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Reduced Temperatures for the Liquid State. General Equations for the Orthobaric Densities as Functions of the Reduced Temperature

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The reduced temperature θ proposed by Bauer, Magat, and Surdin for the liquid state is presented and their work is reviewed. Attention is directed to the fact that a number of empirical power law equations that represent the variation of a property of a liquid as a function of the van der Waals reduced temperature are directly transformable into analogous functions of θ . General equations are derived for the variation of the orthobaric liquid and vapor densities as function of the reduced temperature.

IN developing the concept of corresponding states for liquids it has been customary to employ as the temperature scale the familiar reduced temperature $T_r = T/T_c$. A number of years ago, however, Bauer, Magat, and Surdin¹ defined a new reduced temperature for liquids and undertook to show "that the use of this new variable simplifies the study of the static properties of liquids in the same way as the reduced variables of van der Waals do for gases." The reduced temperature of Bauer, Magat, and Surdin is defined:

$$\theta = (T - T_f)/(T_c - T_f), \quad (1)$$

where T is the Kelvin temperature; T_c , the critical temperature; and T_f , the melting point temperature, or more correctly, the triple point temperature. As can be seen the reduced temperature θ assumes all values between 0 and 1, as the temperature of the liquid varies from T_f to T_c . According to an abstract, another group of investigators, Sibaiya and Rao,² have also hit upon the idea of the reduced temperature θ and are reported to have described it as a "new reduced temperature."

Bauer, Magat, and Surdin based the validity of their reduced temperature θ on a limited number of empirical tests which they carried out as follows. For a given property of a liquid P , values of the ratio P_i/P_f (P_i , value of property P at temperature T ; P_f , value of property at triple point temperature) for a number of different liquids were plotted against θ -values corresponding to temperature T . In a graph constructed in this way for molecular volumes the plotted points for 17 different liquids were shown to fall closely on a common curve for which the authors established the following empirical two-constant formula:

$$V_i/(V_f - 1) = 3.36[1 - (1 - \theta)^{1/10}]. \quad (2)$$

(Two liquids, H_2 and H_2O , were found to be represented by a curve similar to, but slightly lower than, the main curve in the graph.) Combining their relationship with the Eötvös law for surface tension, Bauer, Magat, and

Surdin derived an expression for the variation of surface tension with θ which they showed graphically to hold for the so-called normal liquids. In a plot of values of the ratio of compressibilities β/β_f for 10 different liquids against corresponding θ -values it was found that the plotted points fall on a common curve for which an empirical equation was also established. An analogous test of the specific heat was made with data for only 5 liquids. In the case of this property the curves for mono- and diatomic liquids have the same general shape, but the difference between C_v values, for the same θ is about 2 calories, as it is for perfect gases. Bauer, Magat, and Surdin sought to extend their method to the dynamical properties, viscosity and heat conduction, but found that the points for each liquid formed a separate curve rather than a common one.

The primary purpose of this note is to call attention to the fact that simple functions involving the reduced temperature T/T_c can be transformed readily into functions involving the reduced temperature θ . We shall consider here only one case. The variation of many properties of liquids have been found to be representable by an expression of the form

$$P = P_0(1 - T/T_c)^n, \quad (3)$$

where the power index n is a general constant dependent only on the property being represented; and P_0 is a constant characteristic of each substance. Now at the triple point temperature T_f Eq. (3) becomes

$$P_f = P_0(1 - T_f/T_c)^n. \quad (4)$$

Dividing (3) by (4) we get

$$P/P_f = [(T_c - T)/(T_c - T_f)]^n. \quad (5)$$

Since

$$T_c - T_f = (T_c - T) + (T - T_f), \quad (6)$$

the right-hand term of (5) can be rearranged as follows

$$P/P_f = [(T_c - T_f)/(T_c - T_f) - (T - T_f)/(T_c - T_f)]^n = (1 - \theta)^n. \quad (7)$$

Empirical power law expressions of the type shown in Eq. (3) are known for the following properties of liquids:

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¹ Bauer, Magat, and Surdin, "A discussion on structure and molecular forces in pure liquids," *Trans. Faraday Soc.* (September 1936), p. 81.

² L. Sibaiya and M. R. Rao, *Curr. Sci.* 8, 359 (1939).

orthobaric densities,³ surface tension,⁴ compressibility,⁵ internal latent heat,⁶ total latent heat,⁶ and viscosity.⁷ In the expression for a given property the power-index is found to differ little in value from liquid to liquid, and is generally regarded as a constant. These expressions for the different properties of liquids, therefore, can all be transformed directly into expressions of the type of Eq. (7) in which, for a given property, the ratio P/P_c for all liquids is represented by a single general function of θ .

In passing it may be noted that it should be possible to invent other reduced temperature scales, analogous to the θ -scale, for functions of the type shown in Eq. (3). Obviously, however, no such scale for liquids would have the same general significance or usefulness as the θ -scale of Bauer, Magat, and Surdin.

It will be of interest to indicate the derivations for two expressions representing the variation of the orthobaric liquid and vapor densities in terms of the reduced temperature θ . The starting point of the derivation is the Verschaaffelt equation

$$(D-d) = D_0[1 - (T/T_c)]^n \quad (8)$$

where D is the density of the liquid and d , the density of the vapor in equilibrium with the liquid, at temperature T ; D_0 is a constant, and T_c is again the critical temperature. This empirical equation has had a rather curious history. It was originally proposed by Verschaaffelt³ who set $n = \frac{1}{3}$, and had in place of the constant D_0 , the term mD_c (m = a general constant, and D_c = the density of the substance at the critical temperature). Goldhammer,³ from a rather extensive test of Verschaaffelt's relationship, concluded that, while $n = \frac{1}{3}$, the other constant m was a variable which varied slightly from substance to substance. Sugden³ derived the expression (8) from van der Waals' relationship between surface tension, and MacLeod's relationship between surface tension and $(D-d)$. Sugden's derivation made $n = \frac{3}{10}$. Without any reference to Sugden's work Ferguson and Miller⁸ derived, by the same route, Sugden's equation with $n = \frac{3}{10}$; for their purposes, in place of D_0 , they wrote $4D_c$. Recently, Guggenheim,⁹ from considerations relating to the principle of corresponding states derived Eq. (8) with $n = \frac{1}{3}$ and $D_0 = 7/2D_c$. Apparently Guggenheim was unfamiliar with the previous history of this relationship, for he refers to his equation as "new" and one which, on

certain occasions, "in view of its extreme simplicity and surprisingly high accuracy has much to recommend it."

A decision as to the correct value of the exponent n is complicated by Sugden's manner of treating the equation. Having accepted $\frac{3}{10}$ as the correct value of the exponent Sugden adjusted the value of T_c in order to get the best representation of the experimental data by his equation. In the case of "unassociated" liquids the differences between the experimental and adjusted T_c values were quite small, the maximum difference not exceeding 5°C. In the case of associated liquids the differences were of the order of 15°C. For the time being the present writers are inclined to accept $\frac{3}{10}$ as the best value of the power index and also to recommend Sugden's scheme of using the adjusted T_c values where these can be established conveniently. It is recognized, of course, that a thorough study of the Verschaaffelt equation is desirable and that this might lead to a modification of the views expressed above.

Equation (8) can be transformed, as shown above, into the expression

$$(D-d)/(D_f-d_f) = (1-\theta)^n, \quad (9)$$

where D_f and d_f are the densities of the liquid and vapor, respectively, at the triple point. Since for most liquids d_f would be negligible relative to the density of the liquid at the triple point D_f , the denominator of the left-hand member of the expression can be written simply as D_f . If we may assume a constant value for the index n for all liquids, we have the striking result that the variation of the difference between the orthobaric densities with temperature is represented by a simple general function of θ in which D_f is the only constant characteristic of a particular liquid.

When D/D_f and d/D_f values of a substance are plotted as abscissae against corresponding θ -values as ordinates, the resulting graph resembles the familiar plots of orthobaric densities given in textbooks to illustrate the law of rectilinear diameters. In a plot of this kind the mean density is given quite accurately by a linear relationship which is derivable from the familiar approximate equation of Cailletet and Mathias:

$$\frac{1}{2}(D/D_f + d/D_f) = d_m/D_f = 0.5 - K\theta. \quad (10)$$

But plots of D/D_f and d/D_f values for different substances against θ -values do not yield one common curve because of small differences in values of the constant K in (10). The nature of the differences in K can be seen from the fact that at the critical temperature $\theta = 1$, and d_m becomes D_c , giving for the constant K

$$K = 0.5 - D_c/D_f. \quad (11)$$

Values of the term D_c/D_f for representative liquids fall within the narrow range, 0.31 to 0.38. The constant K will, therefore, have a value 0.12–0.19, depending on the liquid.

³ J. E. Verschaaffelt, Communication of Leiden, No. XXVIII (1896); S. Sugden, J. Chem. Soc. 1780 (1927); D. A. Goldhammer, Zeits. f. physik. Chemie 71, 577 (1910).

⁴ A. Ferguson, Phil. Mag. 31, 37 (1916); A. Ferguson and S. J. Kennedy, Trans. Faraday Soc. 32, 1474 (1936).

⁵ Unpublished studies with James G. Wendel.

⁶ For discussion of these functions see article by W. J. Jones and S. T. Bowden, Phil. Mag. 37, 480 (1946).

⁷ The power-law function for viscosity takes the form $(\eta - \eta_0) = (\eta_0 - \eta_c)(1 - T/T_c)^n$; W. J. Jones and S. T. Bowden, Phil. Mag. 36, 705 (1945); see also reference 6.

⁸ A. Ferguson and J. T. Miller, Proc. Phys. Soc. London 46, 140 (1934).

⁹ E. A. Guggenheim, J. Chem. Phys. 13, 253 (1945).

If we combine Eqs. (9) and (10), by adding and subtracting, we get

$$D/D_f = \frac{1}{2}[1 - 2K\theta + (1 - \theta)^n], \quad (12)$$

and

$$d/D_f = \frac{1}{2}[1 - 2K\theta - (1 - \theta)^n]. \quad (13)$$

It appears, therefore, that D/D_f for all liquids is represented by the same function of the reduced temperature θ with only the single constant K being characteristic of the liquid, assuming, as was discussed above, that the exponent n is identical for all liquids. The same is true for the vapor density ratio d/D_f . If values of $D/D_f + K\theta$ and $d/D_f - K\theta$ are plotted as abscissae against corresponding θ -values, the plotted points should fall on a symmetrical curve represented by $0.5[1 \pm (1 - \theta)^n]$. This fact suggests the possibility of a graphical method for establishing the value of K .

An approximate expression for the characteristic constant K in terms of characteristic properties T_c and T_f of the liquids can be derived by the following argument. Assuming again that the density of the vapor of a liquid is negligible at the triple point, Eq. (8) can be written in the form

$$D_f/D_0 = [(T_c - T_f)/T_c]^n. \quad (14)$$

Now, in his work with Eq. (8), ($n = \frac{3}{10}$), Sugden found the following relationship to hold for all the liquids included in his study

$$D_c = 0.27D_0. \quad (15)$$

Assuming this to be a general relationship we can obtain from (15), (14), and (11) the following expression for the constant K :

$$K = 0.5 - 0.27[T_c/(T_c - T_f)]^n \quad (16)$$

which relates K to the limits involved in the definition of θ .

Since Eqs. (12) and (13) were derived from the Verschaftelt equation and the law of rectilinear diameters, with the temperature expressed as the reduced temperature θ , it might be expected that similar equations would already have been deduced with temperatures expressed in the form of van der Waals' reduced temperatures. So far as the writers are aware this has

been done only by Ferguson and Miller.⁸ They derived an expression for D/D_c as a universal function of T/T_c and pointed out that a relation for d/D_c could be obtained in a similar manner. The equation of Ferguson and Miller can be transformed into a function of θ identical in form to our Eq. (12). The values of the constant factors in the two expressions are not susceptible to a simple comparison. It is significant, however, that Ferguson and Miller, using $n = \frac{3}{10}$, found their equation to represent satisfactorily the density data for thirty organic liquids. Only in the case of alcohols did the value of $\frac{3}{10}$ for the power index n seem unsuitable. It was with this class of liquids, it will be recalled, that Sugden found a significant adjustment of T_c to be necessary.

Equations similar to our Eqs. (12) and (13) have been presented recently by Guggenheim.⁹ Starting on the assumption that the principle of corresponding states would lead one to expect D/D_c and d/D_c to be universal functions of T/T_c , Guggenheim developed empirical expressions to represent the experimental data for argon. His empirical formulas, Guggenheim points out, portray fairly well the experimental data of the other inert gases and also oxygen and nitrogen, but do not fit particularly well the data of carbon monoxide and methane. Although Guggenheim's formula is quite similar in form to that of Ferguson and Miller, he makes no reference to the work of these investigators. Both of Guggenheim's expressions can be transformed into functions of θ identical in form to Eqs. (12) and (13) but with $n = \frac{1}{3}$. The limited evidence which Guggenheim adduces in support of his value of n does not, in our opinion, outweigh the evidence assembled by both Sugden, and Ferguson and Miller in support of the value of $\frac{3}{10}$ for that exponent.

The results presented in this article increase considerably the number of those properties of liquids whose variation with temperature can each be represented by a general function of the reduced temperature θ , and so lend further support to the view, "There is only one simple liquid." An examination of the further implications of these results and also of the transformability of the functions from the van der Waals' scale of reduced temperature to the θ -scale will be taken up in a subsequent note.