Problem 1) a)

$$\tilde{A}(V, T, N_A, N_B, N_C, N_D) = -k_B T \ln Q$$

$$dA = \left(\frac{\partial A}{\partial V}\right)_{T,N} dV + \left(\frac{\partial A}{\partial T}\right)_{V,N} dT + \left(\frac{\partial A}{\partial N_A}\right)_{T,V,N_B,N_C,N_D} dN_A + \left(\frac{\partial A}{\partial N_B}\right) dN_B$$

skipping other subscripts

$$+ \left(\frac{\partial A}{\partial N_C}\right) dN_C + \left(\frac{\partial A}{\partial N_D}\right) dN_D$$

but dV and dT are zero in this process

and $\mu_x = \left(\frac{\partial A}{\partial N_x}\right)$

$$\Rightarrow dA = \left(\mu_A dN_A + \mu_B dN_B + \mu_C dN_C + \mu_D dN_D\right)$$

using $dN_A = a\, d\lambda$, etc as defined in problem, we get

$$dA = d\lambda\,(a\mu_A + b\mu_B - c\mu_C - d\mu_D)$$

at equilibrium $dA/d\lambda = 0$ means

$$a\mu_A + b\mu_B - c\mu_C - d\mu_D = 0 \quad \checkmark$$

$$Q = \underbrace{\frac{q_A^{N_A}}{N_A!}}_{Q_A} \cdot \underbrace{\frac{q_B^{N_B}}{N_B!}}_{Q_B} \cdot \underbrace{\frac{q_C^{N_C}}{N_C!}}_{Q_C} \cdot \underbrace{\frac{q_D^{N_D}}{N_D!}}_{Q_D}$$

$$\mu_A = -k_BT\frac{\partial \log Q_A}{\partial N_A} - k_BT\,\cancel{\frac{\partial \log(Q_B Q_C Q_D)}{\partial N_A}} \to 0$$

$$= -k_BT\frac{\partial}{\partial N_A}\Big(N_A \log q_A - \underbrace{\log N_A!}_{\approx (N_A \log N_A - N_A)}\Big)$$

$$\approx -k_BT \cdot \Big(\log q_A - \big(N_A\cdot\frac{1}{N_A} + \log N_A - 1\big)\Big)$$

$$= -k_BT \log(q_A/N_A)$$

Plugging in to Eqn 4 gives

$$0 = -k_BT\left(a\log q_A/N_A + b\log q_B/N_B - c\log q_C/N_C - d\log q_D/N_D\right)$$

$$\Rightarrow\quad 0 = \log\left[\left(q_A/N_A\right)^a\left(q_B/N_B\right)^b\cdot\left(q_C/N_C\right)^{-c}\cdot\left(\frac{q_D}{N_D}\right)^{-d}\right]$$

exponentiade both sides

$$\Rightarrow\quad 1 = \left[\left(q_A/N_A\right)^a\left(q_B/N_B\right)^b\cdot\left(q_C/N_C\right)^{-c}\cdot\left(\frac{q_D}{N_D}\right)^{-d}\right]$$

note that $q_A/N_A = (q_A/V)/(N_A/V) = \dfrac{(q_A/V)}{\rho_A}$

$$\Rightarrow \left((q_C/V)/\rho_C\right)^c\cdot\left((q_D/V)/\rho_D\right)^d = \left(\frac{(q_A/V)}{\rho_A}\right)^a\left(\frac{(q_B/V)}{\rho_B}\right)^b$$

$$\Rightarrow\quad \frac{\rho_D^d\,\rho_C^c}{\rho_A^a\,\rho_B^b} = \frac{(q_D/V)^d\,(q_C/V)^c}{(q_A/V)^a\,(q_B/V)^b} \equiv K(T)$$

✓

The right side depends only on T because each $q_X = V f(n_X, T)$ as in the problem, so all V dependence cancels out, and no N's. Other side $\rho_X = P_X/k_BT$ where P_X is the partial pressure, see next parts

$$A = -k_B T \log Q$$

$$Q = Q_A Q_B Q_C Q_D \quad \text{as above}$$

$$A = -k_B T \left[\log Q_A + \log Q_B + \log Q_C + \log Q_D\right]$$

$$A_x = -k_B T \log Q_x = -k_B T \log\left(\frac{q_x^{N_x}}{N_x!}\right) \checkmark$$

d) $$P_x = -\frac{\partial A_x}{\partial V} = +k_B T \frac{\partial}{\partial V}\left(\log \frac{q_x^{N_x}}{N_x!}\right)$$

$$= k_B T \frac{\partial}{\partial V}\left(N_x \log V + N_x \log f - \log N!\right)$$

$$= N_x k_B T / V = \rho_x k_B T$$

$$K_P = \frac{P_C^c P_D^d}{P_A^a P_B^b} = \frac{\rho_C^c \rho_D^d}{\rho_A^a \rho_B^b} \cdot (k_B T)^{cd-ab}$$

$$= K(T) \cdot (k_B T)^{cd-ab}$$

Problem 2:

(a) $$L = -k_B \sum_{i=1}^{N} p_i \log p_i - \alpha \sum_{i=1}^{N} p_i - \beta \sum_{i=1}^{N} \epsilon_i p_i$$

product rule

$$\frac{\partial L}{\partial p_k} = -k_B \left[\sum_{i=1}^{N} p_i \underbrace{\frac{\partial \log p_i}{\partial p_k}}_{\frac{1}{p_i}\frac{\partial p_i}{\partial p_k}} + \frac{\partial p_i}{\partial p_k} \cdot \log p_i \right] - \alpha \sum_{i=1}^{N} \frac{\partial p_i}{\partial p_k} - \beta \sum_{i=1}^{N} \epsilon_i \frac{\partial p_i}{\partial p_k}$$

$$\partial p_i / \partial p_k = \begin{cases} 0 & \text{if } i \neq k \\ 1 & \text{if } i = k \end{cases}$$

$$= -k_B \left[1 + \log p_k \right] - \alpha - \beta \epsilon_k$$

$$\partial L / \partial p_k = 0 = -k_B [1 + \log p_k] - \alpha - \beta \epsilon_k$$ if L is to be maximized

$$\Rightarrow 1 + \log p_k = -\alpha / k_B - \beta \epsilon_k / k_B$$

exponentiate

$$\Rightarrow p_k = \underbrace{\left(e^{-1-\alpha/k_B}\right)}_{\text{constant}} \left(e^{-\beta \epsilon_k / k_B}\right)$$. This p_k works for every k

(b) $$\sum_{i=1}^{N} p_i = 1 \Rightarrow 1 = \left[e^{-1-\alpha/k_B}\right] \sum_{i=1}^{N} e^{-\beta \epsilon_i / k_B}$$

$$\Rightarrow \left[e^{-1-\alpha/k_B}\right]^{-1} = \sum_{i=1}^{N} e^{-\beta \epsilon_i / k_B} \equiv Z$$, partition function

So $$p_k = e^{-\beta \epsilon_k / k_B} \Big/ \sum_{i=1}^{N} e^{-\beta \epsilon_i / k_B}$$

(c) $$Z_{\text{canonical}} = \sum_{i=1}^{N} e^{-\epsilon_i / k_B T} \Rightarrow \beta = 1/T$$

(d) without constraint on average energy,

$$L = -k_B \sum_{i=1}^{N} p_i \log p_i - \alpha \sum_{i=1}^{N} p_i$$

$$\partial L / \partial p_k = 0 = -k_B [1 + \log p_k] - \alpha$$

$$\Rightarrow \log p_k = -1 - \alpha / k_B$$

$$p_k = e^{-1 - \alpha / k_B} = \text{const} \equiv A$$

$$\sum_{i=1}^{N} p_i = 1 \Rightarrow 1 = \sum_{i=1}^{N} A = NA$$

$$\Rightarrow A = \frac{1}{N} = p_k \quad \forall k, \text{ so}$$

we have equipartition between states,

this corresponds to microcanonical ensemble

[Note, in microcanonical, $\mathcal{E}$ is const so $\bar{\mathcal{E}} = \mathcal{E}$, but this doesn't come from an extra thermodynamic constraint