<u>Βασικές σχέσεις</u>

1ος Νόμος $dU = dW + dq$

Παραδείγματα εκφράσεων έργου: $-PdV, \gamma dA, HdM, mgdh, EdQ$

Ορισμός εντροπίας και θερμοδυναμικής θερμοκρασίας: $dS = \dfrac{dq_{rev}}{T}$

Θεμελιώδης εξίσωση σε ενεργειακή απεικόνιση: $dU = TdS - PdV$

Η εξάρτηση της εσωτερικής ενέργειας από την μεταφορά ύλης σε ένα σύστημα περιγράφεται με την εισαγωγή του χημικού δυναμικού των c συστατικών και η σχέση γίνεται: $dU = TdS - PdV + \sum_{i=1}^{c} \mu_i dn_i$

Θεμελιώδης εξίσωση σε εντροπική απεικόνιση: $dS = \dfrac{1}{T}dU + \dfrac{P}{T}dV - \sum_{i=1}^{c} \dfrac{\mu_i}{T} dn_i$

Μετασχηματισμοί Legendre:

$$H = U - \left(\frac{\partial U}{\partial V}\right)_S V = U + PV \Rightarrow dH = TdS + VdP + \sum_{i=1}^{c} \mu_i dn_i$$

$$F = U - \left(\frac{\partial U}{\partial S}\right)_V S = U - TS \Rightarrow dF = -SdT - PdV + \sum_{i=1}^{c} \mu_i dn_i$$

$$G = F - \left(\frac{\partial F}{\partial V}\right)_T V = F + PV \Rightarrow dG = -SdT + VdP + \sum_{i=1}^{c} \mu_i dn_i$$

Βασικά πορίσματα των θεμελιωδών εξισώσεων είναι οι καταστατικές εξισώσεις:

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,n_i} = \left(\frac{\partial H}{\partial S}\right)_{P,n_i},\ S = -\left(\frac{\partial F}{\partial T}\right)_{V,n_i} = -\left(\frac{\partial G}{\partial T}\right)_{P,n_i},\ P = -\left(\frac{\partial U}{\partial V}\right)_{S,n_i} = -\left(\frac{\partial F}{\partial V}\right)_{T,n_i},$$

$$V = \left(\frac{\partial H}{\partial P}\right)_{S,n_i} = \left(\frac{\partial G}{\partial P}\right)_{T,n_i},\ \mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_{j\neq i}} = \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_{j\neq i}} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

Από ολοκλήρωση των διαφορικών εξισώσεων προκύπτουν, βάσει του θεωρήματος Euler, οι:

$$U = TS - PV + \sum_{i=1}^{c} \mu_i n_i,\ H = TS + \sum_{i=1}^{c} \mu_i n_i,\ F = -PV + \sum_{i=1}^{c} \mu_i n_i,\ G = \sum_{i=1}^{c} \mu_i n_i$$

Από αυτές σε συνδυασμό με τις θεμελιώδεις προκύπτει η εξίσωση Gibbs-Duhem (Γκιμπς-Ντουέμ):

$$SdT - VdP - \sum_{i=1}^{c} n_i d\mu_i = 0$$

Ειδική περίπτωση αυτής για σύστημα ενός συστατικού: $d\mu = -\dfrac{S}{n}dT + \dfrac{V}{n}dP = -sdT + vdP$

Σχέσεις Maxwell που προκύπτουν από την εφαρμογή του κριτηρίου Euler στις θεμελιώδεις εξισώσεις:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V,\ \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P,\ \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V,\ \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial T}{\partial n_i}\right)_{S,V,n_{j\neq i}} = -\left(\frac{\partial \mu_i}{\partial S}\right)_{V,n_j},\ \left(\frac{\partial P}{\partial n_i}\right)_{S,V,n_{j\neq i}} = -\left(\frac{\partial \mu_i}{\partial V}\right)_{S,n_j},\ \left(\frac{\partial \mu_i}{\partial n_k}\right)_{S,V,n_{j\neq k}} = \left(\frac{\partial \mu_k}{\partial n_i}\right)_{S,V,n_{j\neq i}}$$

$$\left(\frac{\partial T}{\partial n_i}\right)_{S,P,n_{j\neq i}} = -\left(\frac{\partial \mu_i}{\partial S}\right)_{P,n_j},\ \left(\frac{\partial V}{\partial n_i}\right)_{S,P,n_{j\neq i}} = \left(\frac{\partial \mu_i}{\partial P}\right)_{S,n_j},\ \left(\frac{\partial \mu_i}{\partial n_k}\right)_{S,P,n_{j\neq k}} = \left(\frac{\partial \mu_k}{\partial n_i}\right)_{S,P,n_{j\neq i}}$$

$$\left(\frac{\partial S}{\partial n_i}\right)_{T,V,n_{j\neq i}} = -\left(\frac{\partial \mu_i}{\partial T}\right)_{V,n_j},\ \left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{j\neq i}} = -\left(\frac{\partial \mu_i}{\partial V}\right)_{T,n_j},\ \left(\frac{\partial \mu_i}{\partial n_k}\right)_{T,V,n_{j\neq k}} = \left(\frac{\partial \mu_k}{\partial n_i}\right)_{T,V,n_{j\neq i}}$$

$$\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_{j\neq i}} = -\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_j},\ \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_j},\ \left(\frac{\partial \mu_i}{\partial n_k}\right)_{T,P,n_{j\neq k}} = \left(\frac{\partial \mu_k}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

$$\left(\frac{\partial \frac{1}{T}}{\partial V}\right)_{U,n_i} = \left(\frac{\partial \frac{P}{T}}{\partial U}\right)_{V,n_i} \Rightarrow \left(\frac{\partial T}{\partial V}\right)_{U,n_i} = P\left(\frac{\partial T}{\partial U}\right)_{V,n_i} - T\left(\frac{\partial P}{\partial U}\right)_{V,n_i}$$

$$C_X = \left(\frac{dq}{dT}\right)_X = T\left(\frac{\partial S}{\partial T}\right)_X,\ C_V = \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V,\ C_P = \left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P,\ k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T,\ k_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$$

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