PREDICTING THE THERMAL PARAMETERS OF LIQUIDS

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A three-constant equation of state has been used to describe the thermodynamics of the liquid phase for substances with various types of molecular interaction, and a method has been devised for forecasting the thermal parameters of normal and slightly polar liquids, which enables one to predict the density with a mean error of 0.5%.

Rapid advances in technology employ an increasing range of substances and require methods of forecasting thermophysical parameters from minimal data. Optimization calculations on equipment and processes require that these parameters should be represented as simple and compact analytic equations.

For this purpose, we have used the equation of state

$$z = 1 - 1{,}744\,\frac{\varepsilon_l}{kT}\,[(b_{0l}\rho)^2 - 0{,}4654\,(b_{0l}\rho)^4], \tag{1}$$

derived from the cellular model for a liquid in combination with the effective (12, 6) potential containing variables dependent on temperature [1]. It has been shown [2] that (1) contains three constants, because ε_ℓ and $b_{0\ell}$ can be represented as functions of temperature:

$$\varepsilon_l/kT = 0{,}795T_c \exp[c(1 - T/T_c)], \tag{2}$$

$$b_{0l} = \frac{2}{3}\pi N\sigma_l^3;\ \sigma_l^{-3} = a - bT/100. \tag{3}$$

The values of a, b, and c in (2) and (3) are characteristic of a particular liquid and are derived from PVT data. The methods used to determine them incorporate the uneven distribution of the measured points on the PVT surface. Usually, most of the measurements represent the region of the boundary curve for the liquid, where the PVT surface has its maximum curvature. The rest of the liquid region is represented by a relatively small number of points. This point disposition on the PVT surface is equivalent to assigning considerable weight to the low-density region. The parameters in (1) derived from such data provide better description of the parts of the PVT surface examined in detail at the expense of worse agreement with experiment for regions where the measured p, v, and T values are few.

One can offset the effects of the inexplicitly introduced weights for the measurements by a method based on assigning each point a weight inversely proportional to the local point density on the PVT surface.

Let the initial PVT parameters for the liquid be represented by n measured points distributed in any way. Each of them is characterized by coordinates π, τ, ω. Then the distance between points i and j is

$$R_{ij} = [(\pi_i - \pi_j)^2 + (\tau_i - \tau_j)^2 + (\omega_i - \omega_j)^2]^{1/2}. \tag{4}$$

When the R_{ij} are arranged in increasing order, one can take say the first m values, which relate to points lying on the $\pi\tau\omega$ surface near point i. Let $r_{ij} = R_{ij}/R$, where R is the extreme value for the given set of R_{ij}. Then

$$f_i = \frac{1}{m}\sum_{j=1}^{m} r_{ij} \tag{5}$$

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TABLE 1. Parameters in the Equation of State and Description Performance for Liquid Thermal Properties

Substance	T_c, K	$a \cdot 10^2$	$b \cdot 10^3$	c	p_{max}, MPa	$\Delta\tau$	$\overline{\delta\rho}_l$, %	No. of points	Ref.
Ne	44,40	6,828556	51,87415	2,09	100	0,56...1,00	0,19	200	[5]
Ar	150,65	3,976884	9,58571	2,17	100	0,56...1,00	0,06	169	[5]
Kr	209,39	3,270434	5,69100	2,17	100	0,55...1,00	0,10	342	[5]
Xe	289,75	2,524962	3,12925	2,18	100	0,56...1,00	0,13	234	[5]
CH_4	190,77	3,012743	5,72963	2,18	100	0,48...1,10	0,13	240	[6]
N_2	126,20	3,375200	10,09800	2,39	100	0,52...1,00	0,15	776	[7]
O_2	154,58	4,102500	9,89500	2,19	30	0,36...1,00	0,08	260	[8]
CO_2	304,20	3,492295	4,78883	2,83	100	0,72...1,10	0,22		[9]
NH_3	405,55	4,747026	4,64472	1,89	100	0,49...1,10	0,10		[10]
C_2H_4	282,35	2,379882	3,30548	2,43	100	0,39...1,00	0,11	604	[4]
CF_3Br	340,20	1,618441	1,94879	3,01	50	0,50...0,88	0,09	47	[11]
$C_2F_3CL_3$	487,25	0,996983	0,85798	3,26	25	0,52...1,00	0,07	144	[12]
$C_2F_4CL_2$	418,85	1,113835	1,12981	3,09	21	0,77...1,03	0,15	24	[13]
C_2F_5CL	353,15	1,244964	1,48459	3,44	60	0,57...1,10	0,21	322	[14]
$C_2H_4F_2$	386,65	1,889912	2,02538	2,63	50	0,41...1,00	0,09	195	[15]
C_2H_5Br	503,80	1,561330	1,27607	2,85	98	0,56...1,02	0,22	45	[16]
$C_4H_8O_2$ (methyl propionate)	530,60	1,202364	0,98040	3,31	50	0,57...1,13	0,20	36	[17]
$C_4H_8O_2$ (ethyl acetate)	523,20	1,160858	0,89763	3,53	50	0,57...1,02	0,25		[18]
C_5F_{12}	420,59	0,805210	0,95343	3,38	4,4	0,78...0,90	0,16	21	[19]
C_6H_6	562,60	1,267385	0,94589	2,89	60	0,56...1,20	0,15	90	[20]
C_6H_{12} (cyclohexane)	553,40	1,052663	0,81314	3,30	80	0,54...1,26	0,18	113	[21]
C_6H_{12} (1-hexene)	504,00	0,944009	0,80846	3,50	70	0,56...0,94	0,21	99	[22]
C_7H_6O	695,00	1,044931	0,63668	3,10	50	0,42...0,91	0,20	62	[23]
C_7H_8	593,95	1,040525	0,73583	3,14	50	0,29...1,09	0,19	78	[24, 25]
C_7H_{14}(methylcyclohexane)	572,15	0,879715	0,65445	3,63	70	0,49...1,00	0,19	75	[22]
C_8H_{10} (p-xylene)	618,15	0,890343	0,61490	3,33	50	0,52...1,05	0,22	53	[26]
C_8H_{10} (*o*-xylene)	631,59	0,899810	0,59921	3,32	50	0,40...1,03	0,18	72	[27]
C_8H_{10} (m-xylene)	619,15	0,890323	0,60368	3,17	20	0,48...0,76	0,11	57	[28]
C_8H_{10}(ethylbenzene)	619,55	0,897773	0,62404	3,36	50	0,30...0,93	0,18	80	[29]
C_8H_{16} (1-octene)	566,60	0,726993	0,57968	3,83	71	0,50...0,88	0,21	76	[18]
C_9H_{12} (isopropylbenzene)	631,00	0,781387	0,52303	3,65	50	0,45...0,91	0,19	62	[30]

can be taken as an approximate characteristic for the local point density near point i, while as the weight one takes in general $w_i = f^{\gamma}_i$, where $\gamma \geqq 1$. Clearly, the less f_i, the higher the point density.

We minimize the following functional to derive a, b, and c in (1) for numerous substances differing in molecular interaction:

$$s = \sum_{i=1}^{n} w_i \left(z_i^{\text{ex}} - z_i^{\text{cal}}\right)^2 \tag{6}$$

where the Nelder-Mead method [3] was employed. Subsequent reproduction of the liquid densities for the initial P and T showed that the description error increases with temperature in proportion to $1 - \tau^{\alpha}$, where $\alpha \leqq 1$, so in general the weights should be refined on that basis:

$$w_i = \frac{1}{1 - \tau_i^{\alpha}} \left(\frac{1}{m} \sum_{j=1}^{m} r_{ij}\right)^{\nu}. \tag{7}$$

TABLE 2. Forecast Results for Liquid Thermal Parameters

Substance	T_c, K	$\delta\rho'$, %	$\overline{\delta\rho}_l$, %	$\Delta\tau$	p_{max}, MPa	Ref.
Ar	150,65	0,15	0,38	0,56...1,00	100	[5]
Kr	209,39	0,21	0,30	0,55...0,96	100	[5]
Xe	289,75	0,15	0,35	0,56...0,98	100	[5]
N_2	126,20	0,19	0,23	0,52...0,99	100	[7]
C_6H_{14} (n-hexane)	507,40	0,09	0,27	0,36...0,95	30	[32]
C_2H_4	282,35	0,13	0,46	0,39...0,99	100	[11]
C_2H_6	305,50	0,12	0,27	0,30...0,93	60	[33]
CF_3Br	340,20	0,10	0,13	0,50...0,88	50	[12]
CCL_4	556,35	0,12	0,22	0,49...0,91	112	[34—38]
$CFCL_3$	471,15	0,20	0,22	0,52...1,00	20	[39]
CF_2CL_2	388,45	0,25	0,24	0,57...0,83	100	[40]
CF_3CL	301,99	0,12	0,46	0,33...0,98	50	[12]
CF_4	227,50	0,15	0,20	0,40...0,98	57	[41, 42]
$CHCL_3$	536,60	0,01	0,50	0,51...0,65	99	[43]
CHF_2CL	369,30	0,05	0,42	0,36...0,85	50	[12]
CH_2CL_2	518,15	0,003	0,43	0,58...0,67	86	[43]
CH_4	190,77	0,23	0,22	0,48...1,10	100	[6]

One chooses α and γ, as well as the number m of points lying near point i, from considerations of the best description of the measured thermal parameters.

The weights of (7) substantially improve the description of the reference PVT data. For example, (1) with parameters derived from the data of [4] on liquid ethylene can be employed with (6) and (7) to reproduce the initial set (604 points) with a mean density error $\delta\rho_l$ = 0.11%, where $\delta\rho_{max}$ = 0.99%, while the number l of points for which $\delta\rho \geqq 0.3\%$ is 34. If no weights are used ($w_i = 1$), the corresponding characteristics are substantially worse: $\delta\rho_l$ = 0.37%, $\delta\rho_{max}$ = 1.61%, l = 350. Similar pictures occur for the other substances.

Table 1 gives a, b, and c for substances differing greatly in interactions, together with the fit to the PVT data for the liquids. The effective potential with variable parameters enables one to apply (1) to all liquids, including highly polar ones such as NH_3, methyl propionate $C_4H_8O_2$, ethyl acetate $C_4H_8O_2$, difluoroethane $C_2H_4F_2$, and benzaldehyde C_7H_6O, whose dipole moments are 1.5; 1.7; 1.9; 2.3; 2.8 D correspondingly.

As (1) reflects the PVT surface of liquid correctly, it can be used to calculate properties from restricted data. The information most readily available for a pure substance is the PVT data on the saturation line, and the method is as follows.

First, one derives an analytic relationship between c (Table 1) and the Pitzer factor β defined by the Lie-Kessler equation [31]:

$$\beta = \frac{-\ln p_K - 5.92714 + 6.09648\theta^{-1} + 1.28862\ln\theta - 0.169347\theta^6}{15.2518 - 15.6875\theta^{-1} - 13.4721\ln\theta + 0.43577\theta^6}. \tag{8}$$

Least-squares processing of the c data from Table 1 gave c(β) as

$$c = 2.122 + 5.8822\beta - 5.2995\beta^2 + 1.6278\beta^3. \tag{9}$$

In the second stage, the PVT data for the saturated liquid were used with the c derived from (9) to derive a and b by minimizing (6) with w_i = 1.

Table 2 gives the description performance for 17 substances on the liquid boundary line together with the reliability in forecasting PVT for the liquid (mean density error) along with the coordinates of the forecast PVT region.

The results show that this method is quite effective and can be recommended to obtain the properties of normal and slightly polar liquids at high pressures even if one knows only the thermal parameters on the saturation line.

As regards highly polar substances, we note that (9) does not apply so well, and although the sensitivity of the method to errors in c is fairly small, the forecast performance in that case is characterized by $\delta\rho_l$ about 1%.

NOTATION

z, compressibility coefficient, $p/RT\rho$; p, pressure; R, universal gas constant; T, temperature; ρ, molar density; k, Boltzmann constant; T_c, critical temperature; N, Avogadro's number; $\pi = p/p_c$, reduced pressure; p_c, critical pressure; $\tau = T/T_c$, reduced temperature; $\omega = \rho/\rho_\ell$, reduced density; ρ, critical density; z^{ex}, z^{cal}, experimental and predicted values of compressibility coefficient; θ, ratio of the normal boiling point to T_c.

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NONSTATIONARY-FREQUENCY MEASUREMENTS IN RESEARCHING THERMOPHYSICAL PARAMETERS AND PHENOMENA. PART 1. STEPWISE METHODS

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A new approach is illustrated to the theory of thermal conductivity and the use of solutions there, which is a natural consequence of using new nonstationary-frequency methods in experiments.

New industrial processes and process acceleration have made it necessary to produce new substances and materials with preset properties. Correspondingly, there is an increased need for information on the properties of new materials over wide ranges in the state parameters, and measurements of improved accuracy are required.

This has led to extensive researches on the characteristics of gases, liquids, and solids; much of such research in power engineering is concerned with thermophysical parameters, particularly thermal conductivity, specific heat, thermal expansion, and emissivity. The changes in the level and volume of research have naturally led to considerable attention being given to methods, particularly design and implementation of new fast but precise methods of measuring thermophysical parameters. This has led to radical reequipment in experimental thermophysics and to the replacement of cumbersome and slow classical methods by modern fast and highly informative measurement suites. The major trends in experimental techniques here include not only the general one of improving the informativeness but also the following: devising, developing, and implementing methods for the simultaneous determination of several thermophysical parameters, the general use of electronic methods and apparatus, measurement automation (including computerized data acquisition, control, and data processing), the use of nondestructive and contactless methods to provide high throughput in all measurements, including specimen installation and changing, substantial reductions in error levels, improved metrological systems, the design of essentially new methods for indirect measurements based on techniques in molecular optics and acoustics, and substantial extensions to the temperature and pressure ranges covered.

There are two main groups of methods meeting these requirements: a) pulse and stepwise (monotone) heating, and b) periodic heating. These provide a basis for robotic monitoring and control systems for thermophysical parameters of materials and structures in various industrial processes.

The resolving power and response rate are improved if these methods are used with phase and frequency techniques rather than amplitude ones.

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