

① @ $n_{He} = 1000 \text{ moles}$, $n_{Ne} = 2000 \text{ moles}$, $n_{Ar} = 3000 \text{ moles}$

$$n_{\text{total}} = 6000 \text{ moles}, \quad T = 300 \text{ K}$$

Now for each section $V_i = n_i RT/P = (n_i/n) nRT/P$

$$nRT/P = V \Rightarrow V_i = (n_i/n)V \Rightarrow V_{He} = V/6, \quad V_{Ne} = V/3, \quad V_{Ar} = V/2$$

② b) Temperature does not change

$$\Rightarrow \Delta S_i = n_i R \ln(V/V_i)$$

$$\begin{aligned} \Rightarrow \Delta S &= [n_{He} \ln(V/V_{He}) + n_{Ne} \ln(V/V_{Ne}) + n_{Ar} \ln(V/V_{Ar})] R \\ &= (1792 + 2197 + 2079) R \rightarrow \boxed{\Delta S = 50.5 \text{ kJ/K}} \end{aligned}$$

③ c) $dF_i = -P_i dV' = -(nRT/V') dV' \Rightarrow \Delta F_i = -nRT \ln(V/V_i)$

$$\Rightarrow \Delta F_i = -(\Delta S_i)T \Rightarrow \boxed{\Delta F = -(\Delta S)T = -1.51 \times 10^4 \text{ kJ}}$$

② @ $G = n[RT \ln(P/P_0) - f(T, P)]$

$$V = -\left.\frac{\partial G}{\partial P}\right|_{T, n} = \frac{nRT}{P} - n f(T) \Rightarrow \boxed{PV = n[RT - f(T)P]}$$

③ b) $S = -\left.\frac{\partial G}{\partial T}\right|_{P, n} \rightarrow \boxed{S = n\left[P \frac{df}{dT} - R \ln\left(\frac{P}{P_0}\right)\right]}$

③ c) $F = U - TS \quad \text{and} \quad G = U - TS + PV \Rightarrow F = G - PV$

$$\Rightarrow \boxed{F = nRT \left[\ln\left(\frac{P}{P_0}\right) - 1\right]}$$

③ a) $[P + a(N/V)^2][V - bN] = Nk_B T \Rightarrow P = Nk_B T / (V - bN) - a(N/V)^2$

③ b) Isothermal $\rightarrow \Delta F = -\int_{V_1}^{V_2} PdV = -Nk_B T \int_{V_1}^{V_2} \frac{dV}{V - bN} + aN^2 \int_{V_1}^{V_2} \frac{dV}{V^2}$

$$\Rightarrow \boxed{\Delta F = Nk_B T \ln\left(\frac{V_1 - bN}{V_2 - bN}\right) + aN^2 \left(\frac{1}{V_1} - \frac{1}{V_2}\right)}$$

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③ (c) $P = -\frac{\partial F}{\partial V} \Rightarrow F = -\int P dV = -Nk_B T \ln(V-bN) - \frac{aN^2}{V} + f(T)$

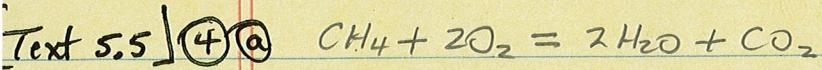
$$\Rightarrow S = -\frac{\partial F}{\partial T} = Nk_B \ln(V-bN) - \frac{df}{dT}$$

(d) For constant T , $\Delta F = \Delta U - T(\Delta S) \Rightarrow \Delta U = \Delta F + T(\Delta S)$

$$\text{Now } \Delta S = Nk_B \ln(V_2 - bN) - Nk_B \ln(V_1 - bN)$$

$$\Rightarrow \Delta U = Nk_B T \ln\left(\frac{V_2 - bN}{V_1 - bN}\right) + Nk_B T \ln\left(\frac{V_1 - bN}{V_2 - bN}\right) + aN^2\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

The \ln terms cancel $\Rightarrow \Delta U = aN^2\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$



$$2 \text{ moles H}_2\text{O} \rightarrow \Delta_f H = -483.64 \text{ kJ}, \Delta_f G = -457.14 \text{ kJ} \quad (\text{gas})$$

$$1 \text{ mole CH}_4 \rightarrow \Delta_f H = -74.81 \text{ kJ}, \Delta_f G = -50.72 \text{ kJ}$$

$$1 \text{ mole CO}_2 \rightarrow \Delta_f H = -393.51 \text{ kJ}, \Delta_f G = -394.36 \text{ kJ}$$

$$2 \text{ moles O}_2 \rightarrow \Delta_f H = \Delta_f G = 0$$

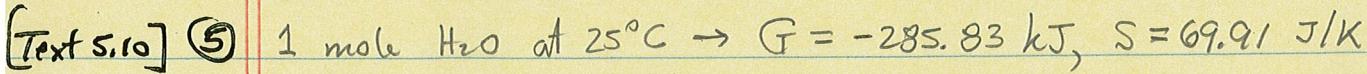
$$\rightarrow \Delta H = \Delta_f H(\text{H}_2\text{O}) + \Delta_f H(\text{CO}_2) - \Delta_f H(\text{CH}_4) \rightarrow \Delta H = -802.34 \text{ kJ}$$

$$\Delta G = \Delta_f G(\text{H}_2\text{O}) + \Delta_f G(\text{CO}_2) - \Delta_f G(\text{CH}_4) \rightarrow \Delta G = -800.78 \text{ kJ}$$

(b) $W_{\text{extracted}} = -\Delta G = 801 \text{ kJ}$ (c) $Q_{\text{extn.}} = \Delta G - \Delta H = 1.56 \text{ kJ}$

(d) $V = W_{\text{extn.}} / (N_A \times \text{charge})$ with charge = 8e

$$\text{Now } W_{\text{extn.}} = 5.0 \times 10^{24} \text{ eV} \Rightarrow V = 1.04 \text{ V}$$



$$\text{and } V = 18.068 \times 10^{-6} \text{ m}^3$$

$$S = -\frac{\partial G}{\partial T} \Big|_{P,n} \Rightarrow \Delta G = -S(\Delta T) \quad (\text{for } S \text{ indep. of } T)$$

$$\Delta T = 5 \text{ K} \rightarrow \boxed{\Delta G = -349.6 \text{ J}}$$

$$V = \frac{\partial G}{\partial P} \Big|_{T,n} \Rightarrow \Delta G = V(\Delta P) \quad (\text{for } V \text{ indep. of } P)$$

To compensate, need $\boxed{\Delta P = -\Delta G/V = 1.935 \times 10^7 \text{ Pa} = 191 \text{ atm}}$

[Text 5.32] ⑥ Clausius - Clapeyron $\rightarrow dP/dT = mL/T(\Delta V)$

$$\Delta V = V_{\text{water}} - V_{\text{ice}} < 0 \Rightarrow dP/dT < 0$$

(b) $p_{\text{ice}} = 917 \text{ kg/m}^3 = m/V_{\text{ice}}$, $p_{\text{final}} = 1000 \text{ kg/m}^3 = m/V_{\text{water}}$
 $\Rightarrow \Delta V/m = 1/p_{\text{water}} - 1/p_{\text{ice}} = -9.05 \times 10^{-5} \text{ m}^3/\text{kg}$
 $L = 3.34 \times 10^5 \text{ J/kg}$, $T = 273 \text{ K} \Rightarrow dP/dT = -1.352 \times 10^7 \text{ Pa/K}$
 $\rightarrow \boxed{\Delta P = (dP/dT)(\Delta T) = 1.35 \times 10^7 \text{ Pa}}$ for $\Delta T = -1 \text{ K}$

(c) $F_g = mg = \rho Vg = \rho A y g$ with $\rho = p_{\text{ice}}$
 $\Rightarrow \Delta P = F_g/A = \rho y g \Rightarrow \boxed{y = \Delta P/\rho g = 1500 \text{ m}}$

(d) $m = 60 \text{ kg}$ and $A = (0.30 \text{ m})(0.005 \text{ m}) = 15 \times 10^{-4} \text{ m}^2$
 $\Rightarrow \Delta P = F_g/A = mg/A = 3.92 \times 10^5 \text{ Pa}$
 $\rightarrow \boxed{\Delta T = \Delta P/(dP/dT) = -0.029 \text{ K}}$

[Text 5.35] ⑦ Clausius - Clapeyron $\rightarrow dP/dT = nL/T(\Delta V)$

Approx. $\Delta V = V_{\text{gas}} = nRT/P \Rightarrow dP/dT = nLP/nRT^2$
 $\Rightarrow dP/P = (L/R) dT/T^2 \Rightarrow \ln P = -L/RT + C$
 $\Rightarrow \boxed{P = (\text{const}) e^{-L/RT}}$

[Text 5.85] ⑧ At temperature T , $\Delta G = \Delta H - T(\Delta S)$ and $\Delta S = -\partial(\Delta G)/\partial T$
 $K = e^{-\Delta G^\circ/RT} \Rightarrow \partial(\ln K)/\partial T = 1/K \partial K/\partial T$
 $= \Delta G^\circ/RT^2 - 1/RT \partial(\Delta G^\circ)/\partial T = \Delta H^\circ/RT^2 - \Delta S^\circ/RT + \Delta S^\circ/RT$
 $\Rightarrow \boxed{\partial(\ln K)/\partial T = \Delta H^\circ/RT^2}$
 $\rightarrow \boxed{\ln[K(T_2)] - \ln[K(T_1)] = (\Delta H^\circ/R)(1/T_1 - 1/T_2)}$

[Text 5.86] ⑨ $T_1 = 25^\circ\text{C} = 298 \text{ K} \rightarrow \Delta H^\circ = -92.22 \text{ kJ}$ and $\Delta G^\circ = -32.90 \text{ kJ}$

$$\text{for 2 moles } NH_3 \Rightarrow K(T_1) = e^{-\Delta G^\circ/RT} = 5.839 \times 10^5$$

$$T_2 = 500^\circ\text{C} = 773 \text{ K} \rightarrow (\Delta H^\circ/R)(1/T_1 - 1/T_2) = -22.87$$

$$\Rightarrow \boxed{K(T_2) = K(T_1) e^{-22.87} = 6.83 \times 10^{-5}}$$