

Example Web5.1. The melting point of sodium (molar mass 22.99 g mol^{-1}) is $97.8 \text{ }^\circ\text{C}$ at 1 atm pressure. The densities at this temperature of the solid and liquid are 0.929 g cm^{-3} and 0.952 g cm^{-3} respectively. The enthalpy of fusion is 3.00 kJ mol^{-1} . Calculate the melting point of sodium at a pressure of 120 atm.

From the Clapeyron equation, Equation 5.3,

$$\frac{dp}{dT} = \frac{\Delta_{\text{fus}} H}{T_m \Delta_{\text{fus}} V}$$

$\Delta_{\text{fus}} H$ is given as $3 \text{ kJ mol}^{-1} = 3.00 \times 10^3 \text{ J mol}^{-1}$ and $T_m = 97.8 \text{ }^\circ\text{C} = 370.95 \text{ K}$.

dp is the change in pressure, $120 \text{ atm} - 1 \text{ atm} = 119 \text{ atm}$. $1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}$.

$\Delta_{\text{fus}} V$ can be found from the densities. It is the difference in molar volumes for liquid and solid.

$$\begin{aligned} \Delta_{\text{fus}} V &= V_m(\text{liquid}) - V_m(\text{solid}) = \left(\frac{22.99 \text{ g mol}^{-1}}{0.929 \text{ g cm}^{-3}} - \frac{22.99 \text{ g mol}^{-1}}{0.952 \text{ g cm}^{-3}} \right) \\ &= 0.598 \text{ cm}^3 \text{ mol}^{-1} \end{aligned}$$

Substituting values and converting to SI units throughout

$$\frac{dp}{dT} = 1.35 \times 10^7 \text{ J m}^{-3} \text{ K}^{-1} = 1.35 \times 10^7 \text{ Pa K}^{-1}$$

This shows that a pressure change of $1.35 \times 10^7 \text{ Pa}$ changes the melting point by 1 K.

When the pressure changes to 120 atm, $dp = 119 \text{ atm} \times 1.013 \times 10^5 \text{ Pa atm}^{-1} = 1.21 \times 10^7 \text{ Pa}$.

The change in melting point is therefore

$$\begin{aligned} \frac{dp}{dT} &= 1.35 \times 10^7 \text{ Pa K}^{-1} \\ dT &= \frac{1.21 \times 10^7 \text{ Pa}}{1.35 \times 10^7 \text{ Pa K}^{-1}} = 0.900 \text{ K} \end{aligned}$$

Thus, T_m increases by 0.900 K so that $T_m(120 \text{ atm})$ is $98.7 \text{ }^\circ\text{C}$.

Example Web5.2 The normal boiling point of benzene is 80.1 °C and the enthalpy of vaporization is 30.8 kJ mol⁻¹. Calculate the boiling point at a pressure of 10.0 kPa.

The normal boiling point is the temperature at which the vapour pressure becomes 1 atm or 1.013 × 10⁵ Pa. Using Equation 5.5.

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

$$\ln\left(\frac{10.0 \times 10^3 \text{ Pa}}{1.013 \times 10^5 \text{ Pa}}\right) = \frac{30.8 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{(273.15 + 80.1) \text{ K}} - \frac{1}{T}\right)$$

Hence $(1/T) = 3.455 \times 10^{-3} \text{ K}^{-1}$

so $T = 289.4 \text{ K}$ or 16.2 °C

Example Web5.3. Calculate the changes in enthalpy, entropy, volume, and Gibbs energy on mixing 1.5 mol of hexane with 2.5 mol of heptane at 25 °C.

Hexane, C₆H₁₄, and heptane, C₇H₁₆, can be assumed to form an ideal mixture.

For ideal solutions: $\Delta_{\text{mix}}H = \Delta_{\text{mix}}V = 0$.

The other functions are given by Equations 5.19 and 5.20.

The mole fraction of hexane is $x_{\text{hexane}} = \frac{n_{\text{hexane}}}{n_{\text{hexane}} + n_{\text{heptane}}} = \frac{1.5}{1.5 + 2.5} = 0.375$

$x_{\text{heptane}} = (1 - 0.375) = 0.625$

$$\Delta_{\text{mix}}G = RT \sum_i x_i \ln x_i = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} \times \{0.375 \ln (0.375) + 0.625 \ln (0.625)\}$$

$$= -1640 \text{ J mol}^{-1}$$

$$\Delta_{\text{mix}}S = -R \sum_i x_i \ln x_i = -8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times \{0.375 \ln (0.375) + 0.625 \ln (0.625)\}$$

$$= +5.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

Note that the formation of the solution is ‘driven’ by the greater disorder in the mixture over that of the pure liquids.