Tut

$\mu \Rightarrow$ Chemical Potential $\left(\frac{\text{Gibbs free energy}}{\text{mole}}\right)$

(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 gm/cm³ under these conditions.

ice $(\Delta\mu) = 1.97\ J/mol^{-1}$
water $(\Delta\mu) = 1.80\ J/mol^{-1}$

$$\rightarrow \quad d\bar{G} = \bar{V}\,dP - \bar{S}\,dT$$

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

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

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

$$\Delta\mu = \frac{M\,dP}{\rho} \qquad \left(\rho = \frac{M}{V_m}\right)$$

$$(\Delta\mu)_{ice} = \frac{(1.802\times10^{-2})\ kg\,mol^{-1}\ (1\times10^{5}\ Pa)}{917\ kg\,m^{-3}}$$

$$(\Delta\mu)_{water} = \frac{(1.802\times10^{-2})\ kg\,mol^{-1}\ (1\times10^{5}\ Pa)}{999\ kg\,m^{-3}}$$

$$P_1T_1 \xrightarrow{\Delta S_1} P_1T_2 \xrightarrow{\Delta S_2} P_2T_2$$

ΔS

(2) 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? ($-7.3\,JK^{-1}$)

As entropy is a state function we can calculate it by breaking into two parts

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

pressure const.

$$\Delta S_1 = \int \frac{dq_{rev}}{T} = \int \frac{nC_{p,m}dT}{T} = nC_{p,m} \ln \frac{T_f}{T_i}$$

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

temp. const.

$$\Delta S_2 = \int \frac{dq_{rev}}{T} = \frac{q_{rev}}{T}$$

$$\Rightarrow \left(q_{rev} = -W = \int PdV = nRT \ln \frac{V_f}{V_i} = nRT \ln \frac{P_i}{P_f}\right)$$

$$\therefore \Delta S_2 = \frac{n R \cancel{T} \ln \frac{P_i}{P_f}}{\cancel{T}} = (2\text{ mol}) \times 8.314\,JK^{-1}mol^{-1} \times \ln\left(\frac{1.5\text{ atm}}{7\text{ atm}}\right)$$

$$\therefore \Delta S_2 = -25.6\,JK^{-1}$$

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

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3. The enthalpy of fusion of mercury is 2.292 kJ mol⁻¹ and its normal freezing point is 243.9 K with the change in molar volume of 0.517 cm³/mol on melting. At what temperature will the bottom of a column of mercury (density = 13.6 g/cm³) of height 10 m be expected to freeze (234.4K).

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

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

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

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

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

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