

$$\bar{M}_i = \left[\frac{\partial (nM)}{\partial n_i} \right]_{T, P, n_j}$$

$$M = f(T, P, n_1, n_2, \dots, n_N)$$

$$d(nM) = \left(\frac{\partial nM}{\partial T} \right)_{P, n} dT + \left(\frac{\partial nM}{\partial P} \right)_{T, n} dP + \sum_i \bar{M}_i dn_i$$

$$d(M) = \left(\frac{\partial M}{\partial T} \right)_{P, X} dT + \left(\frac{\partial M}{\partial P} \right)_{T, X} dP + \sum_i \bar{M}_i dx_i$$

Two results can be obtained from the above equations:

Summability:

$$M = \sum_i x_i \bar{M}_i$$

Gibbs Duhem eq.:

$$\left(\frac{\partial M}{\partial T} \right)_{P, X} dT + \left(\frac{\partial M}{\partial P} \right)_{T, X} dP - \sum_i x_i d\bar{M}_i = 0$$

at const. $T \neq P$ $\sum_i x_i d\bar{M}_i = 0$

For binary solution:

(2)

$$\bar{M}_1 = M + x_2 \frac{dM}{dx_1}$$

$$\bar{M}_2 = M - x_1 \frac{dM}{dx_1}$$

Ideal Gas Mixtures:

Gibbs Theorem $\bar{M}_i^{ig}(T, P) = M_i^{ig}(T, P_i)$

$$M \neq V$$

Enthalpy $\bar{H}_i^{ig}(T, P) = H_i^{ig}(T, P_i) = H_i^{ig}(T, P)$

Entropy: $\bar{S}_i^{ig}(T, P) = S_i^{ig}(T, P_i)$
 $= S_i^{ig}(T, P) - R \ln(y_i)$

Gibbs Energy $\bar{G}_i^{ig} = \bar{H}_i^{ig} + T S_i^{ig}$

$$\Rightarrow \bar{G}_i^{ig}(T, P) = G_i^{ig}(T, P) + RT \ln(y_i)$$

Fugacity For Pure Fluids:

$$G_i^{ig} = \bar{G}_i^*(T) + RT \ln(P) \quad (\text{const. } T)$$

$$G_i^o = \bar{G}_i^*(T) + RT \ln(f_i) \quad (")$$

$$\phi_i^o \equiv \frac{f_i}{P} \quad \ln(\phi_i^o) = \frac{G_i^R}{RT} = \int_0^P (z_i - 1) \frac{dP}{P} \quad (\text{const. } T)$$

Criteria for Equilibrium for Pure species:

(3)

$$f_i^v = f_i^l = f_i^{\text{sat}}$$

$$\Rightarrow \phi_i^v = \phi_i^l = \phi_i^{\text{sat}} \quad ; \quad \phi_i^{\text{sat}} = \frac{f_i^{\text{sat}}}{P_i^{\text{sat}}}$$

$$\ln(\phi_i^{\text{sat}}) = \int_0^{P_i^{\text{sat}}} (z_i - 1) \frac{dP}{P} \quad (\text{const. } T)$$

For $P \neq P_i^{\text{sat}}$

$$f_i = P_i^{\text{sat}} \phi_i^{\text{sat}} \exp \left[\frac{V_i^l (P - P_i^{\text{sat}})}{RT} \right]$$

$$V_i^l = V_{c,i} \left(\frac{1 - T_{r,i}}{Z_{c,i}} \right)^{0.2857} \quad \text{--- (3.63)}$$

Fugacity of species in a solution:

$$\bar{G}_i^{\text{id}} = \bar{G}_i^{\text{id}}(T) + RT \ln(x_i P) \quad (\text{const. } T)$$

$$\bar{G}_i = \bar{G}_i^{\text{id}}(T) + RT \ln(\hat{f}_i) \quad (")$$

$$\hat{\phi}_i = \frac{\hat{f}_i}{x_i P} \quad , \quad \ln(\hat{\phi}_i) = \int_0^P (\bar{z}_i - 1) \frac{dP}{P} \quad (\text{const. } T)$$

see pages 378 to 382 in text book
for evaluation of $\hat{\phi}_i$ using Virial Eq. O.S.

The Ideal Solution

(4)

$$\bar{G}_i^{id} = G_i + RT \ln(x_i)$$

$$\bar{S}_i^{id} = S_i - R \ln(x_i)$$

$$\bar{V}_i^{id} = V_i$$

$$\bar{H}_i^{id} = H_i$$

using $M^{id} = \sum_i x_i \bar{M}_i^{id}$

$$\Rightarrow G^{id} = \sum_i x_i G_i + RT \sum_i x_i \ln(x_i)$$

$$S^{id} = \sum_i x_i S_i - R \sum_i x_i \ln(x_i)$$

$$V^{id} = \sum_i x_i V_i$$

$$H^{id} = \sum_i x_i H_i$$

Fugacity of an Ideal Solution

$$G_i = \mu_i(T) + RT \ln(f_i)$$

(const. T)

$$\bar{G}_i = \mu_i(T) + RT \ln(\hat{f}_i)$$

(s)

$$\bar{G}_i^{id} = \mu_i(T) + RT \ln(\hat{f}_i^{id})$$

(c)

$$\Rightarrow \hat{f}_i^{id} = x_i f_i$$

Lewis / Randal
Rule

also $\hat{\phi}_i^{id} = \phi_i$

Excess Properties

$$M^E \equiv M - M^{id}$$

also,

$$\bar{M}_i^E = \bar{M}_i - \bar{M}_i^{id}$$

$$\Rightarrow \bar{G}_i^E = \bar{G}_i - \bar{G}_i^{id} = RT \ln \left(\frac{\hat{f}_i}{x_i f_i} \right)$$

Definition: $\gamma_i \equiv \frac{\hat{f}_i}{\hat{f}_i^{id}} = \frac{\hat{f}_i}{x_i f_i}$

The Activity Coefficient

$$\ln(\gamma_i) = \frac{\bar{G}_i^E}{RT}$$

summability: $\frac{G^E}{RT} = \sum_i x_i \ln(\gamma_i)$

Gibbs / Duhem at const. T & P

$$\sum_i x_i d\bar{M}_i = 0$$

apply to $\bar{G}_i^E \Rightarrow \sum_i x_i d\bar{G}_i^E = 0$

$$\Rightarrow \sum_i x_i d\bar{G}_i^E = 0 \quad (\text{const. } T \& P) \quad (6)$$

$$\Rightarrow \sum_i x_i d[\ln(\gamma_i)] = 0 \quad (\text{const. } T \& P)$$

Recall,

$$d\left(\frac{nG}{RT}\right) = \frac{nV}{RT} dp - \frac{nH}{RT^2} dT + \sum_i \frac{\bar{G}_i}{RT} dn_i$$

⋮

$$d\left(\frac{nG^E}{RT}\right) = \frac{nV^E}{RT} dp - \frac{nH^E}{RT^2} dT + \sum_i \frac{\bar{G}_i^E}{RT} dn_i$$

$$'' = '' - '' + \sum_i \ln(\gamma_i) dn_i$$

$$\Rightarrow \frac{V^E}{RT} = \left[\frac{\partial (G^E/RT)}{\partial P} \right]_{T, X}$$

$$\frac{H^E}{RT} = -T \left[\frac{\partial (G^E/RT)}{\partial T} \right]_{P, X}$$

$$\ln(\gamma_i) = \left[\frac{\partial (nG^E/RT)}{\partial n_i} \right]_{T, P, n_j}$$