DETERMINATION OF THE THERMOPHYSICAL CHARACTERISTICS OF INCOMPRESSIBLE LIQUIDS

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The author demonstrates the possibility of determining the thermophysical constants of incompressible liquids by the methods of similarity theory and dimensional analysis in general form without the use of critical parameters.

In designing thermal installations, it is necessary to know the physical constants of the heat carriers. In spite of the currently available reference materials, there is at present a partial or complete lack of data on the properties of many liquids.

Since the experimental determination of thermophysical characteristics is very laborious, it is necessary to employ a calculation apparatus. The purely empirical formulas now in use give, as a rule, a simplified dependence of one characteristic on another. The limitations of the method do not permit one to find a form of the functional dependence of the parameter under investigation on a set of other parameters.

The existing method of determining parameters using the principle of corresponding states has the following shortcomings: a) the variables employed do not reflect completely the physical properties of the substance; b) for computation purposes it is necessary to know not only a relation between the reduced parameters of the type

$$p/p_{cr} = f(v/v_{cr}, T/T_{cr}), \qquad (1)$$

but also the values of the critical parameters, the determination of which is difficult.

The present investigation offers a method of determining the thermophysical properties of liquids based on the use of the theory of similarity and dimensional analysis in a more general form than has been available so far.

It develops that for thermodynamically similar substances, it is possible to use the following equation instead of Eq. (1):

$$K_1 = f(K_2, K_3, \ldots, K_7), \qquad (2)$$

where K_1, K_2, K_3, ..., K_7 are dimensionless relative variables—similarity criteria [1]. These are constructed in accordance with dimensional analysis from parameters which do not include p_{cr}, v_{cr}, and T_{cr}.

In developing the criteria, it is necessary to introduce the initial variables which most fully reflect the individual properties of a substance. Equality of the indicated criteria for several substances will characterize the similarity of their states. The parameters included in the criteria will be connected by the well-known relationship

$$p_i = cp_b.$$

Function (2) is exponential. Its specific form is established experimentally for individual substances. Based on the theory of similarity the results of one experiment may be extended to a number of similar systems. In this case they are thermodynamically similar substances.

Let us analyze the application of the given method using the example of the thermophysical properties of the hydrocarbons forming the alkane homologous series.

The following set of quantities characterizes the problem under consideration:

$$T, p, v, c_p, \mu, \lambda, r, \sigma, A, \alpha, l.$$

In accordance with dimensional analysis [2], all the variables expressing the properties of a substance must appear in dimensionless exponential form:

$$T^s \cdot p^t \cdot v^a \cdot c_p^b \cdot \mu^d \cdot \lambda^e \cdot r^f \cdot \sigma^h \cdot A^w \cdot \alpha^k \cdot l^i.$$

Substituting the dimensions of the quantities, we obtain

Comparative Data for Determining the Coefficient of Dynamic Viscosity

Hydrocarbon	Temperature, °K	$\mu_{exp} \cdot 10^{-3}$, N · sec/m² according to [3]	$\mu_{calc} \cdot 10^{-3}$, N · sec/m²	$\frac{\mu_{calc} - \mu_{exp}}{\mu_{calc}} \cdot 100\%$
N-Pentane	283	0.259	0.285	+9.13
	288	0.25	0.277	+9.74
	293	0.24	0.26	+7.7
	298	0.23	0.245	+6.12
	303	0.22	0.235	+6.38
N-Heptane				
	303	0.373	0.39	+ 4.36
	338	0.281	0.283	+ 0.71
	373	0.201	0.203	+ 0.99
	403	0.153	0.151	— 1.33
	433	0.12	0.109	—10.2

$$[\theta]^s \cdot [L^{-1} \cdot M \cdot T^{-2}]^t \cdot [L_3 \cdot M^{-1}]^a [L^{-1} \cdot MT^{-1}]^d \cdot$$
$$\cdot [L^2 \cdot T^{-2}\theta^{-1}]^b \cdot [L \cdot M \cdot T^{-3} \cdot \theta^{-1}]^e \cdot$$
$$\cdot [L^2 \cdot T^{-2}]^f [MT^{-2}]^h \cdot [M]^w \cdot [\theta^{-1}]^k \cdot [L]^i. \quad (3)$$

In expression (3) the sum of exponents for each symbol of the basic units of measurement must equal zero. The problem under study links 11 parameters. Their dimensions are expressed with the use of four basic units. According to the pi-theorem, the total number of criteria will equal seven.

According to the number of primary quantities characterizing the given problem, we obtain a system of four equations for determining the following 11 exponents:

$$s - b - e - k = 0,$$
$$-t + 3a + 2b - d + e + 2f + i = 0,$$
$$-2t - 2b - d - 3e - 2f - 2h = 0,$$
$$t - a + d + e + h + w = 0.$$

Therefore, 7 exponents may be selected arbitrarily. Solving this system by the generally-acepted method of [2], and substituting the values found in expression (3), we obtain the following 7 criteria which link the basic thermophysical characteristics of liquids:

$$K_1 = \sigma^2/\mu\lambda T, \; K_2 = \sigma^2/pv\mu^2, \; K_3 = c_p\mu/\lambda = \mathrm{Pr}, \; K_4 = \mu^2 r/\sigma^2,$$
$$K_5 = N\mu^2\sigma/Mp^2, \; K_6 = a\sigma^2/\mu\lambda, \; K_7 = \sigma/pl.$$

In view of the lack of data on the coefficient of volume expansion for the majority of the hydrocarbons under consideration, it is interesting to find, first of all, the dependence of this quantity on the parameters whose measurement is not complicated and on the parameters characterizing the individual properties of liquids.

To this requirement there corresponds the equation

$$K_\alpha = f(K_\mu),$$

where K_α and K_μ are obtained by combining the initial relative variables, since any such combination produces a new criterion. The processing of the experimental data of [3] on the thermophysical properties of n-octane leads to the following exponential relationship:

$$K_\mu (\alpha T)^n = \mathrm{const},$$

which corresponds to the specific equation

$$K_\mu (\alpha T)^{3.1} = 824 \cdot 10^6. \quad (5)$$

The validity of formula (5) was verified on n-pentane and n-heptane by substituting the value of α and determining μ. The values of α for n-heptane were obtained by extrapolation of the data of [3]. During verification the value of αT was varied from 0.379 to 0.866. The values of μ obtained experimentally and by computation for n-pentane and n-heptane are shown in the table.

Criterial dependence (5) permits the determination of the value of the coefficient of alkane volume expansion, which is essential in finding the specific volume of a liquid as a function of temperature.

Thus, application of similarity theory and dimensional analysis in general form permits the determination of the thermophysical characteristics of incompressible liquids without the use of critical parameters, which decreases the number of initial data.

The degree of accuracy of the results obtained naturally depends on the experimental errors as well as on the number of sections into which we divide the curve of the functional relation between the criteria in processing the experimental results.

NOTATION

T—temperature of liquid; p—pressure; v—specific volume; c_p—isobaric specific heat; μ—coefficient of dynamic viscosity; λ—heat conductivity; σ—surface tension; A = M/N—relative molecular mass; M—kilomole mass; N—Avogadro's number; $l = \sqrt[3]{6n/3.14}$ — characteristic dimension, characterizing the conventional linear dimension of a molecule; l—diameter of sphere whose volume is proportional to the number of atoms in a molecule; n—number of atoms in a molecule; s, t, a, b, d, e, f, h, w, k, and i—exponents; $K_\alpha = \alpha T$, $K_\mu = \frac{N}{M}\frac{\mu^3 l}{\rho}$; p_{cr}, v_{cr}, and T_{cr}—critical parameters; p_i and p_b—parameters of investigated and base substances; c—similarity constant; α—coefficient of volume expansion at constant pressure. Dimensions of all the quantities are given in the international system.

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