

THE COMPRESSIBILITIES OF VAN DER WAALS LIQUIDS*

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An equation relating the compressibility of a van der Waals liquid to the latent heat of vaporization and the coefficient of thermal expansion is derived from thermodynamics. When certain approximations are made this equation reduces to one previously derived by other authors from the van der Waals equation.

The derivation is based on an equation of pure thermodynamics

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P, \quad \dots\dots\dots (1)$$

where T is the absolute temperature, P is the pressure, V is the volume, and E is the internal energy of the liquid. Measurements of $(\partial P/\partial T)_v$ indicate that P is negligible compared with $T(\partial P/\partial T)_v$ for liquids at low pressures and below their boiling points. Further, for a van der Waals liquid

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{\Delta E}{V}v, \quad \dots\dots\dots (2)$$

where ΔE_v is the energy of vaporization (Hildebrand and Scott 1950). The enthalpy of vaporization ΔH_v is given by

$$\Delta H_v = \Delta E_v + P\Delta V, \quad \dots\dots\dots (3)$$

where ΔV is the volume change on vaporization. The volume of a liquid is small compared to the volume of the vapour. If the vapour is assumed to be an ideal gas, equation (3) approximates to

$$\Delta H_v = \Delta E_v + RT. \quad \dots\dots\dots (4)$$

Now

$$\left(\frac{\partial P}{\partial T}\right)_v = -\left(\frac{\partial V}{\partial T}\right)_P \left/\left(\frac{\partial V}{\partial P}\right)_T\right. = \frac{\alpha}{\beta}, \quad \dots\dots\dots (5)$$

where the coefficient of thermal expansion

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

and the compressibility coefficient

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

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Substitution of equations (2), (4), and (5) in equation (1) gives, if P is neglected

$$\beta(\Delta H_v - RT)/\alpha V = T. \quad \dots\dots\dots (6)$$

Wall and Krigbaum (1949) derived the relations

$$\Delta H_v^2 \beta / V = RT, \quad \dots\dots\dots (7)$$

$$\alpha \Delta H_v = R, \quad \dots\dots\dots (8)$$

from the van der Waals equation. Substituting equation (8) in (6), the result is

$$\beta \Delta H_v (\Delta H_v - RT) / V = RT. \quad \dots\dots\dots (9)$$

If RT can be neglected in comparison with ΔH_v , an assumption not strictly valid, the new equation reduces to that of Wall and Krigbaum (1949), namely, equation (7).

Equation (6) gives about the same degree of correlation of published compressibility data as does equation (7). These equations apply to the differential compressibility at 1 atm pressure. There are insufficient data available in the literature to enable extrapolation of the compressibilities of most liquids to 1 atm pressure; Wall and Krigbaum used values in the range 100–300 atm, and the same values were used in checking the new equation.

Wall and Krigbaum derived equation (7) from a second approximation to the volume of a liquid given by the van der Waals equation, which was considered to be valid only if RT is small compared with the heat of vaporization (Wall 1948). This could account for the difference between their equation (7) and (9). The thermodynamic derivation given in this communication places their equation on a firmer basis.

References

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