Post-Lecture Question 4

$$dE = T dS - p dV + \mu dN$$

$$\Rightarrow dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$

$$dS = dS_{\alpha} + dS_{\beta}$$

$$= \frac{1}{T_{\alpha}} dE_{\alpha} + \frac{P_{\alpha}}{T_{\alpha}} dV_{\alpha} - \frac{\mu_{\alpha 1}}{T_{\alpha}} dN_{\alpha 1} - \frac{\mu_{\alpha 2}}{T_{\alpha}} dN_{\alpha 2}$$

$$+ \frac{1}{T_{\beta}} dE_{\beta} + \frac{P_{\beta}}{T_{\beta}} dV_{\beta} - \frac{\mu_{\beta 1}}{T_{\beta}} dN_{\beta 1} - \frac{\mu_{\beta 2}}{T_{\beta}} dN_{\beta 2}$$

$$= 0$$

Have

$$\begin{split} \mathrm{d}E_{\alpha} &= -\,\mathrm{d}E_{\beta} \quad \Rightarrow \quad \left(\frac{1}{T_{\alpha}} - \frac{1}{T_{\beta}}\right) \mathrm{d}E_{\alpha} = 0 \\ \mathrm{d}E_{\alpha} &= -\,\mathrm{d}E_{\beta} \quad \Rightarrow \quad \left(\frac{1}{T_{\alpha}} - \frac{1}{T_{\beta}}\right) \mathrm{d}E_{\alpha} = 0 \\ \mathrm{d}N_{\alpha 1} &= -\,\mathrm{d}N_{\beta 1} \quad \Rightarrow \quad \frac{1}{T}(\mu_{\beta 1} - \mu_{\alpha 1}) \,\mathrm{d}N_{\beta 1} = 0 \\ \mathrm{d}N_{\alpha 2} &= -\,\mathrm{d}N_{\beta 2} \quad \Rightarrow \quad \frac{1}{T}(\mu_{\beta 2} - \mu_{\alpha 2}) \,\mathrm{d}N_{\beta 2} = 0 \end{split}$$

$$\Rightarrow \begin{cases} T_{\alpha} = T_{\beta} = T \\ P_{\alpha} = P_{\beta} = P \\ \mu_{\beta 1} = \mu_{\alpha 1} = \mu_{1} \\ \mu_{\beta 2} = \mu_{\alpha 2} = \mu_{2} \end{cases}$$

It is unnecessary that $\mu_1 = \mu_2$.

(b)
$$\begin{cases} T_{\alpha} = T_{\beta} = T_{\text{bath}} \\ P_{\alpha} = P_{\beta} = P_{\text{bath}} \\ \mu_{\beta 1} = \mu_{\alpha 1} \\ \mu_{\beta 2} = \mu_{\alpha 2} \end{cases}$$

$$dG = -S dT - V dP + \mu dN$$

$$\Delta G_1 = \frac{1}{2} \left(\frac{\partial^2 G_1}{\partial N_{\alpha 1}^2} \right)_{N_2, T, P} (\Delta N_{\alpha 1})^2 + \frac{1}{2} \left(\frac{\partial^2 G_1}{\partial N_{\beta 1}^2} \right)_{N_2, T, P} (\Delta N_{\beta 1})^2$$

$$= \left(\frac{\partial^2 G_1}{\partial N_1^2} \right)_{N_2, T, P} (\Delta N_1)^2$$

$$= \left(\frac{\partial \mu_1}{\partial N_1} \right)_{N_2, T, P} (\Delta N_1)^2 \ge 0$$

$$\Rightarrow \left(\frac{\partial \mu_1}{\partial N_1} \right)_{N_2, T, P} \ge 0$$