

Problem 14-10 Kelvin equation – vapour pressure above a drop

What is the vapour pressure above the liquid drops of diameter of 18 nm at the temperature of 35°C? The density of the liquid at this temperature is 0.022 mol cm⁻³, its surface tension 43.5 mN m⁻¹, normal boiling point 78°C, and the vaporization enthalpy has the value of 37.2 kJ mol⁻¹. You can suppose that the vaporization enthalpy is constant and that the temperature dependence of the vapour pressure is adequately described by Clausius-Clapeyron equation.

$$[p_r^s = 20.315 \text{ kPa}]$$

Solution:

$$\rho_m = 0.022 \text{ mol cm}^{-3} = 2.2 \cdot 10^4 \text{ mol m}^{-3}$$

$$V_m = 1 / \rho_m = 1 / 2.2 \cdot 10^4 \text{ m}^3 \text{ mol}^{-1}$$

$$T_{\text{nbp}} = 78 + 273.15 = 351.15 \text{ K}$$

$$T = 35 + 273.15 = 308.15 \text{ K}$$

$$d = 18 \cdot 10^{-9} \text{ m}$$

$$r = 9 \cdot 10^{-9} \text{ m}$$

$$\Delta_{\text{vap}} H_m = 37.2 \text{ kJ mol}^{-1}$$

$$\ln \frac{p_r^s}{p_\infty^s} = \frac{2 \cdot \gamma \cdot V_m}{RT \cdot r} = \frac{2 \cdot \gamma}{RT \cdot r \cdot \rho_m} = \frac{2 \cdot 0.0435}{8.314 \cdot 308.15 \cdot 9 \cdot 10^{-9} \cdot 2.2 \cdot 10^4} = 0.171507$$

$$p_r^s(308.15 \text{ K}) = 1.18657 \cdot p_\infty^s(308.15 \text{ K})$$

Calculation of the vapour pressure above the curved interface:

$$\ln \frac{p_\infty^s(308.15)}{101.325} = \frac{\Delta_{\text{vap}} H_m}{R} \left(\frac{1}{T_{\text{nbv}}} - \frac{1}{T} \right) = \frac{37.2 \cdot 10^3}{8.314} \left(\frac{1}{351.15} - \frac{1}{308.15} \right) = -1.77806$$

$$p_\infty^s(308.15 \text{ K}) = 0.16897 \cdot 101.325 = 17.12043 \text{ kPa}$$

$$p_r^s(308.15 \text{ K}) = 1.18657 \cdot 17.12043 = 20.315 \text{ kPa}$$