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Temperature Dependence of Lindemann Frequency

RECENTLY we have shown¹ that the surface-tension γ_f of a liquid at its melting-point T_f is given by

$$\nu_f = k \sqrt{\frac{\gamma_f}{m}}$$

where ν_f is the Lindemann frequency and m the mass of the molecule. Assuming that the expression holds at all temperatures, we have at any temperature T ,

$$\nu = k \sqrt{\frac{\gamma}{m}}$$

whence from Eötvös rule we get

$$\nu = k \sqrt{\frac{\gamma V_f^{\frac{2}{3}}}{m V^{\frac{2}{3}}}} = k' \sqrt{\frac{T_c - T}{m V^{\frac{2}{3}}}}$$

and

$$\nu_f = k' \sqrt{\frac{T_c - T_f}{m V_f^{\frac{2}{3}}}}$$

It follows that

$$\frac{\nu}{\nu_f} = \sqrt{\frac{T_c - T}{T_c - T_f}} \left(\frac{V_f}{V}\right)^{\frac{1}{3}} = \left(\frac{V_f}{V}\right)^{\frac{1}{3}} \sqrt{\theta},$$

which shows directly the decrease of ν with rise of temperature.² The surface-tension at any temperature becomes—and it follows also directly from Eötvös rule—

$$\begin{aligned} \gamma &= \frac{1}{k^2} m \nu_f^2 \frac{T_c - T}{T_c - T_f} \left(\frac{V_f}{V}\right)^{\frac{2}{3}} \\ &= \gamma_f \left(\frac{V_f}{V}\right)^{\frac{2}{3}} \theta. \end{aligned}$$

The viscosity at any temperature on Andrade's formula becomes

$$\begin{aligned} \eta &= \eta_f \sqrt{\frac{T_c - T}{T_c - T_f}} \left(\frac{V_f}{V}\right)^{\frac{2}{3}} \\ &= \eta_f \left(\frac{V_f}{V}\right)^{\frac{2}{3}} \sqrt{\theta}. \end{aligned}$$

It has been shown by one of us previously³ that

$$V^{\frac{1.0}{3.0}} (T_c - T) = \text{constant},$$

whence $V = V_f \theta^{-\frac{3}{1.0}}$ (1)
and it follows that

$$\nu = \nu_f \theta^{\frac{3}{3}} (2)$$

$$\gamma = \gamma_f \theta^{\frac{6}{3}} (3)$$

$$\eta = \eta_f \theta^{\frac{7}{3}} (4)$$

and compressibility $\beta = \beta_f \theta^{-1.3}$ (5)
of which the relation (3) is similar to Van der Waals' equation and (4) is of limited applicability.

Thus it is seen that many of the physical properties of the liquids show a temperature dependence directly as function of a new reduced temperature θ defined by $\frac{T_c - T}{T_c - T_f}^{\frac{1}{4}}$.

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¹ Sibaiya and Rama Rao, *Nature*, 1939, 143, 723.
² Macleod, *Proc. Phy. Soc.*, 1938, 53, 788.
³ Sibaiya, *Curr. Sci.*, 1938, 6, 329.
⁴ Bauer, Magat and Surdijn, *Trans. Far. Soc.*, 1937, 33, 81.