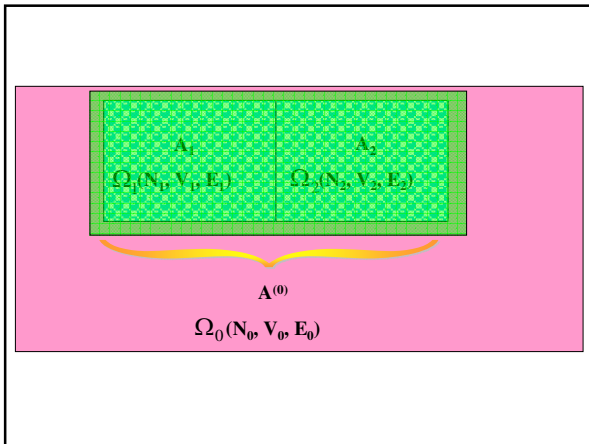
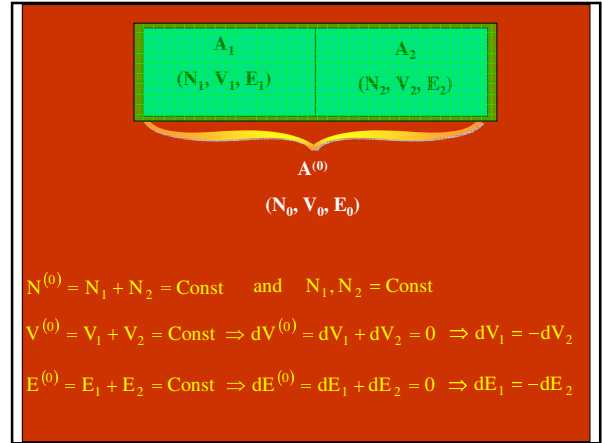
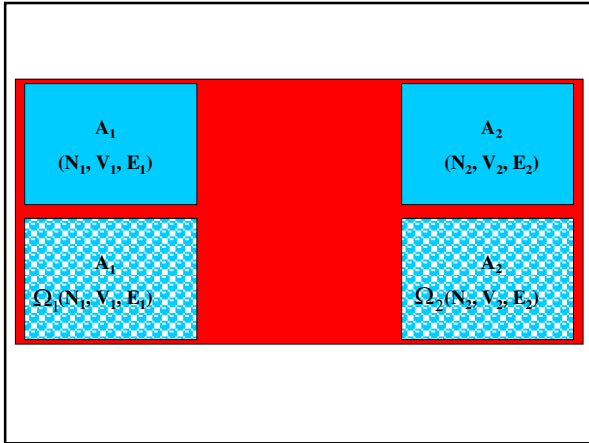


1.3. Further contact between statistics and thermodynamics

In continuation of the preceding considerations, we now examine a more elaborate exchange between the sub-systems A_1 and A_2 . If we assume that the wall separating the two sub-systems is movable as well as conducting, then the respective volumes V_1 and V_2 (of sub-systems A_1 and A_2) also become variable; indeed, the total volume $V^{(0)} (= V_1 + V_2)$ remains constant, so that effectively we have only one more independent variable. Of course, the wall is still assumed to be impenetrable to particles, so the numbers N_1 and N_2 remain fixed. Arguing as before, the state of equilibrium for the composite system $A^{(0)}$ will obtain when the number $\Omega^{(0)}(V^{(0)}, E^{(0)}; V_1, E_1)$ attains its largest value, i.e. when not only

1.3. Further contact between statistics and thermodynamics

In continuation of the preceding considerations, we now examine a more elaborate exchange between the sub-systems A_1 and A_2 . If we assume that the wall separating the two sub-systems is movable as well as conducting, then the respective volumes V_1 and V_2 (of sub-systems A_1 and A_2) also become variable; indeed, the total volume $V^{(0)} (= V_1 + V_2)$ remains constant, so that effectively we have only one more independent variable. Of course, the wall is still assumed to be impenetrable to particles, so the numbers N_1 and N_2 remain fixed. Arguing as before, the state of equilibrium for the composite system $A^{(0)}$ will obtain when the number $\Omega^{(0)}(V^{(0)}, E^{(0)}; V_1, E_1)$ attains its largest value, i.e. when not only



$$\Omega^{(0)}(E_1, V_1, \cancel{N_1}; E_2, V_2, \cancel{N_2}) =$$

$$\begin{aligned} \Omega^{(0)}(E_1, V_1; \cancel{E_2}, \cancel{V_2}) &= \Omega_1(E_1, V_1) \Omega_2(E_2, V_2) \\ &= \Omega_1(E_1, V_1) \Omega_2(E^{(0)} - E_1, V^{(0)} - V_1) \\ &= \Omega_1(E_1, V_1) \Omega_2(E_1, V_1) \\ &= \Omega^{(0)}(E_1, V_1) \end{aligned}$$

Clearly, the number $\Omega^{(0)}$ itself varies with E_1 and V_1 .

تعداد آن دسته از حالت‌های دستگاه $A^{(0)}$ که در آن حالتها انرژی دستگاه A_1 برابر E_1 و حجم آن برابر V_1 است.

$$P(E_1, V_1) = \frac{\Omega^{(0)}(E_1, V_1)}{\Omega_{total}^{(0)}}$$

تعداد کل حالت‌های قابل دسترس دستگاه $A^{(0)}$ مستقل از انرژی و حجم دستگاه A_1 .

$$P(E_1, V_1) = \frac{\Omega^{(0)}(E_1, V_1)}{\Omega_{total}^{(0)}} = C \Omega^{(0)}(E_1, V_1) \quad ; C^{-1} = \Omega_{total}^{(0)}$$

$$= C \Omega_1(E_1, V_1) \Omega_2(E_1, V_1)$$

$$= C \Omega_1(E_1, V_1) \Omega_2(E^{(0)} - E_1, V^{(0)} - V_1)$$

$$= C \Omega_1(E_1, V_1) \Omega_2(E_2, V_2)$$

$$Lnp(E_1, V_1) = LnC + Ln\Omega_1(E_1, V_1) + Ln\Omega_2(E_2, V_2)$$

$$dLnp(E_1, V_1) = 0 + \frac{\partial Ln\Omega_1(E_1, V_1)}{\partial E_1} \Big|_{V_1, N_1, \bar{E}_1} dE_1 + \frac{\partial Ln\Omega_1(E_1, V_1)}{\partial V_1} \Big|_{V_1, N_1, \bar{E}_1} dV_1 +$$

$$+ \frac{\partial Ln\Omega_2(E_2, V_2)}{\partial E_2} \Big|_{N_2, V_2, \bar{E}_2} dE_2 + \frac{\partial Ln\Omega_2(E_2, V_2)}{\partial V_2} \Big|_{N_2, V_2, \bar{E}_2} dV_2 = 0$$

$$dE^{(0)} = 0 \quad \Rightarrow \quad dE_1 + dE_2 = 0 \quad \Rightarrow \quad dE_1 = -dE_2$$

$$dV^{(0)} = 0 \quad \Rightarrow \quad dV_1 + dV_2 = 0 \quad \Rightarrow \quad dV_1 = -dV_2$$

$$\left\{ \frac{\partial Ln\Omega_1(E_1, V_1)}{\partial E_1} \Big|_{N_1, V_1, \bar{E}_1} - \frac{\partial Ln\Omega_2(E_2, V_2)}{\partial E_2} \Big|_{N_2, V_2, \bar{E}_2} \right\} dE_1 +$$

$$+ \left\{ \frac{\partial Ln\Omega_1(E_1, V_1)}{\partial V_1} \Big|_{N_1, E_1, \bar{V}_1} - \frac{\partial Ln\Omega_2(E_2, V_2)}{\partial V_2} \Big|_{N_2, E_2, \bar{V}_2} \right\} dV_1 = 0$$

$$\beta = \frac{\partial Ln\Omega(E, V)}{\partial E} \Big|_{N, V, \bar{E}}$$

$$\eta = \frac{\partial Ln\Omega(E, V)}{\partial V} \Big|_{N, E, \bar{V}}$$

$$\left\{ \frac{\partial Ln\Omega_1(E_1, V_1)}{\partial E_1} \Big|_{N_1, V_1, \bar{E}_1} - \frac{\partial Ln\Omega_2(E_2, V_2)}{\partial E_2} \Big|_{N_2, V_2, \bar{E}_2} \right\} dE_1 +$$

$$+ \left\{ \frac{\partial Ln\Omega_1(E_1, V_1)}{\partial V_1} \Big|_{N_1, E_1, \bar{V}_1} - \frac{\partial Ln\Omega_2(E_2, V_2)}{\partial V_2} \Big|_{N_2, E_2, \bar{V}_2} \right\} dV_1 = 0$$

$$\{\beta_1 - \beta_2\} dE_1 + \{\eta_1 - \eta_2\} dV_1 = 0$$

$$\beta_1 = \beta_2 \quad \eta_1 = \eta_2$$

بررسی مسأله از دیدگاه ترمودینامیکی

A_1
 (N_1, V_1, E_1)

A_2
 (N_2, V_2, E_2)

$\underbrace{\hspace{10em}}$
 $A^{(0)}$
 (N_0, V_0, E_0)

$$E^{(0)} = \sum_{\alpha=1}^2 E_{\alpha} = E_1 + E_2 = \text{Const.} \quad \Rightarrow \quad \Delta E^{(0)} = 0 \quad \Rightarrow \quad \Delta E_1 = -\Delta E_2$$

$$V^{(0)} = \sum_{\alpha=1}^2 V_{\alpha} = V_1 + V_2 = \text{Const.} \quad \Rightarrow \quad \Delta V^{(0)} = 0 \quad \Rightarrow \quad \Delta V_1 = -\Delta V_2$$

$$S^{(0)} = \sum_{\alpha=1}^s S_{\alpha} = S_1 + S_2$$

آنترپی را حول نقطه تعادل بسط تیلور می دهیم:

$$S^{(0)} = S^{(0)} \Big|_0 + \sum_{\alpha=1}^2 \frac{\partial S_{\alpha}}{\partial E_{\alpha}} \Big|_{N_{\alpha}, V_{\alpha}} \Delta E_{\alpha} + \sum_{\alpha=1}^2 \frac{\partial S_{\alpha}}{\partial V_{\alpha}} \Big|_{N_{\alpha}, E_{\alpha}} \Delta V_{\alpha}$$

$$S^{(0)} - S^{(0)} \Big|_0 = \Delta S^{(0)}$$

$$\Delta S^{(0)} = \frac{\partial S_1}{\partial E_1} \Big|_{N_1, V_1} \Delta E_1 + \frac{\partial S_2}{\partial E_2} \Big|_{N_2, V_2} \Delta E_2 + \frac{\partial S_1}{\partial V_1} \Big|_{N_1, E_1} \Delta V_1 + \frac{\partial S_2}{\partial V_2} \Big|_{N_2, E_2} \Delta V_2 + \dots$$

$$\Delta S^{(0)} = \left\{ \frac{\partial S_1}{\partial E_1} \Big|_{N_1, V_1} - \frac{\partial S_2}{\partial E_2} \Big|_{N_2, V_2} \right\} \Delta E_1 + \left\{ \frac{\partial S_1}{\partial V_1} \Big|_{N_1, E_1} - \frac{\partial S_2}{\partial V_2} \Big|_{N_2, E_2} \right\} \Delta V_1 + \dots$$

.....

..... $\langle q \rangle$ $\Rightarrow \Delta S > 0$

.....

$\Delta S^{(0)} > 0$

$\frac{\partial S_1}{\partial E_1} \Big|_{N_1, V_1} - \frac{\partial S_2}{\partial E_2} \Big|_{N_2, V_2} = 0$

?

$\Delta S^{(0)} > 0$

$\frac{\partial S_1}{\partial V_1} \Big|_{N_1, E_1} - \frac{\partial S_2}{\partial V_2} \Big|_{N_2, E_2} = 0$

?

$$\left. \begin{aligned} dE &= dQ - PdV + \mu dN \\ dQ &= TdS \end{aligned} \right\} \Rightarrow dE = TdS - PdV + \mu dN$$

$$\left. \frac{\partial S}{\partial E} \right|_{V,N} = \frac{1}{T} \quad \& \quad \left. \frac{\partial S}{\partial V} \right|_{E,N} = \frac{P}{T}$$

$$\Delta S^{(0)} > 0 \Rightarrow \left. \frac{\partial S_1}{\partial E_1} \right|_{N_1, V_1} - \left. \frac{\partial S_2}{\partial E_2} \right|_{N_2, V_2} = 0 \Rightarrow T_1 = T_2$$

$$\Delta S^{(0)} > 0 \Rightarrow \left. \frac{\partial S_1}{\partial V_1} \right|_{N_1, V_1} - \left. \frac{\partial S_2}{\partial V_2} \right|_{N_2, V_2} = 0 \Rightarrow \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\left. \frac{\partial \text{Ln} \Omega_1(E_1)}{\partial E_1} \right|_{N_1, V_1, \bar{E}_1} = \left. \frac{\partial \text{Ln} \Omega_2(E_2)}{\partial E_2} \right|_{N_2, V_2, \bar{E}_2}$$

$$\beta = \left. \frac{\partial \text{Ln} \Omega(E)}{\partial E} \right|_{N, V, \bar{E}}$$

$$\left. \frac{\partial S_1}{\partial E_1} \right|_{N_1, V_1} = \left. \frac{\partial S_2}{\partial E_2} \right|_{N_2, V_2}$$

$$\left. \frac{\partial S}{\partial E} \right|_{V, N} = \frac{1}{T}$$

$$\left. \frac{\Delta(\text{Ln} \Omega(E))}{\Delta S} \right|_{\bar{E}} = \beta T = \text{const.}$$

$$\left. \frac{\partial \text{Ln} \Omega_1(E_1, V_1)}{\partial V_1} \right|_{N_1, E_1, \bar{V}_1} = \left. \frac{\partial \text{Ln} \Omega_2(E_2, V_2)}{\partial V_2} \right|_{N_2, E_2, \bar{V}_2}$$

$$\eta = \left. \frac{\partial \text{Ln} \Omega(E)}{\partial V} \right|_{N, E, \bar{V}}$$

$$\left. \frac{\partial S_1}{\partial V_1} \right|_{N_1, E_1} = \left. \frac{\partial S_2}{\partial V_2} \right|_{N_2, E_2}$$

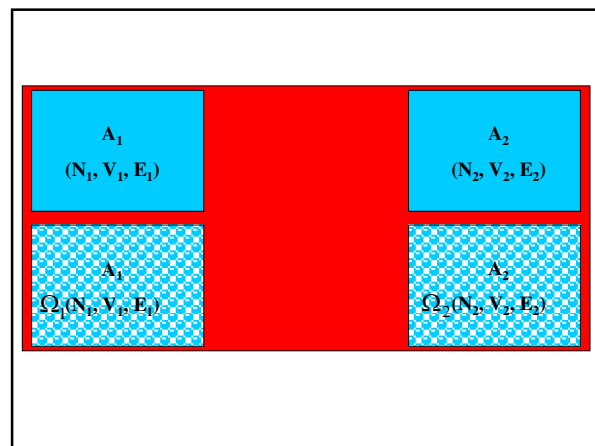
$$\left. \frac{\partial S}{\partial V} \right|_{E, N} = \frac{P}{T}$$

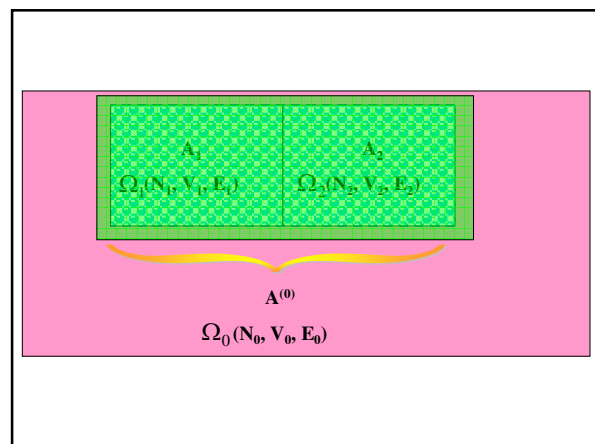
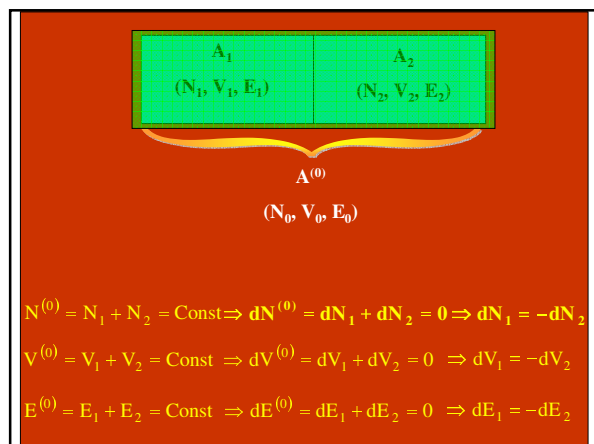
$$\left. \frac{\Delta(\text{Ln} \Omega(E, V))}{\Delta S} \right|_{\bar{E}} = \frac{\eta T}{P} = \text{const.}$$

$$\beta = \frac{1}{kT}$$

$$\left. \begin{aligned} \eta &= \left. \frac{\partial \text{Ln} \Omega(N, V, E)}{\partial V} \right|_{N, E} \\ \left. \frac{\partial S}{\partial V} \right|_{N, E} &= \frac{P}{T} \\ S &= k \text{Ln} \Omega(N, V, E) \end{aligned} \right\} \Rightarrow \eta = \frac{P}{kT}$$

Similarly, if A_1 and A_2 came into contact through a wall which allowed an exchange of particles as well, the conditions for equilibrium would be further augmented by the equality of the parameter ζ_1 of sub-system A_1 and the parameter ζ_2 of sub-system A_2 where, by definition,





$$\begin{aligned}
 \Omega^{(0)}(E_1, V_1, N_1; \cancel{E_2}, \cancel{V_2}, \cancel{N_2}) &= \\
 &= \Omega_1(N_1, E_1, V_1) \Omega_2(N_2, E_2, V_2) \\
 &= \Omega_1(N_1, E_1, V_1) \Omega_2(\cancel{N^{(0)} - N_1}, \cancel{E^{(0)} - E_1}, \cancel{V^{(0)} - V_1}) \\
 &= \Omega_1(N_1, E_1, V_1) \Omega_2(N_1, E_1, V_1) \\
 &= \Omega^{(0)}(N_1, E_1, V_1)
 \end{aligned}$$

Clearly, the number $\Omega^{(0)}$ itself varies with N_1 , E_1 and V_1 .

تعداد آن دسته از حالت‌های دستگاه $A^{(0)}$ که در آن حالت‌ها انرژی دستگاه A_1 برابر E_1 ، حجم آن برابر V_1 و تعداد ذرات آن برابر N_1 است.

$$P(E_1, V_1) = \frac{\Omega^{(0)}(N_1, E_1, V_1)}{\Omega_{\text{total}}^{(0)}}$$

تعداد کل حالت‌های قابل دسترس دستگاه $A^{(0)}$ مستقل از انرژی، حجم و تعداد ذرات دستگاه A_1 است.

$$\begin{aligned}
 P(N_1, E_1, V_1) &= \frac{\Omega^{(0)}(N_1, E_1, V_1)}{\Omega_{\text{total}}^{(0)}} = C \Omega^{(0)}(N_1, E_1, V_1) : C^{-1} = \Omega_{\text{total}}^{(0)} \\
 &= C \Omega_1(N_1, E_1, V_1) \Omega_2(N_1, E_1, V_1) \\
 &= C \Omega_1(N_1, E_1, V_1) \Omega_2(N^{(0)} - N_1, E^{(0)} - E_1, V^{(0)} - V_1) \\
 &= C \Omega_1(N_1, E_1, V_1) \Omega_2(N_2, E_2, V_2)
 \end{aligned}$$

$$\begin{aligned}
 \text{Lnp}(N_1, E_1, V_1) &= \text{Lnc} + \text{Ln}\Omega_1(N_1, E_1, V_1) + \text{Ln}\Omega_2(N_2, E_2, V_2) \\
 d\text{Lnp}(N_1, E_1, V_1) &= 0 + \frac{\partial \text{Ln}\Omega_1(N_1, E_1, V_1)}{\partial E_1} \Big|_{\bar{E}_1, V_1, N_1} dE_1 + \\
 &+ \frac{\partial \text{Ln}\Omega_1(N_1, E_1, V_1)}{\partial V_1} \Big|_{V_1, E_1, N_1} dV_1 + \\
 &+ \frac{\partial \text{Ln}\Omega_1(N_1, E_1, V_1)}{\partial N_1} \Big|_{N_1, E_1, V_1} dN_1 + \\
 &+ \frac{\partial \text{Ln}\Omega_2(N_2, E_2, V_2)}{\partial E_2} \Big|_{\bar{E}_2, V_2, N_2} dE_2 + \\
 &+ \frac{\partial \text{Ln}\Omega_2(N_2, E_2, V_2)}{\partial V_2} \Big|_{V_2, E_2, N_2} dV_2 + \\
 &+ \frac{\partial \text{Ln}\Omega_2(N_2, E_2, V_2)}{\partial N_2} \Big|_{N_2, E_2, V_2} dN_2 \\
 &= 0
 \end{aligned}$$

$$\begin{aligned}
 dE^{(0)} = 0 &\Rightarrow dE_1 + dE_2 = 0 \Rightarrow dE_1 = -dE_2 \\
 dV^{(0)} = 0 &\Rightarrow dV_1 + dV_2 = 0 \Rightarrow dV_1 = -dV_2 \\
 dN^{(0)} = 0 &\Rightarrow dN_1 + dN_2 = 0 \Rightarrow dN_1 = -dN_2 \\
 &\left\{ \frac{\partial \text{Ln}\Omega_1(N_1, E_1, V_1)}{\partial E_1} \Big|_{N_1, V_1, \bar{E}_1} - \frac{\partial \text{Ln}\Omega_2(N_2, E_2, V_2)}{\partial E_2} \Big|_{N_2, V_2, \bar{E}_2} \right\} dE_1 + \\
 &+ \left\{ \frac{\partial \text{Ln}\Omega_1(N_1, E_1, V_1)}{\partial V_1} \Big|_{N_1, E_1, \bar{V}_1} - \frac{\partial \text{Ln}\Omega_2(N_2, E_2, V_2)}{\partial V_2} \Big|_{N_2, E_2, \bar{V}_2} \right\} dV_1 + \\
 &+ \left\{ \frac{\partial \text{Ln}\Omega_1(N_1, E_1, V_1)}{\partial N_1} \Big|_{V_1, E_1, \bar{N}_1} - \frac{\partial \text{Ln}\Omega_2(N_2, E_2, V_2)}{\partial N_2} \Big|_{V_2, E_2, \bar{N}_2} \right\} dN_1 = \\
 &= 0
 \end{aligned}$$

$$\beta = \left. \frac{\partial \text{Ln} \Omega(N, E, V)}{\partial E} \right|_{N, V, \bar{E}} \quad \eta = \left. \frac{\partial \text{Ln} \Omega(N, E, V)}{\partial V} \right|_{N, E, \bar{V}} \quad \xi = \left. \frac{\partial \text{Ln} \Omega(N, E, V)}{\partial N} \right|_{V, E, \bar{N}}$$

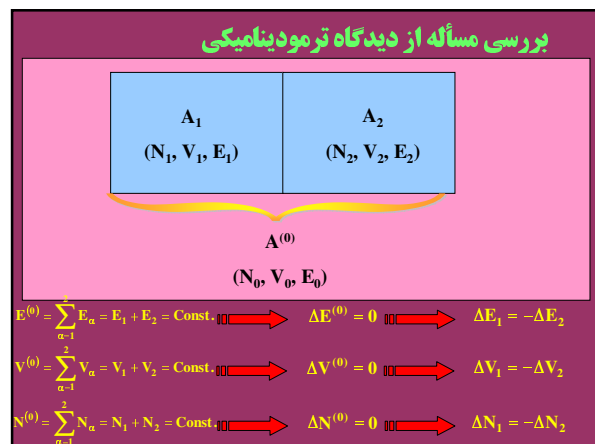
$$\left\{ \frac{\partial \text{Ln} \Omega_1(N_1, E_1, V_1)}{\partial E_1} \Big|_{N_1, V_1, \bar{E}_1} - \frac{\partial \text{Ln} \Omega_2(N_2, E_2, V_2)}{\partial E_2} \Big|_{N_2, V_2, \bar{E}_2} \right\} dE_1 +$$

$$+ \left\{ \frac{\partial \text{Ln} \Omega_1(N_1, E_1, V_1)}{\partial V_1} \Big|_{N_1, E_1, \bar{V}_1} - \frac{\partial \text{Ln} \Omega_2(N_2, E_2, V_2)}{\partial V_2} \Big|_{N_2, E_2, \bar{V}_2} \right\} dV_1 +$$

$$+ \left\{ \frac{\partial \text{Ln} \Omega_1(N_1, E_1, V_1)}{\partial N_1} \Big|_{V_1, E_1, \bar{N}_1} - \frac{\partial \text{Ln} \Omega_2(N_2, E_2, V_2)}{\partial N_2} \Big|_{V_2, E_2, \bar{N}_2} \right\} dN_1 = 0$$

$$\{\beta_1 - \beta_2\} dE_1 + \{\eta_1 - \eta_2\} dV_1 + \{\xi_1 - \xi_2\} dN_1 = 0$$

$$\beta_1 = \beta_2 \quad \eta_1 = \eta_2 \quad \xi_1 = \xi_2$$



$$S^{(0)} = \sum_{\alpha=1}^2 s_{\alpha} = s_1 + s_2$$

آنتروپی را حول نقطه تعادل بسط تیلور می دهیم:

$$S^{(0)} = S^{(0)}|_0 + \sum_{a=1}^2 \left. \frac{\partial S_a}{\partial E_a} \right|_{N_a, V_a} \Delta E_a + \sum_{a=1}^2 \left. \frac{\partial S_a}{\partial V_a} \right|_{N_a, E_a} \Delta V_a + \sum_{a=1}^2 \left. \frac{\partial S_a}{\partial N_a} \right|_{V_a, E_a} \Delta N_a$$

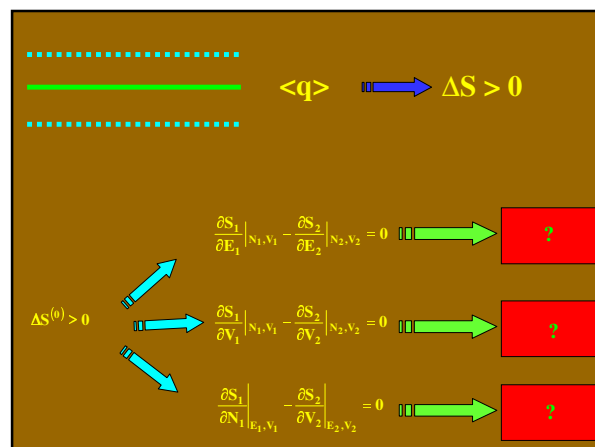
$$S^{(0)} - S^{(0)}|_0 = \Delta S^{(0)}$$

$$\Delta S^{(0)} = \left. \frac{\partial S_1}{\partial E_1} \right|_{N_1, V_1} \Delta E_1 + \left. \frac{\partial S_2}{\partial E_2} \right|_{N_2, V_2} \Delta E_2 + \left. \frac{\partial S_1}{\partial V_1} \right|_{N_1, E_1} \Delta V_1 + \left. \frac{\partial S_2}{\partial V_2} \right|_{N_2, E_2} \Delta V_2 +$$

$$+ \left. \frac{\partial S_1}{\partial N_1} \right|_{V_1, E_1} \Delta N_1 + \left. \frac{\partial S_2}{\partial N_2} \right|_{V_2, E_2} \Delta N_2 + \dots$$

$$\Delta S^{(0)} = \left\{ \left. \frac{\partial S_1}{\partial E_1} \right|_{N_1, V_1} - \left. \frac{\partial S_2}{\partial E_2} \right|_{N_2, V_2} \right\} \Delta E_1 + \left\{ \left. \frac{\partial S_1}{\partial V_1} \right|_{N_1, E_1} - \left. \frac{\partial S_2}{\partial V_2} \right|_{N_2, E_2} \right\} \Delta V_1 +$$

$$+ \left\{ \left. \frac{\partial S_1}{\partial N_1} \right|_{V_1, E_1} - \left. \frac{\partial S_2}{\partial N_2} \right|_{V_2, E_2} \right\} \Delta N_1 + \dots$$



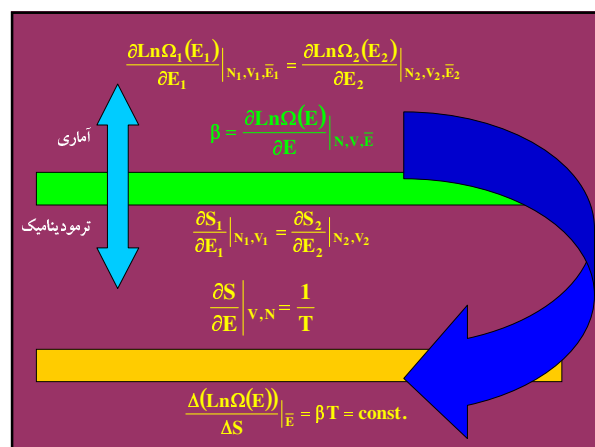
$$\left. \begin{aligned} dE &= dQ - PdV + \mu dN \\ dQ &= TdS \end{aligned} \right\} \implies dE = TdS - PdV + \mu dN$$

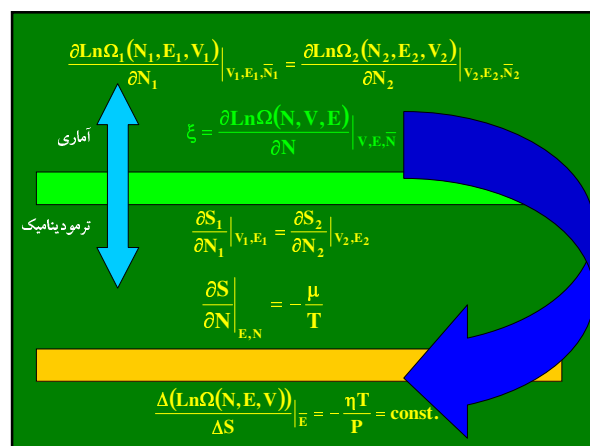
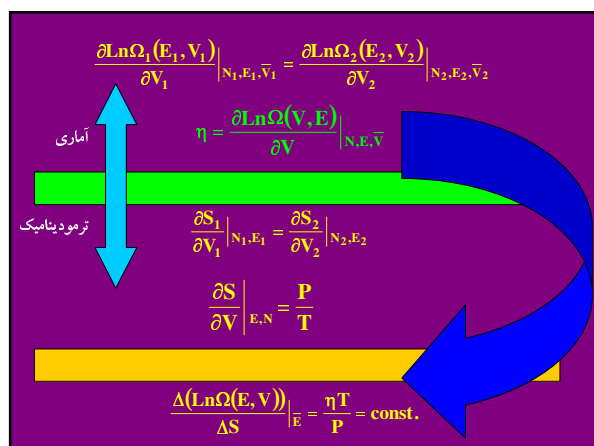
$$\left. \frac{\partial S}{\partial E} \right|_{V, N} = \frac{1}{T} \quad \left. \frac{\partial S}{\partial V} \right|_{E, N} = \frac{P}{T} \quad \left. \frac{\partial S}{\partial N} \right|_{E, V} = -\frac{\mu}{T}$$

$$\Delta S^{(0)} > 0 \implies \left. \frac{\partial S_1}{\partial E_1} \right|_{N_1, V_1} - \left. \frac{\partial S_2}{\partial E_2} \right|_{N_2, V_2} = 0 \implies T_1 = T_2$$

$$\implies \left. \frac{\partial S_1}{\partial V_1} \right|_{N_1, V_1} - \left. \frac{\partial S_2}{\partial V_2} \right|_{N_2, V_2} = 0 \implies \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\implies \left. \frac{\partial S_1}{\partial N_1} \right|_{V_1, E_1} - \left. \frac{\partial S_2}{\partial N_2} \right|_{V_2, E_2} = 0 \implies \frac{\mu_1}{T_1} = \frac{\mu_2}{T_2}$$





$$\beta = \frac{1}{kT} \quad \eta = \frac{P}{kT}$$

$$\left. \begin{aligned} \xi &= \frac{\partial \text{Ln}\Omega(N, V, E)}{\partial N} \Big|_{V, E} \\ \frac{\partial S}{\partial V} \Big|_{N, E} &= -\frac{\mu}{T} \\ S &= k \text{Ln}\Omega(N, V, E) \end{aligned} \right\} \Rightarrow \xi = -\frac{\mu}{kT}$$

$$\begin{pmatrix} \beta \\ \eta \\ \xi \end{pmatrix} = \begin{pmatrix} \frac{\partial \text{Ln}\Omega(N, V, E)}{\partial E} \Big|_{N, V} \\ \frac{\partial \text{Ln}\Omega(N, V, E)}{\partial V} \Big|_{N, E} \\ \frac{\partial \text{Ln}\Omega(N, V, E)}{\partial N} \Big|_{V, E} \end{pmatrix} = \begin{pmatrix} \frac{1}{kT} \\ \frac{P}{kT} \\ -\frac{\mu}{kT} \end{pmatrix}$$

تمرین: شرایط پایداری را در رهیافت ترمودینامیکی با استفاده از بسط تیلور آنتروپی و در نظر گرفتن جملات مرتبه دوم مورد بررسی قرار دهید. (راهنمایی: به کتاب رایشل مراجعه نمایید.)