Problem A

Consider an isolated system in equilibrium with two parts, A and B, having a mixture of particles where $U_{\text{total}} = U_A + U_B$, $V_{\text{total}} = V_A + V_B$, and $N_{\text{total}} = N_A + N_B$ (for each type of particle). Since it is isolated, the change in these parameters is $\mathrm{d}U_{\text{total}} = \mathrm{d}V_{\text{total}} = \mathrm{d}N_{\text{total}} = 0$. The change in entropy can be expressed as

$$\begin{aligned}\Delta S_T = \sum_{\alpha=A}^{B} \Bigg[\left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)^0_{V_\alpha N_\alpha} \Delta U_\alpha + \boxed{\left(\frac{\partial S_\alpha}{\partial V_\alpha}\right)^0_{U_\alpha N_\alpha} \Delta V_\alpha + \left(\frac{\partial S_\alpha}{\partial N_\alpha}\right)^0_{V_\alpha U_\alpha} \Delta N_\alpha} \Bigg] \\ + \frac{1}{2}\left[\Delta \left(\frac{\partial S_\alpha}{\partial U_\alpha}\right)_{V_\alpha N_\alpha} \Delta U_\alpha + \Delta \left(\frac{\partial S_\alpha}{\partial V_\alpha}\right)_{U_\alpha N_\alpha} \Delta V_\alpha + \sum_{j=1}^{l} \Delta \left(\frac{\partial S_\alpha}{\partial N_{\alpha,j}}\right)_{V_\alpha U_\alpha} \Delta N_{\alpha,j} \right] \\ + \dots \end{aligned} \tag{1}$$

Show that the two terms within the red box will yield zero. What conditions between A and B can be derived from these two terms?

Solution:
Using the Born Square, we get the following relation for the change in internal energy:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N \tag{2}$$

Rearranging this, we obtain a relation for the change in entropy:

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}U + \frac{P}{T}\mathrm{d}V - \frac{\mu}{T}\mathrm{d}N \tag{3}$$

Comparing the obtained relation with Eq. (1), we can infer that

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}, \qquad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N}, \qquad \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{V,U} \tag{4}$$

We assume that the interface between parts A and B can transmit heat, mechanical energy and particles of all types. In this case, the thermodynamic variables in both parts of the system (*i.e.* temperature, pressure, and chemical potential for each type of particle) must be the same for the system to be in equilibrium. Thus, the first term in the red box becomes

$$\sum_{\alpha=A}^{B}\left[\left(\frac{\partial S_\alpha}{\partial V_\alpha}\right)_{U^0_\alpha N_\alpha} \Delta V_\alpha\right] = \frac{P_A}{T_A}\Delta V_A + \frac{P_B}{T_B}\Delta V_B = \cancelto{0}{\left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right)} \Delta V_A = 0 \tag{5}$$

and the second term becomes

$$\sum_{\alpha=A}^{B}\left[\left(\frac{\partial S_\alpha}{\partial N_\alpha}\right)^0_{U_\alpha V_\alpha} \Delta N_\alpha\right] = -\frac{\mu_A}{T_A}\Delta N_A - \frac{\mu_B}{T_B}\Delta N_B = \cancelto{0}{\left(\frac{\mu_B}{T_B} - \frac{\mu_A}{T_A}\right)} \Delta N_A = 0 \tag{6}$$

Problem B

Derive the Maxwell's relations from the Gibb's free energy assuming constant number of particles.

Solution:
The total differential of G can be written as

$$\mathrm{d}G = \left(\frac{\partial G}{\partial P}\right)_{T,N} \mathrm{d}P + \left(\frac{\partial G}{\partial T}\right)_{P,N} \mathrm{d}T + \left(\frac{\partial G}{\partial N}\right)_{P,T} \cancelto{0}{\mathrm{d}N} \tag{7}$$

where $\mathrm{d}N = 0$ since there is a constant number of particles. Using the Born Square, we get

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T + \mu\cancelto{0}{\mathrm{d}N} \tag{8}$$

Comparing these two equations, we have the following relations

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N}, \qquad S = -\left(\frac{\partial G}{\partial T}\right)_{P,N} \tag{9}$$

Making use of the symmetry of the second derivatives and applying the relations in Eq. (9), we obtain

$$\left(\frac{\partial}{\partial T}\frac{\partial G}{\partial P}\right)_{P,N} = \left(\frac{\partial}{\partial P}\frac{\partial G}{\partial T}\right)_{T,N} \quad \longrightarrow \quad \left(\frac{\partial V}{\partial T}\right)_{P,N} = -\left(\frac{\partial S}{\partial P}\right)_{T,N} \tag{10}$$

which is the Maxwell's relation derived from Gibb's free energy with fixed N.