EXTRAPOLATION OF EXPERIMENTAL THERMAL DATA TO HIGH PRESSURES

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Inzhenerno-Fizicheskii Zhurnal, Vol. 10, No. 3, pp. 374–381, 1966

UDC 541.1

A method is given for extrapolating thermal data to high pressures. A comparison is made of extrapolated and experimental values of the specific volumes of ten substances.

A number of papers has been devoted to the problem of extrapolating thermal properties of substances to high temperatures [11, 12, 14]. However, no methods have as yet been found permitting reliable extrapolation to high pressures.

It is known that the constants of existing equations of state depend on the method of conputation. For interpolation of test data the methods chosen are those which best satisfy the available test points. As a rule, however, these equations give unreliable values of the extrapolated quantities. It is clear that better results may be achieved by treating the problem of extrapolation as an independent one, and determine the constants as those giving the best description of the P, V, and T properties within the limits of experiment. It is expedient to determine these conditions as follows. Let $y(x)$ be an experimental isotherm, $\bar{y}(x, C_0, \ldots, C_n)$ be a family of approximating curves corresponding to some equation of state or other. We shall designate by x_0 the point up to which the experimental data exist. Then,

$$\begin{aligned} &\bar{y}(x_0, C_0\cdots C_n) = y(x_0),\\ &\bar{y}'(x_0, C_0\cdots C_n) = y'(x_0),\\ &\cdots\cdots\cdots\cdots\\ &\bar{y}^{(n-1)}(x_0, C_0\cdots C_n) = y^{(n-1)}(x_0),\\ &y^{(n)}(x_0, C_0\cdots C_n) = y^{(n)}(x_0), \end{aligned} \tag{1}$$

i. e., the approximation and experimental functions have a common tangent, curvature, etc., at the point x_0.

It should be noted that these are the only conditions which correspond equally to the known part of the isotherm and the unknown part on both sides of the point x_0.

Calculation of the constants $C_0, C_1, \ldots, C_n$ involves determination of high-order derivatives from the tabulated experimental data, and we know that these derivatives are not determined exactly. Nevertheless, the constants $C_0, C_1, \ldots, C_n$ may be determined with considerably greater accuracy than the errors in the derivatives would dictate.

We shall assume that the equalities (1) hold. Solving (1) relative to the constants $C_0, C_1, \ldots, C_n$, we obtain

$$\begin{aligned} &C_0 = \varphi_0[x_0, y(x_0), y'(x_0), \ldots, y^{(n)}(x_0)],\\ &C_1 = \varphi_1[x_0, y(x_0), y'(x_0), \ldots, y^{(n)}(x_0)],\\ &\cdots\cdots\cdots\cdots\cdots\cdots\\ &C_n = \varphi_n[x_0, y(x_0), y'(x_0), \ldots, y^{(n)}(x_0)]. \end{aligned} \tag{2}$$

If the last equation of (1) is dropped, the quantities C_i, apart from x_0 and the derivatives, will depend on C_n and on the parameter

$$C_i = \psi_i[x_0, y(x_0), y'(x_0), \ldots, y^{(n-1)}(x_0), C_n]. \tag{3}$$

Replacing x_0 in (3) by x and substituting the value of C_n calculated from (2), it is easy to show that

$$\left.\frac{d\psi_i}{dx}\right|_{x=x_0} = 0. \tag{4}$$

The functions

$$\begin{aligned} &C_i = \psi_i[x_0, y(x_0),\\ &y'(x_0), \ldots, y^{(n-k)}(x_0), C_{n-k+1}, \ldots, C_n], \end{aligned} \tag{5}$$

have the same property, where $C_{n-k+1}, \ldots, C_n$ are calculated from (2).

As an example, we shall examine the Biron isotherm equation [8]

$$(P+C)(V-A) = B. \tag{6}$$

It has three constants—A, B, C. In this case (1) has the form

$$\begin{aligned} &[B/(P_0+C)] + A = V(P_0),\\ &-\frac{B}{(P_0+C)^2} = \left.\frac{dV}{dP}\right|_{P=P_0} = V'(P_0),\\ &\frac{2B}{(P_0+C)^3} = \left.\frac{d^2V}{dP^2}\right|_{P=P_0} = V''(P_0). \end{aligned} \tag{7}$$

Solving (7) relative to constant C, we obtain

$$C_0 = P + 2V'(P_0)/V''(P_0). \tag{8}$$

Solving the first two equations of (7) relative to A, for example, we have

$$A = \psi_B[P_0, V(P_0), V'(P_0), C] = (P_0 + C)V'(P_0) + V(P_0). \tag{9}$$

It follows from (4) that

$$\left.\frac{d\psi_B}{dP}\right|_{P=P_0} = [(P + C_0)V'(P) + V(P)]' = 0. \tag{10}$$

Therefore, the function ψ_B has an extreme value at the point $P = P_0$. If C_0 has been determined inaccurately because of inaccurate determination of the second derivative $V''(P_0)$, it is clear that the extreme value of function ψ_B will not be at the point P_0, but at some

Table 1

Values of Specific Volume of Liquid Propylene with t = 66° C, P_0 = 700 atm (P, atm; V, amagat)

P	V_{exp} from [2]	V_{theor} from (6)		δ, %	
		by the author's method	by the method of least squares	by the author's method	by the method of least squares
1000	0.003194	0.003195	0.003185	+0.03	−0.28
1500	0.003036	0.003042	0.003077	+0.20	+1.37
2000	0.002920	0.002943	0.003017	+0.80	+3.35

Table 2

Values of Specific Volumes of Ethyl Alcohol and Propylene (P, atm; V, amagat)

P	V_{exp}	V_{calc}		δ, %	
		according to (6)	according to (15)	according to (6)	according to (15)
ethyl alcohol [1], t = 0° C					
1000	0.9344	0.9347	0.9345	+0.03	0.00
2000	0.8954	0.8980	0.8956	+0.29	+0.02
3000	0.8679	0.8740	0.8688	+0.69	+0.10
propylene [2], t = 100° C					
1000	0.003316	0.003318	0.003313	+0.06	−0.10
1500	0.003126	0.003145	0.003124	+0.61	−0.07
2000	0.002993	0.003040	0.003003	+1.57	+0.34
2300	0.002936	0.002995	0.002948	+2.04	+0.42

Table 3

Comparison of Extrapolated Values of Specific Volumes of Substances with Experimental Values (P, atm; V, amagat)

Water [7]					Methyl alcohol [1]				
P	t=50° C, P_0=690.8				P	t=0° C, P_0=700			
	V_{exp}	δ, %				V_{exp}	δ, %		
		from (15)	from (12)	mean			from (15)	from (12)	mean
986.9	0.9734	0.00	0.00	0.00	1000	0.9324	−0.01	0.00	0.00
1935.7	0.9439	+0.04	+0.03	+0.03	2000	0.8923	−0.03	+0.07	+0.02
2903.5	0.9201	+0.01	+0.01	+0.01	3000	0.8640	+0.03	+0.13	+0.08
3871.4	0.8997	+0.06	0.00	+0.03					
4839.2	0.8824	+0.09	−0.07	+0.01					
5807.0	0.8668	+0.22	−0.08	+0.07					

Propylene [2]

P	t=100° C, P_0=300				P	t=150° C, P_0=700			
	V_{exp}	δ, %				V_{exp}	δ, %		
		from (15)	from (12)	mean			from (15)	from (12)	mean
500	0.003662	−0.05	+0.03	−0.01	1000	0.003505	−0.11	+0.03	−0.04
700	0.003489	+0.09	−0.05	+0.02	1500	0.003267	+0.03	+0.06	+0.05
900	0.003367	+0.45	−0.18	+0.14	2000	0.003115	+0.26	−0.13	+0.07
1000	0.003316	+0.70	−0.24	+0.23	2500	0.003010	−0.51	−0.37	−0.07

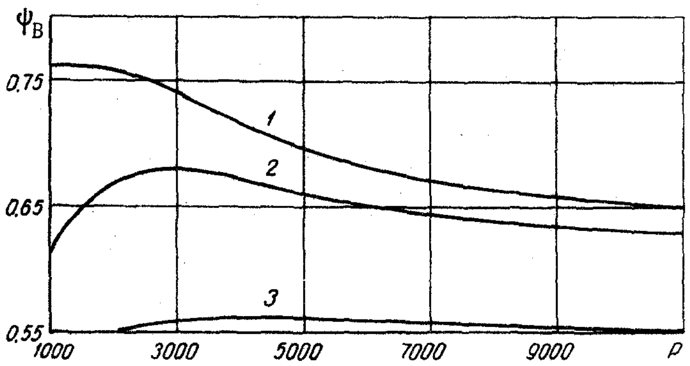

Fig. 1. The function ψ_B for hexane [5] on the isotherm 50° C for values of C of: 1) 1694; 2) 2662; 3) 3629. P) pressure, atm.

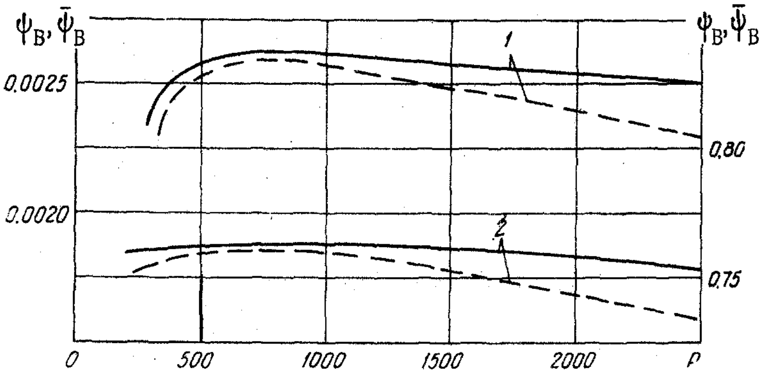

Fig. 2. The functions $-\psi_B$ (continuous lines) and ψ_B (broken lines): 1) propylene [2] at temperature 100° C; 2) ethyl alcohol [1] at temperature 0° C. P in atm.

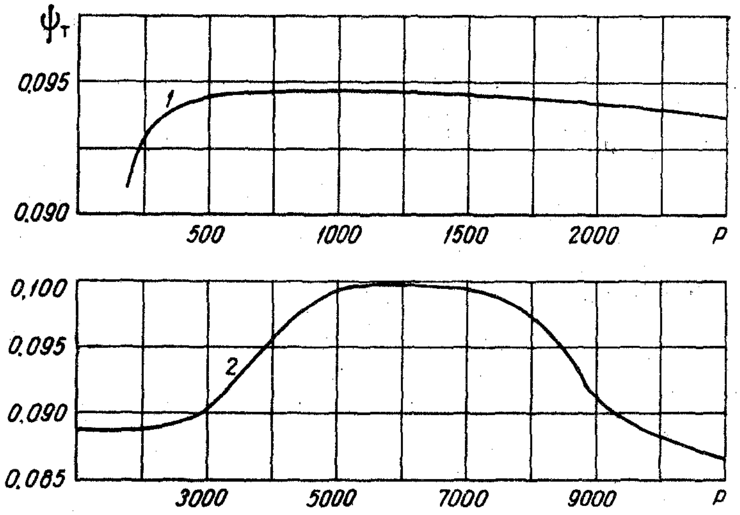

Fig. 3. The functions ψ_T: 1) ethyl alcohol [1] on the isotherm 0° C; 2) hexane [5] on the isotherm 50° C. P in atm.

Table 4

Range of Extrapolation ΔP Within Which the Deviations of the Extrapolated Values of Specific Volumes from the Experimental Values Do Not Exceed ±0.3%

Substance	t, °C	P_0, atm	ΔP, atm	t, °C	P_0, atm	ΔP, atm	Reference
Methyl alcohol	0	700	2300*)	80	1000	4000	[1]
Ethyl alcohol	0	700	2300*)	80	1000	4000	[1]
Acetone	0	700	2300*)				[1]
Diethyl ether	0	700	2300*)				[1]
Water	50	690.8	5300*)				[7]
Hexane	50	967.8	3000				[5]
Heptane	95	967.8	5000	237.78	272.2	400*)	[5]
"	137.78	272.2	400*)	4.6	272.2	400*)	[9]
Propylene	66.3	700	1300*)	100	700	1600	[2]
"	100	300	700	150	700	1800	[2]
Ethylene	50	590	1400				[3]
Nitrogen	0	800	600				[4]

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*The range shown is incomplete because of insufficient experimental data.

other point. In other words, as parameter C changes, the extreme value will move along the P axis. This fact may be used to improve the accuracy of the value of C, by correcting it so that the extremum will correspond to point P_0. Substituting the value of C obtained into (9), we find A. It follows from (5) that the function

$$B = \nu_B(P, V, A_0, C_0) = (P + C_0)(V - A_0) \qquad (11)$$

also has an extremum at the point P when C_0 and A_0 are correctly determined, which makes possible a secondary correction of constants A and C without recourse to the differentiation table.

Two equations have been investigated in this paper: the Biron equation (6), and the Tate equation [10]; the latter has the form

$$V = K\ln(P + L) + E, \qquad (12)$$

where K, L, and E are constants. These equations give a good description of the thermal properties of liquids, while having a small number of constants, which facilitates correction. The investigation was carried out according to experimental thermal data for ten substances: methyl and ethyl alcohol, acetone, diethyl ether, water, hexane, heptane, propylene, ethylene, and nitrogen.

It may be seen from Fig. 1 that the extreme values in the given case are maxima. A similar configuration ψ is also typical for the other substances. Points of inflection correspond to extreme values of the function ν_B.

A comparison is made in Fig. 1 of extrapolated values of specific volumes of liquid propylene at temperature 66° C with the test data of Michels et al [2]. The calculation was carried out according to (6), whose constants were determined by the above-mentioned method with $P_0 = 700$ atm, and by the method of least squares, taking into account all available experimental points from pressure 35.78 to 788.4 atm.

Table 1 shows the advantages of the proposed method of determining the constants for extrapolating thermal data. A similar result is also obtained for the other substances. It is evident that the extrapolation interval will depend on how closely contiguous the experimental isotherm and the approximating function are, i. e., on the size of the horizontal part of the ψ–P graphs. This part may be considerably enlarged by adding to the function ψ_B of equation (6) the term $|A - mV|/n$, in which m is determined from the relation $A - mV = 0$. Verification with the ten substances showed that the quantity n may be assumed equal to 3 for $P_0 < 900$ atm, and 4 for $P_0 > 900$ atm, independently of temperature and the nature of the substance. Equating the function

$$\bar{\psi}_B = \psi_B + |A - mV|/n \qquad (13)$$

to the constant A, we obtain a new approximating function

$$(P + C)\frac{dV}{dP} + V + \frac{|A - mV|}{n} = A, \qquad (14)$$

which after integration takes the form

$$(P + C)(\mu V - \bar{A})^{1/\mu} = \bar{B}. \qquad (15)$$

The constants of (15) are connected with those of (6) by the relations

$$\mu = 1 + m/n;\ \bar{A} = (1 + 1/n)A \text{ when } V > V_0,$$

$$\mu = 1 - m/n;\ \bar{A} = (1 - 1/n)A \text{ when } V < V_0.$$

Equation (15) transforms into (6) when $\mu = 1$.

The functions $\bar{\psi}_B$, and ψ_B for propylene and ethyl alcohol are shown in Fig. 2, and a comparison is made in Table 2 of the extrapolated specific volumes of the same substances, calculated according to (6) and (15), with the experimental data for $P_0 = 700$ atm. It may be seen from the table that the extrapolation interval of (15) is enlarged to several thousand atmospheres.

Let us now turn to Eq. (12). The functions ψ of this equation, which have the form

$$\psi_T = (P + L)\frac{dV}{dP},$$

are shown in Fig. 3.

In contrast to ψ_B, ψ_T do not have any extrema, taking a maximum value for some substances at a given P_0, and a minimum for others. The width of the horizontal parts corresponds to equation (14), and therefore for them the range of extrapolation is of the same order. Table 3 shows the deviations of the extrapolated specific volumes $\delta = \frac{V_{calc} - V_{exp}}{V_{exp}} \cdot 100(\%)$, calculated from (15) and (12), from the experimental values for three substances: propylene [2], methyl alcohol [1], and water [7]. For reasons of space we do not present detailed comparisons for the remaining substances investigated. The results of these investigations are represented in Table 4 by pressure intervals ΔP within which the deviations δ do not exceed 0.3%.

It is interesting to note that for some substances the errors corresponding to each of equations (15) and (12), and increasing with pressure, are opposite in sign. We may clearly establish a reasonable limit of extrapolation from their difference. The sign of δ depends on the type of extreme value of functions ψ. Since ψ_B has only one extreme value, the corresponding deviations are always of one sign—plus. As regards functions ψ_T, negative δ's correspond to their maxima, and positive to their minima. But even in the last case, the limit of extrapolation may be determined. If the deviations δ are plotted against pressure, the curve corresponding to (12) will have a much smaller slope. For all the substances we investigated, the deviations at the point of intersection of these curves did not exceed 0.3%. Thus, for methyl alcohol at 20° C the corresponding $\delta = +0.16\%$; at 80° C, +0.01%; for ethyl alcohol at 20° C, 0.15%; at 80°, 0.12%; for acetone 0.26%; for hexane 0.08%. In Table 4 the extrapolation ranges are established from the mean deviations δ_m.

Because there was not enough experimental material we were not able to investigate the nature of variation of ΔP of one substance in a wide temperature range. Nevertheless, the conclusion may be drawn from Table 4, that ΔP decreases with increasing temperature. Thus, at the same pressure $P_0 = 700$ atm, methyl alcohol has ΔP on the order of 3000 atm at $\tau = 0.532$; propylene has 1800 atm at $\tau = 1.160$; nitrogen has 600 atm at $\tau = 2.217$. This is also to be expected, since equations (6) and (12) were intended to describe substances in the liquid state. It is evident that in the gas region we should use equations which describe the gas better. Since ΔP increases with increase of P_0, we suppose that the method described is applicable also to gases at high enough pressures, when the properties of the gas are close to those of a liquid.

In conclusion we note that the extrapolation method presented was used to supplement the P, V, and T data of Timrot et al. [13] on liquid oxygen from 200 to 400 atm. From the expanded data an equation of state was set up, which described with high accuracy both the experimental and the extrapolated quantities.

NOTATION

P—pressure; T—absolute temperature. T_C—critical temperature; $\tau = T/T_C$—dimensionless temperature; P_0—maximum experimental pressure.

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17 May 1965

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