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Application of a Density/Temperature Relation to Some Nonmetallic Materials in the Liquid State

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One of the most quantitative approaches used to formulate a density/temperature relation is that described by Ree (*1*). By using the van der Waals, the Berthelot, or the Dieterici equations of state and by imposing the condition that the work done in an isothermal reversible cyclic process is zero, Ree derived the equation,

$$\rho_r = 1 + ax^{1/2} + bx + cx^2 + dx^3, \qquad (1)$$

where ρ_r, the reduced liquid density, is the ratio of the density ρ divided by the critical density ρ_c, x is the expression $[1 - (T/T_c)]$ in which T_c is the Kelvin critical temperature, and a, b, c and d are numerical coefficients whose values are dependent on the equation of state used in the derivation of Eq. (1).

It can be shown readily that Eq. (1) can be written in the form

$$\rho = \rho_m \left(\frac{1 + ax^{1/2} + bx + cx^2 + dx^3}{1 + ay^{1/2} + by + cy^2 + dy^3} \right), \qquad (2)$$

where ρ_m is the density of the liquid at the Kelvin melting temperature, T_m, and y is the expression $[1 - (T_m/T_c)]$. This equation shows that if the numerical values of the coefficients a through d are known, then we need only one experimentally determined value, ρ_m, to estimate the density of the liquid as a function of temperature (this is, of course, assuming that T_c is known or can be estimated).

In a previous investigation (*2*) it was found empirically that by using the simple numerical values of 2, $\frac{1}{4}$, -1, and $\frac{3}{4}$ for the coefficients a, b, c and d in Eq. (2), this equation could be fitted to liquid metals.[1]

The present study was undertaken to determine if an equation of the same functional form as Eq. (2) could be fitted to other classes of materials in the liquid state, and, if so, whether the same numerical values for a through d would be applicable (that is, whether the numerical coefficients of the terms in the equation are general materials constants) or whether different numerical values for the coefficients would be needed in order to apply Eq. (2) to different types of materials.

Equation (2) was applied to the substances listed in Table I over the temperature ranges for which density data were available; the above-

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[1] By introducing the indicated values for x and y as well as the empirically determined numerical values for the coefficients a through d into Eq. (2), the actual working equation used to estimate the densities of liquid metals as a function of temperature was

$$\rho = \rho_m \left[\frac{1 + 2(1 - T/T_c)^{1/2} + \frac{1}{4}(1 - T/T_c) - (1 - T/T_c)^2 + \frac{3}{4}(1 - T/T_c)^3}{1 + 2(1 - T_m/T_c)^{1/2} + \frac{1}{4}(1 - T_m/T_c) - (1 - T_m/T_c)^2 + \frac{3}{4}(1 - T_m/T_c)^3} \right].$$

The density ρ is expressed as a function of ρ_m (as well as temperature) rather than in terms of the density at some higher temperature because it is possible in many instances to estimate ρ_m from a knowledge of the densities of solid materials when density data for materials in the liquid state are not available. Over the temperature ranges for which experimental data were available, the differences between experimental and calculated values were found to be less than 3% for most of the liquid metals to which this equation was applied.

mentioned values for the coefficients *a* through *d* were used. Reference (*3*) was the source of the density data used.[2] The elements and compounds listed in the table represent a number of different classes of organic and inorganic materials. For the substances listed, experimental liquid densities were compared with those calculated using Eq. (2) over the indicated portions of the liquid ranges. The densities used for the comparison were chosen near the melting point, intermediate values between the melting point and the critical point, and a value near the critical point (when such data were available). It was found that the differences between experimental and calculated densities were less than 8% for nine of the materials listed and less than 5% for the remaining 23 substances. This is considered to be a rather good fit of Eq. (2) especially when one takes into consideration that (a) the density data in Ref. (*3*) are derived from various sources, (b) the substances listed in Table I do represent a number of different types of materials, and (c) Eq. (2) was applied over temperature ranges exceeding 90% of the liquid range for most of the materials listed.

Although the present study was not very extensive (32 substances is not a very large sample size for this type of study), the results still indicate that not only is an equation of the same functional form as Eq. (2) applicable to different classes of materials in the liquid state, but, additionally, that the coefficients of the terms in the equation have constant numerical values. Thus, the tentative conclusions of this study (subject to further verification) are that (a) the numerical coefficients of the terms in Eq. (2) are general rather than specific materials constants, and (b) Eq. (2) should be applicable to many classes of liquids over large portions of the liquid range.

TABLE I

MATERIALS IN THE LIQUID STATE TO WHICH EQUATION (2) WAS APPLIED

Material[a]			
Name	Chemical formula	A[b]	B[c]
Neon	Ne	93.4	2.3
Argon	Ar	95.9	1.4
Krypton	Kr	98.8	2.1
Xenon	Xe	99.5	1.1
Hydrogen	H_2	88.4	4.6
Oxygen	O_2	98.4	3.3
Nitrogen	N_2	98.5	0.9
Chlorine	Cl_2	92.3	4.7
Carbon monoxide	CO	97.7	3.3
Water	H_2O	98.9	4.7
Ammonia	NH_3	95.5	6.9
Sulfur dioxide	SO_2	97.5	7.3
Hydrogen chloride	HCl	96.1	5.7
Hydrogen iodide	HI	67.7	0.2
Aluminum bromide	Al_2Br_6	97.8	5.5
Osmium tetroxide	OsO_4	40.8	0.4
Tin tetrachloride	$SnCl_4$	89.0	5.9
Tetrachloromethane	CCl_4	99.0	3.7
Ethylamine	C_2H_7N	86.3	4.4
Diethyl sulfide	$C_4H_{10}S$	97.2	3.8
1,1,2-Trifluoro-1,2,2-trichloroethane	$C_2F_3Cl_3$	98.1	3.9
Methyl propionate	$C_4H_8O_2$	97.9	5.6
2,3-Dimethylbutane	C_6H_{14}	99.3	3.8
Octane	C_8H_{18}	98.2	7.4
Butadiene-1,3	C_4H_6	95.4	4.4
Benzene	C_6H_6	97.0	3.7
Fluorobenzene	C_6H_5F	98.0	4.7
Chlorobenzene	C_6H_5Cl	97.4	5.2
Bromobenzene	C_6H_5Br	70.3	4.4
Iodobenzene	C_6H_5I	62.9	4.7
Diphenyl ether	$C_{12}H_{10}O$	99.1	5.7
Naphthalene	$C_{10}H_8$	98.4	4.8

[a] The name and formula designations used are those given in Ref. (*3*).

[b] A = Percentage of the liquid range over which densities calculated using Eq. (2) were compared with values reported in Ref. (*3*).

[c] B = Absolute magnitude of the maximum percentage difference between experimental and calculated densities over the indicated portion of the liquid range.

References

1. F. H. REE, *J. Chem. Phys.* **36**, 3373 (1962).
2. S. W. STRAUSS, *Nucl. Sci. Eng.* **18**, 280 (1964).
3. LANDOLT–BORNSTEIN, "Physikalisch-Chemische Tabellen," Band II, Teil 2, pp. 185–215 (1960).

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[2] Reference (*3*) includes data on ρ_c for most of the materials listed in Table I, but we shall not be concerned with ρ_c in the present communication.