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

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

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

$$\vdots$$

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

Two results can be obtained from the above equations:

Summability:

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

Gibbs Duhem eq.:

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

at const. T & P $\quad \sum_i x_i \, d\overline{M}_i = 0$

For binary solution:

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

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

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 $\boxed{\text{Pure}}$ Fluids:

$$G_i^{ig} = \Gamma_i(T) + RT\ln(P) \qquad (\text{const. } T)$$

$$G_i = \Gamma_i(T) + RT\ln(f_i) \qquad (\text{''})$$

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

Criteria for Equilibrium for Pure species:

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

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

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

For $P \neq P_i^{sat}$

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

$$V_i^{l} = V_{c_i}\,Z_{c_i}^{(1-T_{r_i})^{0.2857}} \quad --- \ (3.63)$$

Fugacity of species in a Solution:

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

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

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

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

The Ideal Solution

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

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

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

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

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

$$G_i = \Gamma_i(T) + RT\ln(f_i) \qquad \text{(const. } T\text{)}$$

$$\bar{G}_i = \Gamma_i(T) + RT\ln(\hat{f}_i) \qquad (\;\text{"}\;)$$

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

$$\Rightarrow \hat{f}_i^{id} = x_i f_i$$ 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: $\underbrace{\gamma_i}_{\text{The Activity Coefficient}} \equiv \frac{\hat{f}_i}{\hat{f}_i^{id}} = \frac{\hat{f}_i}{x_i f_i}$

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

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

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

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

<u>Recall,</u>

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

$$\vdots$$

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

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

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

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

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