1) The vapour pressure of a substance at 50.0°C is 43.0 kPa and its enthalpy of vaporization is 42.2 kJ mol^{-1}. Estimate the temperature at which its vapour pressure is 96.0 kPa.

Assume vapour is a perfect gas and $\Delta_{vap}H$ is independent of temperature

$$\ln\frac{p^*}{p} = +\frac{\Delta_{vap}H}{R}\left(\frac{1}{T}-\frac{1}{T^*}\right)$$

$$\frac{1}{T} = \frac{1}{T^*} + \frac{R}{\Delta_{vap}H}\ln\frac{p^*}{p}$$

$$= \frac{1}{323.2\,\text{K}} + \frac{8.314\,\text{J K}^{-1}\,\text{mol}^{-1}}{42.2\times10^3\,\text{J mol}^{-1}}\times\ln\left(\frac{43.0}{96.0}\right)$$

$$= 2.936\times10^{-3}\,\text{K}^{-1}$$

$$T = \frac{1}{2.93\bar{6}\times10^{-3}\,\text{K}^{-1}} = 341\,\text{K} = \boxed{68^\circ\text{C}}$$

2) The normal boiling point of heptane is 98.4°C. Estimate (a) its enthalpy of vaporization and (b) its vapour pressure at 37°C and 84°C.

(a) According to Trouton's rule (Section 3.3(b), eqn 3.16)

$$\Delta_{vap}H = \left(85\,\text{J K}^{-1}\,\text{mol}^{-1}\right)\times T_b = \left(85\,\text{J K}^{-1}\,\text{mol}^{-1}\right)\times(371.6\,\text{K}) = \boxed{31.\bar{6}\,\text{kJ mol}^{-1}}$$

(b) Use the Clausius–Clapeyron equation [Exercise 4.8(a)]

$$\ln\left(\frac{p_2}{p_1}\right) = \frac{\Delta_{vap}H}{R}\times\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

At $T_2 = 371.6\,\text{K}, p_2 = 1.000$ atm; thus at 37°C

$$\ln p_1 = -\left(\frac{31.\bar{6}\times10^3\,\text{J mol}^{-1}}{8.314\,\text{J K}^{-1}\,\text{mol}^{-1}}\right)\times\left(\frac{1}{310.2\,\text{K}}-\frac{1}{371.6\,\text{K}}\right) = -2.02\overline{45}$$

$$p_1 = \boxed{0.13\bar{2}\text{ atm}} = 10\bar{0}\text{ Torr}$$

At 60°C,

$$\ln p_1 = -\left(\frac{31.\bar{6}\times10^3\,\text{J mol}^{-1}}{8.314\,\text{J K}^{-1}\,\text{mol}^{-1}}\right)\times\left(\frac{1}{357.2\,\text{K}}-\frac{1}{371.6\,\text{K}}\right) = -0.41\overline{23}$$

$$p_1 = \boxed{0.66\bar{2}\,\text{atm}} = 50\bar{3}\,\text{Torr}$$

3) The molar volume of a certain solid is 122.0 cm^3 mol^{-1} at 1.00 atm and 483.15 K, its melting temperature. The molar volume of the liquid at this temperature and pressure is 142.6 cm^3 mol^{-1}. At 1.29 MPa the melting temperature changes to 485.34 K. Calculate the enthalpy and entropy of fusion of the solid.

$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m}$$

$$\Delta_{fus} S = \Delta V_m \left(\frac{dp}{dT}\right) \approx \Delta V_m \frac{\Delta p}{\Delta T}$$

assuming $\Delta_{fus} S$ and ΔV_m independent of temperature.

$$\Delta_{fus} S = \left(142.6\,\text{cm}^3\,\text{mol}^{-1} - 122.0\,\text{cm}^3\,\text{mol}^{-1}\right) \times \frac{\left(1.26\times10^6\,\text{Pa}\right) - \left(1.01\times10^5\,\text{Pa}\right)}{485.34\,\text{K} - 483.15\,\text{K}}$$

$$= \left(20.6\,\text{cm}^3\,\text{mol}^{-1}\right) \times \left(\frac{1\,\text{m}^3}{10^6\,\text{cm}^3}\right) \times \left(5.29\times10^5\,\text{Pa}\,\text{K}^{-1}\right)$$

$$= 10.90\,\text{Pa}\,\text{m}^3\,\text{K}^{-1}\,\text{mol}^{-1} = \boxed{10.9\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}}$$

$$\Delta_{fus} H = T_f \Delta S = \left(483.15\,\text{K}\right) \times \left(10.9\bar{0}\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}\right)$$

$$= \boxed{5.27\,\text{kJ}\,\text{mol}^{-1}}$$