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Equation of State for Compressed Liquids and Their Mixtures from the Cohesive Energy Density[1]

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A procedure is presented, based on statistical-mechanical theory, for predicting the equation of state of compressed normal liquids and their mixtures from two scaling constants that are available from measurements at ordinary pressures and temperatures. The theoretical equation of state is that of Ihm, Song, and Mason, and the two constants are the enthalpy of vaporization and the liquid density at the triple point, which are related to the cohesive energy density of regular solution theory. The procedure is tested on a number of substances ranging in complexity from Ar and CO_2 to *n*-heptane and toluene. The results indicate that the liquid density at any pressure and temperature can be predicted within about 5%, over the range from T_{tp} to T_c and up to the freezing line. Possible methods of determining the scaling constants are discussed, as well as other possible choices for scaling constants.

KEY WORDS: cohesive energy; compressed liquids and mixtures; equation of state; statistical mechanics.

1. INTRODUCTION

The mechanical behavior of compressed liquids—that is, the equation of state– is needed for the design and analysis of many processes at high pressures. Many equations of state, dating back to the work of P. G. Tait over 100 years ago, have been proposed for the correlation and prediction of the p-v-T properties of compressed liquids [1–6]. However, almost all require at least a few measurements at high pressure for any particular liquid of interest; many also require knowledge of the critical constants. For example, many of the empirical equations of state are based on some

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variation of the fact that the isothermal bulk modulus (reciprocal compressibility) is very nearly linear in the pressure over the whole range from the vapor pressure curve to the freezing line. Thus each p-ρ isotherm involves at least four constants: the pressure and density of some reference state (such as the vapor pressure and the density of the saturated liquid) and the two constants needed to characterize such a linear relationship. Unfortunately, all four constants are temperature dependent.

The purpose of this paper is to present a method for predicting the equation of state of a compressed liquid from properties that are readily available at ordinary pressures and temperatures. In particular, we use the latent heat of vaporization and the liquid density at the triple point as two numbers that can correlate and predict the behavior of the compressed liquid. These two numbers, if not directly available, can be obtained with sufficient accuracy from two measured vapor pressures and liquid densities. (The latent heat and liquid density are closely related to the cohesive energy density of regular solution theory [7], hence the title of this paper.)

2. THEORY

The theoretical background is as follows. The linear relation between liquid bulk modulus and pressure, due essentially to Tait [1, 3, 4, 6], remained empirical until very recently, when it was shown how the relation could be obtained from an equation of state that had been derived from statistical-mechanical theory [8]. This demonstration was restricted to fluids whose particles interacted with pairwise central foces—specifically, argon and a Lennard–Jones (12, 6) fluid. In molar units, this equation of state has the form [9, 10]

$$\frac{p}{\rho RT} = 1 + B\rho + \alpha\rho[g(\sigma) - 1] \tag{1}$$

where p is the pressure, ρ is the molar density, RT has its usual meaning, B is the second virial coefficient, α is a temperature-dependent parameter that scales for the softness of the repulsive forces, b is a temperature-dependent analogue of the van der Waals covolume related to α by $b = d(\alpha T)/dT$, and $g(\sigma)$ is the pair distribution function at contact for equivalent hard spheres of diameter σ. The parameters B, α, and b are related to the intermolecular potential by integrations, but we do not need to write down the expressions here. The diameter σ is related to b by $b = (2\pi N_0/3)\,\sigma^3$, where N_0 is Avogadro's number. The function $g(\sigma)$

depends on the single variable $b\rho$, and its form was taken from the Carnahan–Starling equation of state for hard spheres,

$$g(b\rho)=\frac{1-\eta/2}{(1-\eta)^3}, \qquad \eta=b\rho/4 \tag{2}$$

where η is the packing fraction.

The extension of Eq. (1) to molecular fluids turned out to be fairly straightforward, with the same general mathematical form being retained [10, 11]

$$\frac{p}{\rho RT}=1+B\rho+\alpha\rho[G(b\rho)-1] \tag{3}$$

where the fundamental expressions for B, α, and b now involve integrations over molecular orientation angles, and $G(b\rho)$ is an average pair distribution function at contact for equivalent hard nonspherical convex bodies. The form adopted for $G(b\rho)$ was a generalization to nonspherical bodies of the Carnahan–Starling formula of Eq. (2) for hard spheres [12], with at least one adjustable constant to characterize the nonsphericity. We do not need to write down any of these expressions here. The difficulty with the direct use of Eq. (3) is that intermolecular forces for most nonspherical molecules are known only poorly, if at all. However, $B(T)$ can be found experimentally, and $\alpha(T)$ and $b(T)$ can be calculated from $B(T)$ by means of simple two-constant scaling rules [10, 11]. The reason is that α and b depend only on the intermolecular repulsive forces and are therefore relatively insensitive to the details of the shape of the intermolecular potential; they can be characterized by two constants corresponding to an average potential range and strength.

Thus the minimum input information needed to use Eq. (3) consists of experimental values of $B(T)$ plus some high-density data to fix the value of an adjustable "shape" constant in $G(b\rho)$. It is easy to show that Eq. (3) still predicts a nearly linear dependence of the liquid bulk modulus on the pressure and, therefore, extends the statistical-mechanical basis of the Tait relation to molecular liquids.

A new strong principle of corresponding states is contained in Eq. (3), and this principle has led to an appreciable improvement in both accuracy and simplicity [13]. The basic idea is that the form of $G(b\rho)$ does not need to be specified according to some model of a fluid composed of hard convex bodies but that Eq. (3) can be solved for $G(b\rho)$ in terms of $Z\equiv p/\rho RT$, ρ, B, and α, all of which can be determined from experiment, and this particular combination of quantities is then predicted to be a function of the single variable $b\rho$. A whole p-v-T surface is thereby collapsed to a single curve by plotting the data in this special way.

Analysis of experimental data according to this principle showed the need for a small correction to Eq. (3) to account for some effects of attractive forces, of the form $\delta b\rho^2(\alpha - B)/(1 + \delta b\rho)$, where δ is a small constant, equal to or less than 0.10. When this correction term is added to Eq. (3), the resulting solution for $G(b\rho)$ is

$$G(b\rho) = \frac{1}{\alpha\rho}\left[Z - 1 + \frac{(\alpha - B)\,\rho}{1 + \delta b\rho}\right] \tag{4}$$

Plots of p-v-T data for a number of fluids according to Eq. (4) showed not only that the right-hand side was indeed a function of the single variable $b\rho$, but also that G^{-1} vs $b\rho$ was a straight line rather than the curve predicted for a hard-body fluid. The latter result was interpreted to be an effect of many-body forces [13], but theory has as yet offered no explanation of why G^{-1} vs $b\rho$ is a straight line rather than some other curve. This linear result has been found to hold for a wide variety of substances, including noble gases, diatomic molecules, various polyatomic inorganic molecules, and a number of hydrocarbons [13, 14], but with slopes that depend on the particular substance.

The foregoing results culminate in the equation of state that is the starting point for the present work:

$$\frac{p}{\rho RT} = 1 + \frac{(B - \alpha)\,\rho}{1 + \delta b\rho} + \frac{\alpha\rho}{1 - \lambda b\rho} \tag{5}$$

Here λ is the absolute value of the slope of G^{-1} vs $b\rho$, equal to 0.454 for noble-gas fluids and less for more complex fluids, and it has been found that δ can be taken equal to 0.22 λ with sufficient accuracy [13, 14]. The nearly linear dependence of the liquid bulk modulus on pressure is still predicted by Eq. (5).

The remaining problem is how to use Eq. (5) to predict the behavior of a compressed liquid on the basis of minimal input information. In particular, for many liquids likely to be encountered the second virial coefficient of the vapor is probably not known, or even the critical constants. We now turn to a correlation scheme for circumventing these difficulties.

3. CORRELATION PROCEDURE

The second virial coefficient $B(T)$ plays a central role in the application of Eq. (5): it is used both directly and as the source of scaling constants for the calculation of $\alpha(T)$ and $b(T)$. Given $B(T)$ for the vapor, and some high-density information to fix the value of λ, the entire p-v-T surface of a fluid can be predicted, including the properties of the compressed liquid. Although accurate direct measurements of B are best, in their absence there are several correlation schemes, usually based on a principle of corresponding states, by which B can be estimated with reasonable accuracy. The best of these require three constants [15, 16]: the critical temperature (T_c), the critical pressure (p_c), and the Pitzer acentric factor (ω). In the simplest scheme the dimensionless quantities Bp_c/RT_c vs T/T_c form a universal family of curves indexed by the constant ω. The value of ω is determined from the vapor pressure at a temperature of about $T \approx 0.7\,T_c$. Using such a scheme, Tao and Mason [14] have shown how T_c, p_c, and ω can be used with Eq. (5) to predict the equation of state for normal fluids over their entire density range, for both single substances and mixtures. This is the recommended procedure when accurate measurements of $B(T)$ are unavailable, and values of these three constants are available for many substances [17].

However, the problem we wish to consider here involves predictions for liquids for which T_c and p_c are not known, either because they have merely not been measured or because the liquid decomposes at high temperatures.

The problem thus reduces to finding at least two scaling constants available from simple measurements at ordinary temperatures and pressures—an energy constant (the analogue of RT_c) and a volume or density constant (the analogue of the pseudocritical molar volume, RT_c/p_c). These would be used to estimate $B(T)$ from a corresponding-states correlation, with the energy constant used to form a dimensionless temperature and the volume constant to form a dimensionless second virial coefficient. A third constant analogous to ω might then be added as a refinement.

Constants of this sort have been used for many years in the theory of solutions of nonelectrolytes, in particular the cohesive energy and the cohesive energy density ("internal pressure") [7, 18, 19]. "The cohesive energy is the enthalpy of evaporation plus the change in enthalpy in expanding from the vapor pressure to the ideal-gas state minus RT" [19]. We have found empirically that the enthalpy of vaporization itself works just as well as the cohesive energy in furnishing a temperature scale for the calculation of $B(T)$; our temperature scale constant is therefore simply $\Delta H_{\mathrm{vap}}/R$. The cohesive energy density furnishes a pressure scale; on converting this to a volume scale with the chosen temperature scale, we simply recover the molar volume v_l of the liquid. Since both ΔH_{vap} and v_l depend somewhat on temperature, we need to pick a reference temperature at which to fix the scaling constants. The only unique point on the liquid–

vapor coexistence curve other than the critical point is the triple point, and we accordingly adopt the triple-point temperature as our reference. It should be emphasized that this is not a crucial choice, merely a convenient one. The ordinary freezing point would probably work as well, inasmuch as our final correlation scheme tends to be self-correcting, as explained later. In any case, our two scaling constants here are $\Delta H_{\text{vap}}/R$ and ρ_{tp}, the molar density at the triple point.

We can now check experimental data to see whether a dimensionless plot of $B\rho_{\text{tp}}$ as a function of $RT/\Delta H_{\text{vap}}$ results in a universal curve or, at least, a close family of curves that can be indexed by a third constant like ω. It comes as somewhat of a surprise that a single curve serves to correlate a wide variety of nonpolar fluids with sufficient accuracy for our purposes. This is illustrated in Fig. 1 for a selection of substances having values of ω ranging from 0 (argon) to 0.394 (n-octane). Apparently the "shape" effects

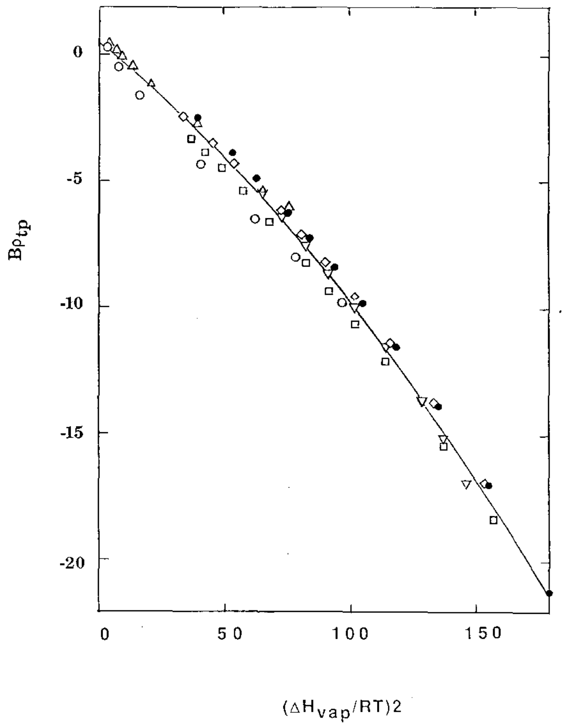

Fig. 1. Correlation plot for the second virial coefficient. ○, Ar ($\omega = 0.000$); △, CO_2 ($\omega = 0.225$); □, C_6H_6 ($\omega = 0.212$); ▽, n-C_6H_{14} ($\omega = 0.296$); ◇, n-C_7H_{16} ($\omega = 0.351$); ●, n-C_8H_{18} ($\omega = 0.394$). The curve is given by Eq. (6).

described by ω affect ΔH_{vap} and ρ_{tp} in such a way as to tend to compensate for their influence on B.

In constructing Fig. 1 we have taken ρ_{tp} (often approximated by ρ_{fp}) from the tabulations of Vargaftik [20] and used his vapor-pressure tabulations to calculate $\Delta H_{\text{vap}}/R$ from the Clausius–Clapeyron equation. The values used are collected in Table I, together with the values of λ used to construct Fig. 2, obtained as described below. The second virial coefficients were taken from the compilation of Dymond and Smith [21].

The resulting correlation for B can be represented by the empirical expression

$$B\rho_{\text{tp}} = 0.403891 - 0.076484(\Delta H_{\text{vap}}/RT)^2 - 0.0002504(\Delta H_{\text{vap}}/RT)^4 \quad (6)$$

which is shown as the curve in Fig. 1. This expression can be used to predict B over the temperature range from T_{tp} to T_c. Once $B(T)$ is known, the parameters $\alpha(T)$ and $b(T)$ follow from almost any reasonable two-constant effective pair potential; the results can also be scaled by ρ_{tp} and $\Delta H_{\text{vap}}/R$ and are fitted by the expressions

Table I. Parameters Used

Substance	$\Delta H_{\text{vap}}/R$ (K)	ρ_{tp} ($\text{mol} \cdot \text{l}^{-1}$)	T_{tp} (K)	λ
Ar	797	35.42	83.81	0.381
Xe	1532	22.73	161.3	0.381
N_2	702	30.98	63.17	0.413
O_2	868	40.82	54.36	
CO_2	1999	26.79	216.6	0.374
CH_4	1022	28.16	90.70	
C_2H_6	1796	21.91	89.88	
C_3H_8	2337	16.64	85.6	0.494
n-C_4H_{10}	2875	12.65	134.9	0.491
n-C_6H_{14}	3628	8.781	177.8	0.497
n-C_7H_{16}	4039	7.720	182.6	0.513
n-C_8H_{18}	4356	6.753	216.4	0.514
C_2H_4	1748	23.39	104.0	
C_6H_6	3633	11.48	278.7	0.435
$C_6H_5CH_3$	4283	10.44	178.2	0.508

$$\alpha\rho_{tp} = a_1 \exp[-c_1(RT/\Delta H_{vap})] + a_2\{1 - \exp[-c_2(\Delta H_{vap}/RT)^{1/4}]\} \quad (7)$$

$$b\rho_{tp} = a_1[1 - c_1(RT/\Delta H_{vap})] \exp[-c_1(RT/\Delta H_{vap})] + a_2\{1 - [1 + \tfrac{1}{4}c_2(\Delta H_{vap}/RT)^{1/4}] \exp[-c_2(\Delta H_{vap}/RT)^{1/4}]\} \quad (8)$$

$$a_1 = -0.1053, \qquad c_1 = 5.7862$$

$$a_2 = 2.9359, \qquad c_2 = 0.7966$$

These expressions are based on results obtained with a Lennard-Jones (12, 6) potential [10].

It remains to find the constant λ in order to use Eq. (5). Once B, α, and b are known, it takes only one experimental point to calculate λ from Eq. (5). For this purpose we can use the same data that was used to find ΔH_{vap}—for example, the vapor pressure and liquid density at the triple point or the freezing point. This method for determining λ makes the whole procedure self-correcting. If the correlation of Eq. (6) produces values of B that are somewhat in error, or if the input values of ΔH_{vap} and ρ_{tp} are not accurate, the defects will be largely compensated by the determination of λ. Thus the scatter evident in Fig. 1 is not a serious problem.

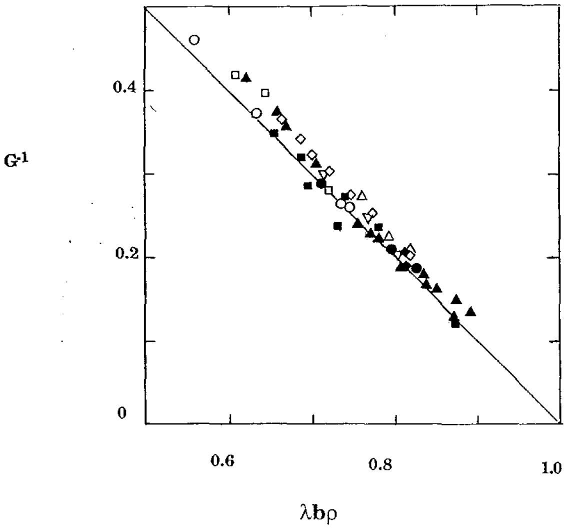

Fig. 2. Correlation plot of G^{-1} vs $\lambda b\rho$ for different fluids according to Eq. (9), covering the range between the triple and the critical temperatures. The points are from experimental p-v-T data: ○, Ar; ●, Xe; △, N_2; □, CO_2; ▽, C_3H_8; ◇, n-C_4H_{10}; ▼, n-C_6H_{14}; ■, n-C_7H_{16}; ▲, C_6H_6; ◆, $C_6H_5CH_3$. The solid line is $1 - \lambda b\rho$.

4. RESULTS

A simple way of plotting experimental data for many diverse compressed liquids on a single graph is as G^{-1} vs $\lambda b\rho$, where

$$\frac{1}{G} \equiv \alpha\rho \left[Z - 1 + \frac{(\alpha - B)\,\rho}{1 + 0.22\lambda b\rho} \right]^{-1} = 1 - \lambda b\rho \tag{9}$$

Note that $\alpha\rho$ can be written as a product of dimensionless quantities, $\alpha\rho_{\text{tp}}$ and ρ/ρ_{tp}, and similarly for $B\rho$ and $b\rho$. According to Eq. (5) all the measurements should fall on the straight line given by $1 - \lambda b\rho$. Such a graph is shown in Fig. 2 for 10 substances, ranging in character from Ar and CO_2 to heptane and toluene. The experimental density region that is covered in Fig. 2 ranges from the vapor-pressure curve to the freezing curve at various temperatures between T_{tp} and T_c. The data were taken from several compilations [20, 22–25]. Data from near the critical point are omitted because Eq. (5) is not expected to be very accurate in this region, inasmuch as it is an analytic expression whereas the critical region is known to be nonanalytic.

The points in Fig. 2 do indeed fall close to a single straight line, as predicted, although they are somewhat closer to a line of slope -0.98 (not shown) than to the predicted one of slope -1.00. From the scatter it can be concluded that the density of a compressed liquid at any specified pressure and temperature can be predicted within an accuracy of better than about 5%. This is about the same as the accuracy of the predictions based on the constants T_c, p_c, and ω [14].

These results show that the equation of state of compressed liquids can be predicted from knowledge of just two constants, ΔH_{vap} and ρ_{tp}, which can be obtained from measurements of the vapor pressures and saturated liquid densities at two temperatures.

5. MIXTURES

The present correlation procedure can be generalized to mixtures of any number of components, a result which should have great predictive power. We present the formulas and procedures for mixtures here, although extensive testing by comparison with measurements on compressed liquid mixtures remains for future work.

The formal extension of Eq. (5) to mixtures can be written in the form [26]

$$p/\rho RT = 1 + \rho \sum_{ij} x_i x_j (B_{ij} - \alpha_{ij})\, F_{ij} + \rho \sum_{ij} x_i x_j \alpha_{ij} G_{ij} \tag{10}$$

where ρ is the total molar density, x_i and x_j are mole fractions, and the double summations run over all the components. For a single substance $F^{-1} = 1 + \delta b\rho$ and $G^{-1} = 1 - \lambda b\rho$.

The interaction parameters B_{ij}, α_{ij}, and b_{ij} for $i \neq j$ correspond to a hypothetical single substance whose molecules interact according to a pairwise $i-j$ potential. For $i = j$, the parameters are those for the corresponding pure substance i. To find the interaction parameters for $i \neq j$, we use in principle effective pair potentials, such as those used to predict $\alpha(T)$ and $b(T)$ from $B(T)$, although the potentials do not need to enter the calculations explicitly. The potential strength is characterized by an average well depth ε, and the potential range by an average potential-minimum position r_m; the corresponding quantities in the present calculation are $\Delta H_{\text{vap}} \sim \varepsilon$ and $\rho_{\text{tp}} \sim r_{\text{m}}^{-3}$. The simplest combining rules for predicting unlike-molecule interactions from the like-molecule interactions are a geometric mean for ε and an arithmetic mean for r_{m}, so that our combining rules would be

$$(\Delta H_{\text{vap}})_{ij} = [(\Delta H_{\text{vap}})_i \, (\Delta H_{\text{vap}})_j]^{1/2} \tag{11}$$

$$(\rho_{\text{tp}})_{ij}^{-1/3} = \tfrac{1}{2}[(\rho_{\text{tp}})_i^{-1/3} + (\rho_{\text{tp}})_j^{-1/3}] \tag{12}$$

Once $(\Delta H_{\text{vap}})_{ij}$ and $(\rho_{\text{tp}})_{ij}$ are known, the values of B_{ij}, α_{ij}, and b_{ij} follow from Eqs. (6)–(8) as for single substances.

For mixtures the quantities G_{ij} and F_{ij} are given by [26]

$$G_{ij} = \frac{1}{1-\eta} + \left(\frac{b_i b_j}{b_{ij}}\right)^{1/3} \frac{\rho \sum_k x_k b_k^{2/3}(\lambda_k - 1/4)}{(1-\eta)(1 - \rho \sum_k x_k b_k \lambda_k)} \tag{13}$$

$$F_{ij} = \frac{1}{1-\eta} - \left(\frac{b_i b_j}{b_{ij}}\right)^{1/3} \frac{\rho \sum_k x_k b_k^{2/3}(\delta_k + 1/4)}{(1-\eta)(1 + \rho \sum_k x_k b_k \delta_k)} \tag{14}$$

where η is the packing fraction for the mixture,

$$\eta = (\rho/4) \sum_k x_k b_k \tag{15}$$

and $\delta_k = 0.22\lambda_k$ as before. Here the single summations run over all the components. Notice that the only interaction parameter in these expressions is b_{ij} but that, nevertheless, G_{ij} and F_{ij} depend on all the components of the mixture.

The general formulas for fluid mixtures, Eqs. (10) and (13)–(15), have been shown to give accurate results for small molecules [26]. What still needs to be tested are the combining rules given by Eqs. (11) and (12), and their application to compressed liquid mixtures of large molecules, but this remains for future work.

6. DISCUSSION

Our essential result is that the equation of state for a compressed liquid or liquid mixture can be predicted over the entire liquid range without the need for any high-pressure measurements. Two constants are needed for each pure component, ΔH_{vap} and ρ_{tp}, and it is worthwhile to discuss the availability of these quantities.

There is seldom any difficulty in determining liquid densities; only simple measurements are needed if values cannot be found in the literature. The temperature constant $\Delta H_{\text{vap}}/R$ is more difficult. Direct calorimetric measurements of ΔH_{vap} are usually not very accurate unless considerable care is taken. It is easier to measure the vapor pressure at two (or more) temperatures and calculate ΔH_{vap} from the Clausius–Clapeyron equation,

$$\ln p = C - \Delta H_{\text{vap}}/RT \tag{16}$$

where C is a constant. This is the procedure we have used in our present examples.

If vapor-pressure data are lacking and it is too much trouble to measure the vapor pressures, perhaps because only some rough preliminary estimates on a compressed liquid are wanted, then ΔH_{vap} can be estimated from the boiling point temperature, T_{bp}. The simplest estimate follows from Trouton's rule, that the entropy of vaporization at the boiling point is approximately the same for all "normal" liquids. This is equivalent to the statement that C in Eq. (16) is the same for all normal liquids, and the result is

$$\Delta H_{\text{vap}}/R \approx 10.2\, T_{\text{bp}} \tag{17}$$

where $10.2\, R \approx 85$ J/mol-K is the entropy of vaporization, obtained from experimental data on a number of liquids [27]. This gives the value of ΔH_{vap} at T_{bp}.

A more accurate variation of Trouton's rule is due to Hildebrand, who stated that the entropy of vaporization for normal liquids is the same at the temperature at which the molar density of the vapor is the same, rather than at the temperature at which the vapor pressure is 1 atm. An empirical formula embodying this rule, obtained by fitting data for a large number of substances, is [28]

$$\Delta H_{\text{vap}}(25^\circ\text{C})/R \approx -1485 + 11.9\, T_{\text{bp}} + 0.010\, T_{\text{bp}}^2 \tag{18}$$

Thus ΔH_{vap} at 25°C can be found if only T_{bp} is known.

If T_{bp} is so high that decomposition is a problem, then the Hildebrand rule can still be used to obtain an expression by which ΔH_{vap} can be estimated from the boiling point at some other pressure. Scatchard found that low vapor pressures could be well estimated by a relation between $\ln(p/T)$ and $1/T$ instead of between $\ln p$ and $1/T$ as in Eq. (16). His result is [19, 29]

$$\ln(p/T) = Y/(1+0.05Y) \tag{19}$$

$$Y = 10.8 - A/RT \tag{20}$$

where p is in Torr. Here A depends on the particular substance, but the constant 10.8 is universal for normal liquids. (It has different values for various polar liquids.) Application of the relation $d\ln p/dT = -\Delta H_{\text{vap}}/RT^2$ then yields

$$\frac{\Delta H_{\text{vap}}}{R} \approx T + \frac{T(10.8-Y)}{(1+0.05Y)^2} \tag{21}$$

Thus knowledge of T at some fixed low p determines Y and hence ΔH_{vap}.

All of the foregoing procedures yield only approximate values of $\Delta H_{\text{vap}}/R$ and, hence, of B, α, and b from Eqs. (6)–(8). However, errors will be compensated by choosing λ to fit the known liquid density.

Finally, it should be mentioned that $\Delta H_{\text{vap}}/R$ is not the only reasonable possibility for a temperature scale constant. For example, it is well-known that the surface tension γ is related to ΔH_{vap}. The reason is that ΔH_{vap} can also be considered to be the surface energy required to carve 1 mol of liquid into N_0 tiny cubes of edge d, each one containing one molecule of diameter d [30]. Then $\Delta H_{\text{vap}} \approx N_0(6d^2\gamma)$, since each cube has six faces, and the molar volume is approximately $v = 1/\rho \approx N_0 d^3$. Eliminating d between these two relations, we obtain

$$\Delta H_{\text{vap}} \approx 6N_0^{1/3}\gamma/\rho^{2/3} \tag{22}$$

The numerical factor in this expression is very approximate, and we do not recommend Eq. (22) as a way to find ΔH_{vap}, but the relation clearly suggests that a reasonable characteristic reference temperature could be defined as

$$RT_{\text{ref}} = \gamma/\rho^{2/3} \tag{23}$$

This definition would properly require a new correlation for B to replace Eq. (6), but then Eqs. (7) and (8) for α and b follow immediately by scaling, and the rest of the calculation proceeds as before. Such a new correlation remains for future work.

In summary, statistical-mechanical theory now allows the equation of state of compressed liquids and their mixtures to be predicted from simple measurements at ordinary pressures and temperatures.

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