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A METHOD FOR CALCULATING HEAT CAPACITY AND THERMAL CONDUCTIVITY OF LIQUIDS

L. P. Filippov

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Methods employing easily obtainable empirical data are described for calculation of heat capacity, speed of sound, and thermal conductivity of liquids.

The methods proposed in this study for calculation of thermophysical properties are based on the theory of thermodynamic similarity. Use of thermodynamic similarity principles for description of the thermal properties of liquids and gases reveals a number of important principles and makes it possible to develop effective methods for computation of a large number of properties [1, 2]. One of the most important principles is the one-parameter law of corresponding states for the class of normal, nonassociated substances, i.e., the existence of one and only one dimensionless parameter (the defining criterion) that characterizes the individuality of the substance in the dimensionless equation of state [1].

The basis for description of thermal properties using thermodynamic similarity theory is the so-called expanded law of corresponding states [3], according to which the differences between values of the thermodynamic properties under given conditions and the same values for the ideal gas state at the same temperature must obey the rules of thermodynamic similarity. In the case of heat capacity, on the saturation line the expanded law of corresponding states for normal substances should have the form

$$C_p = C_p^0 + \Delta C_p(\tau, A),$$
$$C_v = C_v^0 + \Delta C_v(\tau, A), \quad (1)$$

where C_p and C_V are the molar heat capacities on the saturation line (for the liquid or vapor branch); C_p^0 and C_V^0 are the corresponding values in the ideal gas state) and ΔC_p and ΔC_V are the configuration heat capacities, which must be identical functions of the dimensionless temperature $\tau = T/T_{cr}$ and the defining criterion A for the entire class of materials considered.

The functions $\Delta C_p(\tau, A)$ and $\Delta C_V(\tau, A)$ for the liquid state were studied using available data on 60 materials and are presented in Table 1. [numerator, ΔC_p; denominator, ΔC_V, J/(mole•°K)].

For practical calculation of configuration heat capacity it is not obligatory to know explicitly the critical temperature and parameter A. Methods may be used to determine these

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TABLE 1. ΔC_p (numerator) and ΔC_v (denominator) versus τ and log A

τ	log A				
	−0,2	−0,1	0	0,1	0,2
0,5	82, (5)	75/26, (5)	67, (5)/24	60/21, (5)	52, (5)/19
0,55		70/25, (5)	63, (5)/23	57, (5)/20, (5)	50, (5)/18
0,6			60, (5)/22	56/19, (5)	50, (5)/17
0,65			60/21	55, (5)/18, (5)	50, (5)/16
0,7			61, (5)/20	56, (5)/17, (5)	52/15
0,75				59	54
0,8				62, (5)	57
0,85				69	63
0,9				79	75

τ	log A			
	0,3	0,4	0,5	0,6
0,5	45/17	38/15	30, (5)/13	23, (5)/11, (5)
0,55	44, (5)/16	37, (5)/14	30/12	23, (5)/10, (5)
0,6	44, (5)/15	37, (5)/13	29/11	23, (5)/9, (5)
0,65	45/14	37, (5)/12	30/10	24/8, (5)
0,7	45, (5)/13	38, (5)/11	31, (5)/9, (5)	25/8
0,75	47, (5)	40, (5)	33, (5)	27, (5)
0,8	50, (5)	44	38	32, (5)
0,85	57	51	45	40
0,9	69, (5)	63	56, (5)	52, (5)

quantities based on easily obtainable empirical information. In [1] the author described methods for calculation of critical parameters and the criterion A, commencing from two given values of vapor pressure and one density value or from two density values and one vapor pressure value. Either of these sets of data may be used for calculation of configuration heat capacities. The total heat capacity C_p and C_v may be calculated by using theoretical or empirical methods for calculating C_p^0 together with the configuration heat capacity values.

We will present examples of heat capacity calculations. We will consider the liquids n-hexane (which also served as an example in [1] and [2]) and Freon-11 as examples of a liquids of industrial importance. We will use the first of the sets of data referred to above. The data are as follows: for hexane, t_{boil} = 68.7°C, P = 121 mm Hg at 20°C, and ρ = 0.6594 g/cm^3 [1]; for Freon, t_{boil} = 23.7°C, and p = 0.403 barr at 0°C, and ρ = 3.445 g/cm^3 [5]. For calculation of C_p^0 of hexane, following the recommendation of [4], we use the method of Sauders et al., while for Freon (also as recommended in [4]), we use the method of Richani and Doresveimi. The results of the calculations are presented and compared with data from the literature in Table 2. Calculations of heat capacity ratios by the method described here are compared with calculations by the simple empirical formula proposed by the author previously:

$$\frac{C_p}{C_v} = 1 + \frac{56.5}{C_p} \tag{2}$$

[C_p in J(mole•°K)] and with thermodynamic computations from [10].

Examination of Table 2 will reveal that the proposed method gives results agreeing with experiment to within 5%.

For thermal conductivity calculations we require data on the speed of sound. These data may also be obtained by calculations based on the previously determined C_p/C_v and isothermal compressibility β_T. For calculation of the latter quantity we have proposed methods using the same set of initial data as used above. This calculation is based on yet another fundamental principle predicted by the theory of thermodynamic similarity: the universality of the dependence of the complex $\mathscr{P} = \beta_T(RT\rho/M)$ on the dimensionless volume $\varphi^{-1} = \rho/\rho_{cr}$. The function of one variable $\mathscr{P}(\varphi)$ identical for all normal liquids, then gives the isothermal compressibility β_T as a function of temperature and pressure.

We have proposed two formulas for approximation of $\mathscr{P}(\varphi)$ [1, 8]:

$$\mathscr{P} = 0.201\,\frac{(\varphi - 0.256)^2}{(0.538 - \varphi)\,\varphi}, \tag{3}$$

TABLE 2. Calculation of Properties of Hexane and Freon-11

t, °C	C_p, J/(mole·°K), calc.	C_v, J/(mole·°K), [5]	C_v, J/(mole·°K), calc.	C_p/C_v, calc.	C_p/C_v, Eq. (2)	C_p/C_v, [10]	u, m/sec, calc.	u, m/sec, [10, 11]	λ, W/(m·°K), calc.	λ, W/(m·°K), [9]
				Hexane						
0	185	183	142	1,30	1,30	1,29	1192	1189	0,132	
10	188	186	146	1,29	1,30	1,29	1144	1143	0,130	
20	192	189	150	1,28	1,29	1,29	1096	1098	0,128	0,125
30	196		153	1,28	1,29	1,29	1052	1054	0,126	0,123
40	199		156	1,28	1,28		1012	1010	0,124	0,120
50	203		160	1,27	1,28		967		0,122	0,118
60	207		163	1,27	1,27		926	921	0,120	0,116
70	211		166	1,27	1,27		881		0,118	
80	215		169	1,27	1,26		840	834	0,116	
90	219									
100	224									
110	228									
120	233									
130	238									
140	243									
150	249									
160	254									
170	263									
180	273									

t, °C	C_p, J/(mole·°K), calc.	C_p, J/(mole·°K), exp.	C_v, J/(mole·°K), calc.	C_p/C_v, calc.	C_p/C_v, Eq. (2)	u, m/sec, calc.	λ, W/(m·°K), calc.	λ, W/(m·°K), table
				Freon-11				
—40	106		71	1,50	1,53	924	0,094	0,105
—30	108		72,5	1,49	1,52	887	0,092	0,103
—20	109		73,5	1,49	1,52	858	0,091	0,101
—10	110		74,5	1,48	1,51	830	0,090	0,098
0	112		75	1,48	1,51	794	0,089	0,096
10	113		76	1,48	1,50	764	0,087	0,093
20	114		77	1,49	1,49	736	0,085	0,091
30	116	119 [6]	78	1,48	1,49	703	0,084	0,089
40	117	125 [12]	79	1,48	1,48	678	0,082	0,086
50	118		79,5	1,49	1,48	642	0,080	0,084
60	120	129 [12]						
70	122							
80	124	132 [12]						
90	127							
100	130	136 [12]						
110	133							
120	136	142 [12]						
130	139							
140	143	154 [12]						

$$\mathscr{P} = 72\varphi^{7.5} \quad (4)$$

In the range $0.32 \geq \varphi \geq 0.45$ these formulas give similar results. Data on isothermal compressibility were used in calculations of the speed of sound. Results are also presented in Table 2. It is evident from the example of hexane that the results agree well with experimental data.

Thermal conductivity on the saturation line can then be determined with the aid of the formula previously proposed by the author [9]:

$$\lambda = 2.12u(c_p\rho)^{2/3}k^{1/3}\left(\frac{\rho_{cr}}{\rho}\right)^{5/3}, \quad (5)$$

where c_p is specific heat capacity.

The critical density value ρ_{cr} appearing in this formula is determined from the same initial data used above by a method described in [1]. Results of the calculations and a comparison with data from the literature are presented in Table 2. The divergence does not exceed the accuracy of the calculations, which comprises approximately 10%.

In the above discussion we have limited ourselves to calculation of liquid properties on the saturation line. It is clear, however, that analogous calculations may be performed over a wider range of states. In the case of heat capacity, well-known thermodynamic relationships may be used together with methods for calculating p, v, T relationships on the basis of the same set of initial data, while for thermal conductivity the fact may be used that in the dense liquid region the dependence of thermal conductivity on density is given in the first approximation by the dependence on temperature and pressure.

NOTATION

C_p, molar heat capacity at constant pressure; C_v, molar heat capacity at constant volume; T_{cr}, ρ_{cr}, critical temperature and density; A, defining criterion of thermodynamic similarity; u, speed of sound; k, Boltzmann's constant.

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