

Tut

$\mu \Rightarrow$ Chemical Potential (Gibbs free energy per mole)

(1)

Calculate the effect on the chemical potentials of ice and water at increasing the pressure from 1.00 bar to 2.00 bar at 273K. The density of ice is 0.917 g/cm³ and that of liquid water is 0.999 g/cm³ under these conditions.

$$\text{ice } (\Delta H) = 1.97 \text{ J/mol}^{-1}$$

$$\text{water } (\Delta H) = 1.80 \text{ J/mol}^{-1}$$

$$\Rightarrow d\bar{G} = \bar{V}dP - \bar{S}dT$$

$$\Rightarrow d\mu = \bar{V}dP - \bar{S}dT$$

$$\Rightarrow \frac{d\mu}{dP} = \bar{V} = V_m$$

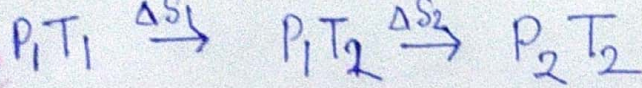
$$\Rightarrow \Delta\mu = V_m dP$$

$$\Delta\mu = \frac{M dP}{\rho}$$

$$\left(\rho = \frac{M}{V_m} \right)$$

$$(\Delta\mu)_{\text{ice}} = \frac{(1.802 \times 10^2) \text{ kg mol}^{-1} (1 \times 10^5 \text{ Pa})}{917 \text{ kg m}^{-3}}$$

$$(\Delta\mu)_{\text{water}} = \frac{(1.802 \times 10^2) \text{ kg mol}^{-1} (1 \times 10^5 \text{ Pa})}{999 \text{ kg m}^{-3}}$$



(e)

Calculate ΔS (for the system) when the state of 2.00 mol diatomic perfect gas molecules, for which $C_{p,m} = \frac{7}{2}R$, is changed from 25°C and 1.50 atm to 135°C and 7.00 atm. How do you rationalize the sign of ΔS ? (-7.3 J K^{-1})

As entropy is a state

function we can calculate it by breaking into two parts

$$\Rightarrow \Delta S = \overset{\text{(pressure)}}{\Delta S_1} + \overset{\text{(temp.)}}{\Delta S_2}$$

$$\text{pressure const.} \quad \Delta S_1 = \int \frac{dq_{\text{rev}}}{T} = \int \frac{n C_{p,m} dT}{T} = n C_{p,m} \ln \frac{T_f}{T_i}$$

$$\Delta S_1 = (2 \text{ mol}) \left(\frac{7}{2} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \right) \ln \frac{(135+273)}{(25+273)} = 18.3 \text{ J K}^{-1}$$

$$\text{temp. const.} \quad \Delta S_2 = \int \frac{dq_{\text{rev}}}{T} = \frac{q_{\text{rev}}}{T}$$

$$\Rightarrow (q_{\text{rev}} = -W = \int P dV = nRT \ln \frac{V_f}{V_i} = nRT \ln \frac{P_i}{P_f})$$

$$\therefore \Delta S_2 = \frac{nRT \ln \frac{P_i}{P_f}}{T} = (2 \text{ mol}) \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln \left(\frac{1.5 \text{ atm}}{7 \text{ atm}} \right)$$

$$\therefore \Delta S_2 = -25.6 \text{ J K}^{-1}$$

$$\therefore \Delta S = \Delta S_1 + \Delta S_2 = [18.3 + (-25.6)] = -7.3 \text{ J K}^{-1}$$

3. The enthalpy of fusion of mercury is $2.292 \text{ kJ mol}^{-1}$ and its normal freezing point is 243.9 K with the change in molar volume of $0.517 \text{ cm}^3/\text{mol}$ on melting. At what temperature will the bottom of a column of mercury (density = 13.6 g/cm^3 of height 10 m be expected to freeze. (234.4 K)

$$\Rightarrow \frac{dP}{dT} = \frac{\Delta_{\text{fus}} S}{\Delta_{\text{fus}} V} = \frac{\Delta_{\text{fus}} H}{T \Delta_{\text{fus}} V}$$

$$\int dP = \frac{\Delta_{\text{fus}} H}{\Delta_{\text{fus}} V} \int \frac{dT}{T} \Rightarrow P_2 - P_1 = \frac{\Delta_{\text{fus}} H}{\Delta_{\text{fus}} V} \ln \frac{T_2}{T_1}$$

$$\left(13.6 \times 10^3 \frac{\text{kg}}{\text{m}^3}\right) (9.81 \frac{\text{m}}{\text{s}^2}) (10 \text{ m})$$

$$= \frac{2.292 \times 10^3 \text{ J/mol}}{0.517 \times 10^{-6} \text{ m}^3/\text{mol}} \cdot \ln \left(\frac{T_2}{243.9 \text{ K}} \right)$$

$$\Rightarrow \ln \left(\frac{T_2}{243.9 \text{ K}} \right) = \frac{13.6 \times 9.81 \times 10 \times 0.517}{2.292 \times 10^6}$$

$$\Rightarrow T_2 = 243.9 e^{3.0094 \times 10^{-4}}$$