

Equations in polynomial form

$$F_k = \sum_{i=1}^{m} \sum_{j=0}^{n_i} a_{ij} \frac{\omega^i}{\tau^j} \tag{1}$$

are extensively used, where

$$F_1 = \frac{pv}{RT} - 1 \tag{2}$$

for the equation of state, and

$$F_2 = \ln \frac{\eta_{p,T}}{\eta_T}, \tag{3}$$

$$F_3 = \eta_{p,T} - \eta_T, \tag{4}$$

$$F_4 = \frac{\eta_{p,T}}{\eta_T} - 1, \tag{5}$$

$$F_5 = \frac{\omega}{\eta_{p,T}}. \tag{6}$$

TABLE 2. Coefficients of a Single Equation for the Coefficient of Dynamic Viscosity for Ethylene (η, 10^{-6} Pa·sec)

i	j	a_{ij}	i	j	a_{ij}
1	0	$0,46828\cdot10^{1}$	4	0	$0,17807\cdot10^{1}$
2	0	$0,75363\cdot10^{1}$		2	$-0,32034\cdot10^{1}$
			5	2	$0,11442\cdot10^{1}$

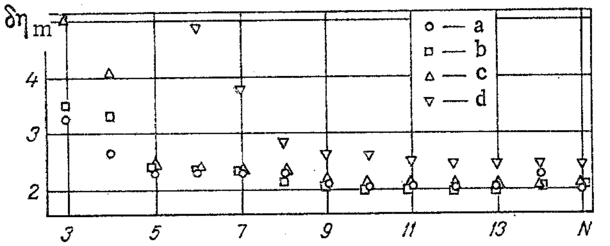

Fig. 3. Dependence of the rms deviation of experimental data on the viscosity of ethylene on the number of coefficients for different equations: a) (3); b) (4); c) (5); d) (6). $\delta\eta_m$, %.

for the most widespread equations of the transport properties. In place of the variable ω ordinarily used in the right side of (1) to describe the transport properties, there is $\bar{\omega} = \omega(p, T) - \omega(0.1, T)$, which is necessary in order to satisfy the limit condition ($\eta_{p,T} = \eta_T$ for $p = 0.1$ MPa). Forms analogous to (3)-(6) are used in the equations for the coefficient of heat conductivity also. The maximum values of the exponents i and j are determined by a regression analysis of the data on the most extended isochores and isotherms. The question of the expediency of using the complete set of coefficients a_{ij} is of interest.

The problem of composing an equation containing just substantially significant coefficients is a typical optimization problem in several contradictory criteria. In our case the criteria are accuracy of describing the data and the number of coefficients. However, correct formulation of the optimization problem presumes the presence of just one criterion. Hence, we set a threshold for the growth of the variance of the test data and optimized the number of coefficients.

The significance of the coefficient is determined by the magnitude of the ratio of the absolute value of the coefficient and its error σ_{ij} defined by the formula

$$\sigma_{ij} = \sqrt{D/w_{ij}}, \tag{7}$$

where D is the weighted variance, and w_{ij} is the weight of the coefficient computed according to [5]. The coefficient for which the ratio $|a_{ij}|/\sigma_{ij}$ is minimal is an exception.

Because of the close correlation between the coefficients of the empirical equation, it is revised after elimination of the least significant coefficient, then the ratio $|a_{ij}|/\sigma_{ij}$ is determined, and again the least significant coefficient is eliminated. This procedure is repeated automatically until the ratio between the weighted variance of the test data for the next and initial equations exceeds the threshold value determined by the Fisher criterion. Revision of the equation after elimination of the next coefficient assures conservation of the approximation of the data for the limited quantity of coefficients. We consequently obtain an optimal equation of definite form for the set of test points used.

The method was verified in [6] on the basis of tabulated data on the thermal and caloric properties of argon. Of considerable interest is the application of the method to arrays of experimental data obtained by different authors and characterized by different accuracy.

In compiling a single equation of state for ethylene by means of experimental p, v, T data [7-16] and 54 values of the derivative $(\partial p/\partial v)_T$ from [12], the number of coefficients was reduced from 52 in the initial to 38 in the optimal equation for a rms error of $\delta\rho_m = 0.11\%$ in the description of the density data (Fig. 2). The equation describes the overwhelming majority of experimental data with high accuracy, and permits reliable computation of the caloric properties. The coefficients of the optimized equation of state of ethylene that are valid in the 105-450°K temperature and up to 320 MPa pressure ranges are presented in Table 1.

The method for optimizing the number of coefficients permits objective comparison of the efficiency of equations of a different kind. This can be illustrated by the example of single equations of the coefficient of dynamic viscosity of ethylene.

Experimental data [17-22] are used in composing the equations whose left sides are represented in the form (3)-(6). The results of optimizing the number of coefficients show

(Fig. 3) that equations of the form (3)-(5) that are equivalent in the accuracy of description are of greatest interest for the description of data on viscosity in broad parameter ranges.

To estimate the influence of optimization on the extrapolation properties of the equations, computations were performed on the basis of values of the ethylene viscosity coefficient that we tabulated and separated into a number of groups including different sections of the surface being described. This permitted confirmation of the extrapolation in the temperature and pressure in both broad and narrow limits of variation of the parameters.

Confirmation showed that optimization of the number of coefficients reduces the value of the rms error by 1.3-1.6 times in the extrapolation domain. Equation (4) possesses the best extrapolation possibilities, especially in the pressure. The coefficients of a single equation for the dynamic viscosity of ethylene, composed in the form (4) for 200-550°K temperatures and 0.1-200 MPa pressures, are represented in Table 2.

Therefore, the investigation conducted showed that logical reduction in the number of test data being used to compose the equations, and the number of empirical coefficients, will contribute to raising the accuracy in describing the data and will assure the possibility of more reliable interpolation in the parameter range not investigated experimentally.

NOTATION

p, pressure; v, specific volume; ρ, density; T, absolute temperature; C_V, specific heat at constant volume; $\eta_{p,T}$, dynamic viscosity of a substance at the pressure p and temperature T; η_T, dynamic viscosity of a gas at the pressure 0.1 MPa and temperature T; $\omega = \rho/\rho_{cr}$, reduced density; $\tau = T/T_{cr}$, reduced temperature; and a_{ij}, coefficient of the equation for the i-th power of ω and the j-th power of τ.

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HEAT CAPACITY OF LIQUID ORGANIC COMPOUNDS: EXPERIMENTAL DETERMINATION AND METHOD OF GROUP APPROXIMATION OF ITS TEMPERATURE DEPENDENCE

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The article describes the experimental method and presents results of the investigation of the heat capacity of liquid n-alcohols and esters. It examines the method of group approximation of the temperature dependence on the example of n-alkanes and n-alkenes.

A calorimetric device was designed and made at the research institute VNIIFTRI. This device makes it possible rapidly and with sufficient accuracy to determine the heat capacity of small quantities (up to 12 cm^3) of both liquids and solids in the temperature interval 40-350°C. The device has the following main component units: an adiabatic calorimeter, a vacuum system, an automatic system of maintaining adiabatic conditions, and a potentiometric measuring console.

The adiabatic calorimeter is schematically illustrated in Fig. 1. The calorimetric cup 1 is made of two thin-walled copper tubes, each of which has a bottom of the same material soldered to it. Fixedly mounted between the tubes is a heater assembled on a mica frame and insulated on each side by mica plates. On top the cup is covered by a lid and suspended inside the massive block 3 by steel braces.

Block 3 is an adiabatic shell consisting of a thick-walled copper cylinder and massive bottom and lid with sliding fit. Heaters are situated on the outer surface of the cylinder, the bottom, and the lid. A differential Chromel–Constantan thermocouple is provided for registering possible temperature gradients between the upper, central, and lower parts of the block. The junctions of this thermocouple are situated in special holes and fixed with a heat-resisting paste (Fig. 1 does not show the position of this thermocouple). Block 3 is mounted inside furnace 4 on thin stainless-steel tubes 7. Furnace 4 is made of a thick-

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