DETERMINATION OF THE COEFFICIENT OF VOLUME EXPANSION FOR LIQUIDS

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We present a theoretical method for an approximate determination of the coefficient of volume expansion for liquids at the saturation line. The theory of similarity and the molecular characteristics of the materials serve as the basis for the derivation of quantitative relationships.

The lack of experimental data for most substances serves as the impetus for the development of theoretical methods to determine the coefficient of volume expansion α.

Below we propose a method of determining α, this method based on the following premises.

The contemporary state of the theory of liquids does not allow for an analytical determination of α with the accuracy required for engineering calculations. The use of purely empirical formulas cannot yield results valid for an entire group of materials. We therefore make use of the theory of similarity.

According to the theory of similarity [1], the critical equation should express the relationship between the dimensionless coefficient of volume expansion and the relative complexes composed of known thermophysical characteristics of the material. The limited nature of experimental data on the physical constants hinders the direct application of the theory of similarity. To eliminate this shortcoming, we propose the use of a characteristic which expresses the individual properties of each substance.

The proposed characteristic is based on the Mendeleev periodic table of elements. It is demonstrated in [2] that the physical properties of a substance may be associated with the size of the structural particles. This also follows from the Kammerlingh–Onnes principle of mechanical similarity [5], according to which substances made up of molecules of some identical shape and size exhibit identical volume properties.

In addition, it should be pointed out that the quantity inversely proportional to the density ρ for the packing of the elementary particles in the molecule can be taken as the determining nominal volume of the molecules.

The packing density, in turn, according to [7, 8], is directly proportional to the mass number M of the molecules, and to the sum of the valences ΣE (the group numbers of the periodic table) for all atoms of the molecule; it is inversely proportional to $\Sigma 3$, i.e., the sum of electrons for all the atoms of the molecule, and to ΣC, i.e., to the sum of the electron layers for all of the atoms of the molecule.

Thus,

$$\rho = \frac{M\Sigma E}{\Sigma C \Sigma 3}. \tag{1}$$

Taking the quantity inversely proportional to (1) as the determining nominal volume of the molecule, we find

$$V_{\text{nom}} = \frac{\Sigma C \Sigma 3}{M \Sigma E}. \tag{2}$$

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TABLE 1. Molecular Characteristics of the Liquids

Liquid	ΣC,m	$\Sigma 3$,m	M,kg	ΣE,m^{-1}	$l^3_,$ m^{3}kg^{-1}	L
Freon 12 CF_2Cl_2	12	58	121	32	0,180	0,647
Water H_2O	4	10	18	8	0,278	1,000
Benzene C_6H_6	18	42	78	30	0,320	1,163
Diethyl ether $C_2H_5OC_2H_5$	20	42	74	32	0,356	1,280
Ammonia NH_3	5	10	17	8	0,367	1,323
Ethane C_2H_6	10	18	30	14	0,429	1,543
Diborane B_2H_6	10	16	27,7	12	0,485	1,748
Mercury Hg	6	80	200,6	2	1,153	4,300

It should be noted that in [7, 8], as well as in this paper, we use the conventional linear dimension

$$l = \left(\frac{\Sigma C \Sigma 3}{M \Sigma E} \right)^{1/3}, \tag{3}$$

from which $V_{nom} = l^3$.

Table 1 lists the magnitudes of the nominal volume and the molecular characteristics obtained from (2) for certain liquids.

Let us construct the relative dimensionless variable containing the unknown – the coefficient of volume expansion at constant pressure. We will use one of the statements of the theory of similarity [3]: any combination of relative variable and of the criterion of similarity represents a dimensionless form of the variable. Applying this property to earlier derived and utilized variables [7], we obtain the following as a function of the dimensionless criterion:

$$K_\alpha = \frac{\alpha T l^3}{V}, \tag{4}$$

which contains the unknown.

The reduced pressure may serve as the argument:

$$\pi = \frac{p}{p_{cr}}. \tag{5}$$

We thus obtain the general form for the relationships between these variables, i.e.,

$$K_\alpha = f_1(\pi). \tag{6}$$

The specific form of the equation is based on the processing of experimental data for water [4]. The narrow range of temperatures from 273 to 277°K, in which water exhibits anomalous properties, is not considered here.

The experimental data for water on the saturation line are approximated by the criterial equations:

a) for $\pi = 0.05-0.2$

$$K_\alpha = 525\pi + 112{,}5, \tag{7}$$

b) for $\pi = 0.2-0.65$

$$K_\alpha = 156 \cdot 10^{0.84\pi}. \tag{8}$$

According to [1], the coordinates of the curve $K_{\alpha\,\text{stand}} = f_2(\pi)$ of the test liquid can be found by multiplying the coordinates of the standard liquid by conversion factors for the coordinate axes K_α and π. The correction factor N in this case is a function of the conversion factors. As is well known, the explicit form of this function of the theory of similarity is not determined, but found experimentally by mathematical processing, in this case, of the coordinates of the family of curves found from (6) for a large number of liquids.

In this paper we have been confronted with the practical necessity of introducing a single correction factor N, and namely

$$K_{\text{test}} = K_{\text{st}} N, \tag{9}$$

TABLE 2. Comparative Data on the Coefficient of Volume Expansion for Certain Liquids

Liquid	$p_{cr}\cdot 10^{-5}$ N/m^2	T, °K	$p\cdot 10^{-5}$, N/m^2	$V\cdot 10^3$ m^3/kg	π	$a_p\cdot 10^3$ deg^{-1}	$a_{exp}\cdot 10^3$ deg^{-1}	$\Delta = (a_{theor} - a_{exp})/a_{exp}\cdot 100$, %
Freon CF_2Cl_2	41,2	273,15	3,09	0,7173	0,075	2,335	2,363	+1,21
		338,15	16,9	0,8741	0,411	4,212	4,435	+5,30
		358,15	25,15	0,968	0,612	6,210	6,647	+7,05
Water H_2O	221,29	533,15	46,94	1,2755	0,212	2,000	2,020	+1,00
		563,15	74,45	1,3655	0,336	2,607	2,607	0,00
		593,15	112,90	1,499	0,510	3,803	3,795	—0,18
		613,15	146,08	1,639	0,660	5,308	5,345	+0,70
Benzene C_2H_6	47,7	418,15	5,105	1,357	0,107	1,695	1,732	+2,22
		478,15	14,93	1,535	0,313	2,606	2,684	+3,0
		528,15	31,08	1,829	0,647	5,139	5,172	+0,65
Diethyl ether $C_2H_5OC_2H_5$	36,1	328,15	1,65	1,475	0,0456	1,695	1,783	+5,25
		403,15	11,85	1,79	0,328	3,355	3,466	+3,3
		433,15	20,35	2,022	0,564	5,366	5,151	—4,0
Ammonia NH_3	109,5	285	6,41	1,607	0,0585	2,300	2,434	+5,85
		355	42,1	1,95	0,384	4,380	4,460	+1,8
		385	76,5	2,39	0,698	8,770	8,147	—7,1
Ethane C_2H_6	48,6	228,15	6,56	2,062	0,135	2,900	2,900	0,0
		268,15	21,25	2,364	0,434	5,200	5,181	—0,36
		288,15	33,7	2,706	0,693	9,670	9,143	—5,45
Diborane B_2H_6	38,8	200	2,565	2,466	0,0661	2,960	2,513	—15,1
		250	14,63	2,984	0,377	5,278	4,676	—11,4
		270	24,6	3,418	0,633	9,252	8,000	—13,5
Mercury Hg	10,21	953,15	45,1	0,08354	0,0442	1,630	1,369	—15,9

where

$$N = f_3\left(\frac{l^3_{te}}{l^3_{st}}\right).$$

The explicit form of the correction factor has been found experimentally, i.e.,

$$N = \frac{L^2}{0.1\cdot 10^{0.9709L}}, \tag{10}$$

where L^3_{test}/l^3_{stand}.

In using the working formulas (7) and (8), with introduction of the correction factor (10), according to (9), we found the magnitudes for the coefficient of volume expansion for all of the substances under discussion to be overstated by 10-15%.

In this connection, Eqs. (7) and (8) have been altered slightly to yield more exact results with respect to α. The range of applicability for the working formulas has thus been changed.

The working formulas (7) and (8), with the correction and the introduction of the correction factor N, have the form:

a) for $\pi = 0.05-0.35$

$$K_\alpha = \frac{525\pi + 111.9}{0.91(1+0.175\pi)}\;\frac{L^2}{0,1\cdot 10^{0.9709L}}, \tag{11}$$

b) for $\pi = 0.35-0.65$

$$K_\alpha = \frac{146.5\cdot 10^{0,805\pi}}{0.91(1+0,175\pi)}\;\frac{L^2}{0,1\cdot 10^{0.9709L}}. \tag{12}$$

The use of (7) and (8) to determine the coefficient of volume expansion for water at the saturation line and the use of (11) and (12) for other liquids, whether organic or inorganic, with pronounced difference in molecular structure, shows that the scattering of the theoretical points in comparison with the experimental values of these points is comparatively slight.

Table 2 shows the comparative data for a number of liquids at the saturation line.

Because the coefficient of volume expansion α is not available in explicit form at the saturation line for most substances, it is calculated on the basis of tabulated data [4, 6] according to a formula yielding an average value:

$$\bar{\alpha} = \alpha_{\text{theor}} = \frac{1}{\bar{V}}\left(\frac{\Delta V}{\Delta T}\right)_{\bar{p}} . \qquad (13)$$

To increase the accuracy of the resulting values of $\bar{\alpha}$, we used the smallest possible range for the averaging parameters.

NOTATION

p, V, T	are, respectively, the pressure, the volume, and the temperature of the liquid at the saturation line;
p_{cr}	is the liquid pressure at the critical points;
$K_{\alpha\text{test}}$, $K_{\alpha\text{stand}}$	are, respectively, the critical determined for the test and standard liquids;
α_{theor}, α_{exp}	are, respectively, the theoretical and experimental values for the coefficient of liquid volume expansion;
Δv	is the change in the specific volume of the liquid with a change in liquid temperature by ΔT;
$\bar{\alpha}$, $\bar{v}$, $\bar{p}$	are the average values of these quantities;
l^3_{test}, l^3_{stand}	are, respectively, the determining nominal volumes of the molecules for the test and standard liquids.

LITERATURE CITED

1. A. A. Gukhman, Introduction to the Theory of Similarity [in Russian], Vysshaya Shkola (1963).
2. M. Kh. Karapet'yants and S. I. Drakin, The Structure of Matter [in Russian], Vysshaya Shkola (1967).
3. A. A. Gukhman, Khim. Promyshl., No. 7 (1965).
4. M. P. Vukalovich, Tables of Thermodynamic Properties for Water and Water Vapor [in Russian], Energiya (1965).
5. G. Hirschfelder, C. Curtiss, and R. Bird, The Molecular Theory of Gases and Liquids [Russian translation], IL (1961).
6. N. B. Vargaftik, Handbook on Thermophysical Properties of Gases and Liquids [in Russian], FM (1963).
7. I. A. Cherepennikov, Trudy TIKhM, No. I, VNIIRTMASh, Tambov (1967).
8. I. A. Cherepennikov, Trudy TIKhM, No. II, VNIIRTMASh, Tambov (1968).