

9/12/10

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Stat Phys

Problem Set #4

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4.1 1000g water $20^\circ\text{C} = 293.15\text{K}$, $\text{HB} = 80^\circ\text{C} = 353.15\text{K} = T_0$

$$\Delta S_w = C \int_{T_i}^{T_2} \frac{dT}{T} = Mc \int_{T_i}^{T_2} \frac{dT}{T} = mc \ln\left(\frac{T_2}{T_i}\right)$$

$$= (1000\text{g}) (4.2\text{Jg}^{-1}\text{K}^{-1}) \ln \frac{353.15}{293.15} = 782.1\text{JK}^{-1}$$

$$\Delta S_{\text{HB}} = -\frac{Q}{T_0} = -\frac{Mc(T_0 - T_i)}{T_0} =$$

$$= -\frac{(1000\text{g})(4.2\text{Jg}^{-1}\text{K}^{-1})(353.15 - 293.15)\text{K}}{353.15\text{K}} = -713.6\text{JK}^{-1}$$

$$\Delta S = \Delta S_w + \Delta S_{\text{HB}} = (782.1 - 713.6)\text{JK}^{-1} = 68.5\text{JK}^{-1}$$

$$T_{01} = 50^\circ\text{C} = 323.15\text{K} \quad T_{02} = 80^\circ\text{C} = 353.15\text{K}$$

$$\Delta S_1 = Mc \left[\ln\left(\frac{T_{01}}{T_i}\right) - \frac{(T_{01} - T_i)}{T_{01}} \right] = 4200\text{JK}^{-1} \left[\ln\left(\frac{323.15}{293.15}\right) - \frac{323.15 - 293.15}{323.15} \right]$$

$$\Delta S_1 = (1000\text{g})(4.2\text{Jg}^{-1}\text{K}^{-1}) \left[\ln\left(\frac{323.15}{293.15}\right) - \frac{323.15 - 293.15}{323.15} \right]$$

$$= 19.46\text{JK}^{-1}$$

$$\Delta S_2 = (1000\text{g})(4.2\text{Jg}^{-1}\text{K}^{-1}) \left[\ln\left(\frac{353.15}{323.15}\right) - \frac{353.15 - 323.15}{353.15} \right]$$

$$= 16.28\text{JK}^{-1}$$

$$\Delta S = \Delta S_1 + \Delta S_2 = 35.74\text{JK}^{-1} \quad \checkmark \quad \checkmark$$

$$4.2 \quad T_A, T_B \quad P_A = P_B = P \quad N = N_A = N_B$$

$$T_F = \frac{1}{2}(T_A + T_B)$$

$$\Delta S = \Delta S_A + \Delta S_B = Nc_p \int_{T_A}^{T_F} \frac{dT}{T} + Nc_p \int_{T_B}^{T_F} \frac{dT}{T}$$

$$= Nc_p \left[\ln\left(\frac{T_F}{T_A}\right) + \ln\left(\frac{T_F}{T_B}\right) \right]$$

$$C = Nc_p \left[\ln \frac{T_F^2}{T_A T_B} \right]$$

if $\frac{T_F^2}{T_A T_B} > 1$ then ΔS is positive, is $T_F^2 > T_A T_B$?

$$T_F^2 = \frac{1}{4}(T_A + T_B)^2 = \frac{1}{4}(T_A^2 + T_B^2 + 2T_A T_B)$$

$$T_F^2 > T_A T_B \rightarrow T_F^2 - T_A T_B > 0$$

$$\frac{1}{4}(T_A^2 + T_B^2 - 2T_A T_B) > 0$$

$$\frac{1}{4}(T_A - T_B)(T_A - T_B) > 0$$

$$\text{if } |T_A - T_B|^2 > 0$$

then $\Delta S > 0$

4.3

$$\begin{array}{|c|c|} \hline N_1 & N_2 \\ \hline P_1, T & P_2, T \\ \hline \end{array} \rightarrow \begin{array}{|c|} \hline N = N_1 + N_2 \\ \hline P \\ \hline V = V_1 + V_2 \\ \hline T \\ \hline \end{array}$$

$$P_1 V_1 = N_1 k T = P_2 V_2 = N_2 k T \quad \text{initial}$$

$$P(V_1 + V_2) = (N_1 + N_2) k T = \text{final}$$

$$T(V_1 + V_2) = T(V_1 + V_2)$$

$$P(V_1 + V_2) = P_1 V_1 + P_2 V_2$$

$$\Delta T = 0 \Rightarrow dE = 0$$

$$P dV + V dP = N k dT = 0 \Rightarrow P dV = -V dP$$

$$\Delta S = \int \frac{dQ}{T} = - \int \frac{V dP}{T} = -Nk \int_{P_1}^{P_2} \frac{dP}{P}$$

$$\Delta S_{\text{tot}} = \Delta S_1 + \Delta S_2 = -N_1 k \int_{P_1}^P \frac{dP}{P} - N_2 k \int_{P_2}^P \frac{dP}{P}$$

$$\Delta S_{\text{tot}} = -N_1 k \ln\left(\frac{P}{P_1}\right) - N_2 k \ln\left(\frac{P}{P_2}\right) = N_1 k \ln\left(\frac{P_1}{P}\right) + N_2 k \ln\left(\frac{P_2}{P}\right)$$

$$\Delta S_{\text{tot}} = N_1 k \left[\ln \frac{P_1}{P} \right] + (N - N_1) \left[k \ln \frac{P_2}{P} \right]$$

$$= N_1 k \left(\ln \frac{P_1}{P} - \ln \frac{P_2}{P} \right) + N \ln \frac{P_2}{P}$$

$$= N_1 k \ln \frac{P_1}{P_2} + N \ln \frac{P_2}{P}$$

$$= N_1 k \ln \frac{N_1 k T}{V P}$$

$$N_1 k \ln \left(\frac{N_1 (N k)}{V P} \right) + N_2 k \ln \left(\frac{N_2 (N_1)}{V P} \right) > 0$$

$$4.4 \quad 25^\circ\text{C} \Rightarrow 298.15\text{K} = T_f = T_i, 1\text{atm}$$
$$\Delta S = 76\text{JK}^{-1} \quad \Delta H = -8.2 \cdot 10^4\text{J}$$

$$G \equiv E + PV - TS = H - TS$$

$$\Delta G \equiv \Delta H - T\Delta S = -8.2 \cdot 10^4\text{J} - 298.15\text{K}(76\text{JK}^{-1})$$

$$\Delta G = -104,659\text{J} = -1.05 \cdot 10^5\text{J}$$

Since the Gibb's energy decreased

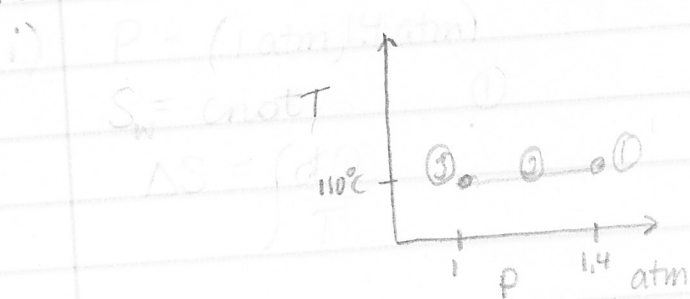
$T = \text{constant}$ - $\Delta P = 0$ - $\Delta V = 0$ - $\Delta H = 0$ - $\Delta S = \text{maximized}$

$P = \text{constant}$ $\therefore \Delta H = 0$ $\therefore S = \text{maximized}$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T = 0 \quad S \text{ extremum}$$

Since G decreased and S is an extreme these are equilibrium conditions

4.5 1 mole Superheated water $110^\circ\text{C} = 383.15\text{K}$



$$R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$$

① $P_1 = 1.4 \text{ atm}$ $P_2 = 1 \text{ atm}$ $S_w = \text{const}$

② Latent heat = $\frac{4 \cdot 10^4 \text{ J}}{\text{mol}}$ at 110°C vapor + water at eq.

③ Water vapor at 110°C behaves as a perfect gas.

$$\Delta S_{\text{phase change}} = \frac{dQ}{T} = \frac{(4 \cdot 10^4 \frac{\text{J}}{\text{mol}})(1 \text{ mol})}{383.15 \text{ K}} = 104 \frac{\text{J}}{\text{K}}$$

ideal gas:

$$\Delta S_{\text{val/pressure change}} = \int \frac{P dV}{T} = R \int \frac{dV}{V} = R \ln\left(\frac{V_2}{V_1}\right) = R \ln\left(\frac{P_1}{P_2}\right)$$

$$= R \ln(1.4) = 2.8 \text{ J K}^{-1}$$

$$\Delta S = \Delta S_{\text{phase}} + \Delta S_{\text{vol}} = 106.8 \text{ J K}^{-1} \quad \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + 0.46 \text{ cm}^3 \text{ K}^{-1}$$

non-ideal gas:

$$\Delta S_{\text{vol}} = - \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial T}\right)_P dP = R \ln\left(\frac{P_1}{P_2}\right) + 0.46(P_1 - P_2)$$

$$\Delta S_{\text{ideal}} - \Delta S_{\text{non ideal}} = 0.46(P_1 - P_2) = .46(1.4 \text{ atm cm}^3 \text{ K}^{-1}) = 0.019 \text{ J/K}$$

4.6 allotropic forms α, β, γ

$$\alpha \rightarrow \beta = 49.43 \text{ K} \quad \alpha \rightarrow \gamma = 30.29 \text{ K} \quad \gamma \rightarrow \alpha = 30.29 \text{ K}$$

$$S_d = 34.03 \text{ J mol}^{-1} \text{ K}^{-1} \quad \text{when } T = 49.43 \text{ K}$$

$$S(\gamma) \quad T_0 = 0 \text{ K, to } T_1 = 30.29 \text{ K} \quad \text{is } 11.22 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S(\alpha) \quad \text{heat } 30.29 \text{ K to } 49.43 \text{ K} = 20.10 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta S(\alpha \rightarrow \gamma, T = 49.43 \text{ K}) = 34.03 \text{ J K}^{-1} = \Delta S_{\text{TOT}}$$

$$\Delta S_{\text{TOT}} = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$\Delta S_1 = \text{heat in } \gamma \text{ form from } 0 \text{ K to } 30.29 \text{ K} = 11.22 \text{ J K}^{-1}$$

$$\Delta S_2 = \frac{\Delta Q}{T_1} = \frac{L}{T_1} = \frac{L}{30.29 \text{ K}} = \text{entropy change due to latent heat released as form changes } \gamma \text{ to } \alpha.$$

$$\Delta S_3 = \text{heat in } \alpha \text{ form from } 30.29 \text{ K to } 49.43 \text{ K} = 20.10 \text{ J K}^{-1}$$

$$\Delta S_{\text{TOT}} = \Delta S_1 + \frac{L}{T_1} + \Delta S_3$$

$$L = T_1 (\Delta S_{\text{TOT}} - \Delta S_1 - \Delta S_3)$$

$$L = (30.29 \text{ K})(34.03 - 11.22 - 20.10) \text{ J K}^{-1}$$

$$L = 82.1 \text{ J}$$