Thermodynamics II

Department of Chemical Engineering

Prof. Kim, Jong Hak

연세대학교
YONSEI UNIVERSITY

11.5 Fugacity & Fugacity Coefficient : Pure Species

μ_i => · provides fundamental criterion for phase equilibrium
· not easy to apply to solve problem

Limitation of Egn (11.29) (G = H – TS)
P –> 0 or y_i –> 0 => $\mu_i \longrightarrow -\infty$ (which is not true for ideal gas)

Egn (11.27) => valid only for pure species i in the ideal gas

For real gas, fugacity is introduced instead of P

$$G_i \equiv \Gamma_i(T) + RT \ln f_i$$

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

$$G_i - G_i^{ig} = RT \ln \frac{f_i}{P} = RT \ln \varphi_i$$

(φ_i : fugacity coefficient)

$$\therefore G_i^R = RT \ln \varphi_i \qquad (11.33)$$

For an ideal gas, $f_i^{ig} = P,\quad G_i^R = 0\ \&\quad \varphi_i = 1$

In chapter 6, $\left(\frac{G_i^R}{RT}\right)_{P=0} = J,\quad \frac{G_i^R}{RT} \equiv J + \int_0^P (z_i - 1)\frac{dP}{P}$

$$\therefore \lim_{P\to 0}\left(\frac{G_i^R}{RT}\right) = \lim_{P\to 0} \ln\varphi_i = J$$

set J as zero, $\lim_{P\to 0} \ln\varphi_i = \lim_{P\to 0} \ln\left(\frac{f_i}{P}\right) = 0$ which means that $\lim_{P\to 0} \varphi_i = \lim_{P\to 0} \frac{f_i}{P} = 1$

From egn (6.49) $\frac{G_i^R}{RT} = \int_0^P (z_i - 1)\frac{dP}{P},\ \ln\varphi_i = \int_0^P (z_i - 1)\frac{dP}{P}$

=> φ_i : obtained from PVT data or from compressibility factor $z_i - 1 = \frac{B_{ii}P}{RT}$

$$\ln\varphi_i = \int_0^P \frac{B_{ii}}{RT}dP = \frac{B_{ii}}{RT}\int_0^P dP = \frac{B_{ii}P}{RT}$$

$$\therefore \ln\varphi_i = \frac{B_{ii}P}{RT}$$

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Evaluation of fugacity coeff. from Cubic EOS

$$G_i^R = RT\ln\varphi_i \qquad (11.33)$$

$$\frac{G^R}{RT} = Z - 1 - \ln(Z - \beta) - qI \qquad (6.66)$$

$$\therefore \ln\varphi_i = Z - 1 - \ln(Z - \beta) - q_i I_i \qquad (11.37)$$

where $\beta_i = \frac{b_i P}{RT}$ (3.50) $\quad q_i = \frac{a_i(T)}{b_i RT}$ (3.51) $\quad I_i = \frac{1}{\delta_i - \varepsilon_i}\ln\left(\frac{Z_i t \delta_i \beta_i}{Z_i t \varepsilon_i \beta_i}\right)$ (6.65b)

$$Z_i = \frac{P}{\rho_i RT} \qquad (11.37)$$

If, $\delta = \varepsilon$

$$I_i = \frac{\rho_i b_i}{1 + \varepsilon_i \beta_i b_i} = \frac{\beta_i}{Z_i + \varepsilon_i \beta_i}$$

■ Vapor-Liquid equilibrium for pure species

Consider vapor liquid equilibrium

For species i as a saturated vapor, using eqn(11.3)

$$G_i^v = \Gamma_i(T) + RT \ln f_i^v \qquad (11.38a)$$

For species i as a saturated liquid

$$G_i^l = \Gamma_i(T) + RT \ln f_i^l \qquad (11.38b)$$

$$\therefore dG = G_i^v - G_i^l = RT \ln \frac{f_i^v}{f_i^l} = 0 \qquad \text{at equilibrium}$$

$$\therefore f_i^v = f_i^l = f_i^{sat} \qquad (\ f_i^{sat} : \text{either saturated liquid or vapor})$$

Alternative formulation

$$\varphi_i^{sat} = \frac{f_i^{sat}}{p_i^{sat}} \qquad \therefore \varphi_i^v = \varphi_i^l = \varphi_i^{sat}$$

=> Criterion of VLE for pure species G, μ, f, Φ

■ Fugacity of a pure liquid

- Fugacity of pure species i as a compressed Liq.
  => calculated from the product of easily evaluated ratio

$$f_i^l(P) = \frac{f_i^v(P_i^{sat})}{P_i^{sat}} \frac{f_i^l(P_i^{sat})}{f_i^v(P_i^{sat})} \frac{f_i^l(P)}{f_i^l(P_i^{sat})} P_i^{sat} \qquad \text{at const T}$$

A B C

Ratio A => vapor phase fugacity coeff., φ_i^{sat} at VLE

$$\ln \varphi_i^{sat} = \int_0^{P_i^{sat}} (z_i^v - 1) \frac{dP}{P}$$

Ratio B => 1 since $f_i^v = f_i^l$ at VLE

Ratio C => the effect of pressure on the fugacity of pure liquid ;

$$dG = VdP \qquad \text{(6.10) at const T}$$

$$G_i - G_i^{sat} = \int_{p_i^{sat}}^{p} V_i dP$$

from (11-31) $G_i = \Gamma_i(T) + RT\ln f_i$ $\therefore G_i - G_i^{sat} = RT\ln\frac{f_i}{f_i^{sat}}$

$$\therefore RT\ln\frac{f_i}{f^{sat}} = \int_{p_i^{sat}}^{p} V_i^l dP$$

Ratio C, $$\frac{f_i^l(P)}{f_i^{sat}(P_i^{sat})} = \exp\left(\frac{1}{RT}\int_{P_i^{sat}}^{P} V_i^l dP\right)$$

since $f_i^l(P) = A \bullet B \bullet C \bullet P_i^{sat}$ $f_i^l = \varphi_i^{sat} p_i^{sat} \exp\left(\frac{1}{RT}\int_{P_i^{sat}}^{P} V_i^l dP\right)$

Because V_i^l is a very weak function of P => assumed constant

$$\therefore f_i^l = \varphi_i^{sat} p_i^{sat} \exp\left(\frac{V_i^l(P - P_i^{sat})}{RT}\right)$$

→ Poynting factor

φ_i^{sat} : can be calculated from Z_i^V, $Z_i - 1 = \frac{B_{ii}P}{RT}$ $\therefore \varphi_i^{sat} = EXP\left(\frac{B_{ii}P_i^{sat}}{RT}\right)$

V_i^l : value for saturated liquid

P_i^{sat} : Antoine eqn.

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11.6 Fugacity & Fugacity Coefficient : Species in Solution

For species i in a mixture of real gas or in a solution of liquid

$$\mu_i \equiv \Gamma_i(T) + RT \ln \hat{f}_i \qquad (11.46)$$

$\hat{f}_i$: Fugacity of species i in solution (replacing partial pressure)

at equilibrium, the fugacity of each component is the same in all phases

$$\hat{f}_i^{\alpha} = \hat{f}_i^{\beta} = \ldots = \hat{f}_i^{\pi}$$

-> Multicomponent VLE, $\hat{f}_i^{v} = \hat{f}_i^{l}$

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Residual property $M^R = M - M^{ig}$

Multiply n and differentiate with respect to n_i at constant T, P, n_j

$$\left[\frac{\partial (nM)^R}{\partial n_i}\right]_{P,T,n_j} = \left[\frac{\partial (nM)}{\partial n_i}\right]_{P,T,n_j} - \left[\frac{\partial (nM^{ig})}{\partial n_i}\right]_{P,T,n_j}$$

$$\Rightarrow \overline{M}_i^R = \overline{M}_i - \overline{M}_i^{ig}$$

Written for G, $\overline{G}_i^R = \overline{G}_i - \overline{G}_i^{ig}$

From egn(11.29)

$$\mu_i^{ig} = \overline{G}_i^{ig} = \Gamma_i(T) + RT\ln(y_i P)$$

$$\mu_i = \Gamma_i(T) + RT\ln\hat{f}_i \qquad (11.46)$$

$$\mu_i - \mu_i^{ig} = RT\ln\frac{\hat{f}_i}{y_i P}, \quad \mu_i - \mu_i^{ig} = \overline{G}_i^R \quad (\text{since } \mu_i \equiv \overline{G}_i)$$

$$\therefore \overline{G}_i^R = RT\ln\hat{\varphi}_i \qquad (\hat{\varphi}_i = \frac{\hat{f}_i}{y_i P})$$

$\overline{\varphi}_i$: fugacity coeff. of species in solution

For ideal gas : $\overline{G}_i^R = 0$ & $\hat{\varphi}_i^{ig} = 1$ $\Rightarrow \hat{f}_i^{ig} = y_i P$

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The fundamental residual-property relation

$$d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i dn_i$$

Alternative form $d\left(\frac{nG}{RT}\right) \equiv \frac{1}{RT}d(nG) - \frac{nG}{RT^2}dT$ $\quad (G = H - TS$, $dG = VdP - SdT)$

$$d\left(\frac{nG}{RT}\right) = \frac{nV}{RT}dP - \frac{nH}{RT^2}dT + \sum_i \frac{\overline{G}_i}{RT}dn_i \qquad (11.54)$$

$\therefore \left(\frac{nG}{RT}\right) \rightarrow$ Function of all of i canonical variable (T, P, n_j)

=> Allow evaluation of all other thermodynamic properties

compare (6.37) $\quad d\left(\frac{G}{RT}\right) = \frac{V}{RT}dP - \frac{H}{RT_o}dT$

Special case of 1 mol of a constant-composition

=> Since we cannot evaluate absolute value of thermodynamic propertyes
=> use residual property

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For ideal gas

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

Subtracting this eqn from (11.54)

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

=> The fundamental residual-property relation

by introducing fugacity coeff. $(\overline{G}_i^R = RT\ln\hat{\varphi}_i)$

$$d\left(\frac{nG^{R}}{RT}\right) = \frac{nV^{R}}{RT}dP - \frac{nH^{R}}{RT^2}dT + \sum_i \ln\hat{\varphi}_i dn_i$$

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

=> Use eqn (6.46), (6.48), (6.49) for the calculation

$$\ln\hat{\varphi} = \left[\frac{\partial(nG^R/RT)}{\partial n_i}\right]_{P,T,n_j} \Rightarrow \ln\hat{\varphi}_i$$: partial property of G^R/RT

For n mol of constant – composition mixture

$$\frac{nG^R}{RT} = \int_0^P (nZ - n)\frac{dP}{P}$$

Differentiation with respect to n_j at constant T, P, n_j

$$\ln\hat{\varphi}_i = \int_0^P [\frac{\partial(nZ - n)}{\partial n_j}]_{P,T,n_j}\frac{dP}{P}$$

since, $\frac{\partial(nZ)}{\partial n_i} = \overline{Z_i}, \quad \frac{\partial n}{\partial n_i} = 1$

$$\therefore \ln\hat{\varphi}_i = \int_0^P (\overline{Z_i} - 1)\frac{dP}{P} \qquad (11.60)$$

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■ Fugacity coefficients from the virial equation of state

Evolution of value of $\hat{\varphi}_i$ from EOS

Simplest form of virial eqn $\ln\varphi = \int_0^P (z-1)\frac{dP}{P}$ (11.60)

$$z = 1 + \frac{BP}{RT}$$ (3.38) where B=f(T) composition second virial coeff.

$$B = \sum_i \sum_j y_i y_j B_{ij}$$ (11.61) where B_{ij} : characterize bimolecular interaction b/w i and j ($B_{ij} = B_{ji}$)

For binary mixture

$$B = y_1y_1B_{11} + y_1y_2B_{12} + y_2y_1B_{21} + y_2y_2B_{22}$$

$$= y^2{}_1B_{11} + 2y_1y_1B_{12} + y^2{}_2B_{22}$$ (11.62)

(B_{11}, B_{22}) : virial coeff. of pure species
(B_{12}) : cross coeff (mixture property)

For n mol of binary gas mixture eqn(3.38) becomes

$$nZ = n + \frac{nBP}{RT}$$

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Differentiation with respect to n_1

$$\bar{z}_1 \equiv \left[\frac{\partial(nz)}{\partial n_1}\right]_{P,T,n_2} = 1 + \frac{P}{RT}\left[\frac{\partial(nB)}{\partial n_1}\right]_{T,n_2}$$

From eqn (11.60)

$$\ln\hat{\varphi}_i = \frac{1}{RT}\int_0^P \left[\frac{\partial(nB)}{\partial n_1}\right]_{T,n_2} dP \Rightarrow \frac{P}{RT}\left[\frac{\partial(nB)}{\partial n_1}\right]_{T,n_2}$$

Second virial coeff. can be written

$$B = y_1(1 - y_2)B_{11} + 2y_1y_2B_{12} + y_2(1 - y_1)B_{22}$$

$$= y_1B_{11} - y_1y_2B_{11} + 2y_1y_2B_{12} + y_2B_{22} - y_1y_2B_{22}$$

$$= y_1B_{11} + y_2B_{22} + y_1y_2\delta_{12}, \quad \delta_{12} \equiv 2B_{12} - B_{11} - B_{22}$$

since $y_i = n_i / n$, multiplying by n $\quad nB = n_1B_{11} + n_2B_{22} + \frac{n_1n_2}{n}\delta_{12}$

by differentiation

$$\left[\frac{\partial(nB)}{\partial n_1}\right]_{T,n_2} = B_{11} + \left(\frac{1}{n} - \frac{n_1}{n_2}\right)n_2\delta_{12} = B_{11} + (1 - y_1)y_2\delta_{12} = B_{11} + y_2^2\delta_{12}$$

$$\therefore \ln\hat{\varphi}_1 = \frac{P}{RT}(B_{11} + y_2^2\delta_{12})$$

by similar method $\quad \ln\hat{\varphi}_2 = \frac{P}{RT}(B_{22} + y_1^2\delta_{12})$

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For multicomponent gas mixture, the general eqns.

$$\ln \hat{\varphi}_k = \frac{P}{RT}[B_{kk} + \frac{1}{2} \sum_I \sum_J y_i y_j (2\delta_{ik} - \delta_{ij})]$$

$$\delta_{ik} \equiv 2B_{ik} - B_{ii} - B_{kk} \qquad \delta_{ii} = 0 \qquad \delta_{ki} = \delta_{ik}$$

$$\delta_{ij} \equiv 2B_{ij} - B_{ii} - B_{jj} \qquad \delta_{kk} = 0$$

11.7 Generalized Correlations for the Fugacity Coefficient

To calculate Φ, use Generalized methods for compressibility factor Z

Correlation for $z = z^0 + \omega z^1$ (3.57)

where $\omega \equiv -1.0 - \log(P_r^{sat})_{Tr=0.7}$

Eqn (11.35) $\ln \varphi_i = \int_0^P (z-1)\frac{dP}{P}$ (const T) transformed into generalize form

using $P = P_c P_r$, $dP = P_c dP_r$ $\Rightarrow \therefore \ln \Phi_i = \int_0^{P_r} (z_i - 1)\frac{dP_r}{P_r}$ (11.65)

Using eqn (3.57)

$$\ln \varphi = \int_0^{Pr} (z^0 - 1)\frac{dP_r}{P_r} + \omega \int_0^{P_r} z^1 \frac{dP_r}{P_r}$$

$\Rightarrow \ln \varphi = \ln \varphi^0 + \omega \ln \varphi^1 \Rightarrow$ Three parameter generalized correlation for Φ

$\therefore \varphi = (\varphi^0)(\varphi^1)^\omega \Rightarrow$ use table E13 ~ E14

Using Pitzer correlations for the second virial coeff.

$$Z = 1 + \hat{B}\frac{P_r}{T_r} \quad (3.61) \qquad \hat{B} = B^0 + \omega B^1 \quad (3.63)$$

$$\therefore Z - 1 = \frac{P_r}{T_r}(B^0 + \omega B^1)$$ => Insert into eqn(11.15) and integrate

$$\ln\varphi = \frac{P_r}{T_r}(B^0 + \omega B^1) \Rightarrow \varphi = \exp[\frac{P_r}{T_r}(B^0 + \omega B^1)]$$

where $B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}$, $B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$

■ Generalized correlations for fugacity coefficient in gas mixture

$$\ln\hat{\varphi}_k = \frac{P}{RT}[B_{kk} + \frac{1}{2}\sum_i\sum_j(2\delta_{ik} - \delta_{ij})]$$

$T_{rij} = T / T_{Cij}$

More general form for coeff. $\hat{B}_{ij} = B^0 + \omega_{ij}B^1$ => B^0, B^1 -> function of T_{rij}

$$B_{ij} \equiv \frac{B_{ij}P_{Cij}}{RT_{Cij}} \quad (11.69)$$

=>use Prausnitz's combining rule for the calculation of $\omega_{ij}, T_{Cij}, R_{Cij}$

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$$\omega_{ij} = \frac{\omega_i + \omega_j}{2} \quad (11.70) \qquad T_{cij} = (T_{ci}T_{cj})^{1/2}(1 - k_{ij}) \quad (11.71)$$

$$P_{cij} = \frac{z_{cij}RT_{cij}}{V_{cij}} \quad (11.72) \qquad z_{cij} = \frac{z_{ci} + z_{cj}}{2} \quad (11.73)$$

Where k_{ij} = empirical interaction parameter

if i=j and for chemically similar species k_{ij}=0 -> all eqns reduce to value for pure species

Procedure to obtain $\hat{\varphi}_i$

① Find value of B_{ij} from (11.69)

② insert Bij into eqn(11.61) $B = \sum_i \sum_j y_i y_j B_{ij}$

③ using eqn(11.14) $\ln\hat{\varphi}_k = \frac{P}{RT}[B_{kk} + \frac{1}{2}\sum_i \sum_j y_i y_j (2\delta_{ik} - \delta_{ij})]$ =>find B

obtain φ value of $\ln\hat{\varphi}_i$

value of the pure-species virial coeff. B_{kk}, B_{ii} for eqn

$$\hat{B} = \frac{BP_C}{RT_C} = B^0 + \omega B^1$$

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10-8. The ideal solution model

Definition : ▪ all molecules are of the same size
▪ all forces b/w molecules (like and unlike) are equal

The chemical potential from ideal-gas mixture model

$$\mu_i^{ig} \equiv \overline{G}_i^{ig} = G_i^{ig}(T,P) + RT\ln y_i \qquad (11.24)$$

=> Only applicable for ideal gas

replace $G_i^{ig}(T,P) \Rightarrow G_i(T,P)$ (Gibbs energy of pure i in its real physical state of gas liquid, solid)

■ chemical potential of an ideal solution

$$\mu_i^{id} \equiv \overline{G}_i^{id} = G_i(T,P) + RT\ln x_i \qquad (11.75)$$

=> applicable gas, liquid, solid

From eqn(11.18) $\left(\frac{\partial \overline{G}_i^{id}}{\partial P}\right)_{T,x} = \overline{V}_i$

$$\overline{V}_i^{id} = \left(\frac{\partial \overline{G}_i^{id}}{\partial P}\right)_{T,x} = \left(\frac{\partial \overline{G}_i}{\partial P}\right)_T = V_i \qquad \therefore \overline{V}_i^{id} = V_i \qquad (11.76)$$

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From eqn(11.19) $\left(\frac{\partial \overline{G}_i}{\partial T}\right)_{P,x} = -\overline{S}_i$

$$\overline{S}_i^{id} = -\left(\frac{\partial \overline{G}_i^{id}}{\partial T}\right)_{P,x} = -\left(\frac{\partial G_i}{\partial T}\right)_p - R\ln x_i = S_i - R\ln x_i \qquad (11.77)$$

For $\overline{H}_i^{id}$, $\overline{H}_i^{id} = \overline{G}_i^{id} + TS_i^{id}$, using (11.75) (11.77)

$$\overline{H}_i^{id} = G_i + RT\ln x_i + TS_i - RT\ln x_i$$

$$= G_i + TS_i = H_i$$

by summability relation, $M = \sum_i x_i \overline{M}_i$

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

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

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

$$V^{id} = \sum_i x_i V_i \qquad , H^{id} = \sum_i x_i H_i$$

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The Lewis / Randall Rule

From eqn (11.46) $\mu_i \equiv \Gamma_i(T) + RT\ln\hat{f}_i$ (11.31) $G_i \equiv \Gamma_i(T) + RT\ln f_i$

(11.46−11.31) => $\mu_i^{id} = \overline{G}_i^{id} = G_i + RT\ln(\frac{\hat{f}_i^{id}}{f_i})$

For the special case of an ideal solution

$$\mu_i = G_i + RT\ln(\frac{\hat{f}_i}{f_i})$$

If compared with eqn(11.75) $\mu_i^{id} = G_i + RT\ln x_i$

$\hat{f}_i^{id} = x_i f_i$ (11.83) => Show the composition dependence of the fugacity in an ideal solution (Lewis/Randall rule)

Lewis/Randall Rule : fugacity of each species ∝ mole fraction
proportional constant = fugacity of pure species i

Alternative form of Lewis/Randall Rule : $\therefore \hat{\varphi}_i^{id} = \varphi_i$ (11-81)
(divide 11.83 with Px_i)

Fugacity coeff. of species i in an ideal solution
= fugacity coeff. of pure species i

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11.9. Excess Properties

Recall the relation b/w $G^R, \varphi_i, \hat{\varphi}_i$ and PVT data

$$\frac{G_i^R}{RT} = \int_0^P (z_i - 1)\frac{dP}{P} \qquad (6.49)$$

$$\ln \varphi_i = \int_0^P (z_i - 1)\frac{dP}{P} \qquad (11.35) \qquad \ln \hat{\varphi}_i = \int_0^P (\bar{z}_i - 1)\frac{dP}{P} \qquad (11.60)$$

-> obtain thermodynamic property using Residual properties

In the case of liquid, measure the departure from ideality not from ideal gas, but from ideal solution => excess property

Mathematical formulation

$$M^E \equiv M - M^{id}$$ (Difference b/w actual property and ideal solution)

For example, $G^E = G - G^{id}$, $H^E = H - H^{id}$, $S^E = S - S^{id}$, $G^E = H^E - TS^E$

considering $M^R = M - M^{ig}$ Pure species $M^E = 0$

$$M^E - M^R = -(M^{id} - M^{ig})$$

(ideal gas mixture => ideal solution of ideal gas) $G^{ig} = \sum_i x_i G_i^{ig} + RT \sum x_i \ln x_i$

Compare M^{ig} and M^{id}

$$H^{ig} = \sum y_i H_i^{ig} \qquad H^{id} = \sum x_i H_i$$

$$S^{ig} = \sum y_i S_i^{ig} - R \sum y_i \ln y_i \qquad S^{id} = \sum x_i S_i - R \sum x_i \ln x_i$$

$$G^{ig} = \sum y_i G_i^{ig} - RT \sum y_i \ln y_i \qquad G^{id} = \sum x_i G_i - RT \sum x_i \ln x_i$$

$$\therefore M^{id} - M^{ig} = \sum_i x_i M_i - \sum_i x_i M_i^{ig} = \sum_i x_i M_i^R$$

$$M^{id} - M^{ig} \Rightarrow M^R - M^E \qquad \therefore M^E = M^R - \sum_i x_i M_i^R$$

※ Excess Property : applied to only mixture
Residual property : applied to both pure species & mixture

For partial excess property : $\bar{M}_i^E = \bar{M}_i^E - \bar{M}_i^{id}$

※ Fundamental excess-property relation

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

=> Similar to fundamental residual-property relation

■ The Excess Gibbs Energy and the Activity Coefficient

From eqn (11.46) $\bar{\mu}_i = \Gamma_i(T) + RT\ln\hat{f}_i$ $\qquad \bar{G}_i = \Gamma_i(T) + RT\ln\hat{f}_i$

From Lewis/Randall rule, for an ideal solution

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

Difference $\qquad \bar{G}_i - \bar{G}_i^{id} = \bar{G}_i^E = RT\ln\frac{\hat{f}_i}{x_i f_i}$

activity coefficient $(\gamma_i) \equiv \frac{\hat{f}_i}{x_i f_i}$ (11.90) $\qquad \therefore \bar{G}_i^E \equiv RT\ln\gamma_i$ (11.91)

$\bar{G}_i^R = RT\ln\hat{\varphi}_i$, for ideal solution $\bar{G}_i^E = 0, \gamma_i = 1$

To device chemical potential of mixture

$\bar{G}_i - \bar{G}_i^{id} = RT\ln\gamma_i, \quad \bar{G}_i^{id} = G_i + RT\ln x_i$ (11.75) $\qquad \bar{G}_i = G_i + RT\ln\gamma_i x_i$ (11.92)

Comparison of three equations defining chemical potential

$\mu_i^{ig} = G_i^{ig} + RT\ln y_i$ (11.24)

$\mu_i^{id} = G_i + RT\ln x_i$ (11.75)

$\mu_i^{i} = G_i + RT\ln\gamma_i x_i$ (11.92)

1st Eqn : ideal gas mixture model
2nd Eqn : ideal solution model

Excess-property Relation

In fundamental excess property relation

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

$$= \frac{nV^E}{RT}dP - \frac{nH^E}{RT^2}dT + \sum_i \ln\gamma_i dn_i \quad (\overline{G}^E = RT\ln\gamma_i)$$

$$\therefore \frac{V^E}{RT} = \left[\frac{\partial(G^E/RT)}{\partial P}\right]_{T,x}$$ (11.90),

$$\frac{H^E}{RT} = -T\left[\frac{\partial(G^E/RT)}{\partial T}\right]_{P,x}$$ (11.91)

=> Effect of T, P on the G^E

$$\ln\gamma_i = \left[\frac{\partial(nG^E/RT)}{\partial n_i}\right]_{P,T,n_j}$$ (11.96)

=> $\ln\gamma_i$: partial properties of $\frac{G^R}{n_i}$

=> Similar to eqn for Residual property

※ Difference : in the case of relation to G^R -> we can use experimental PVT data ~ EOS to calculate Residual property

V^E, H^E, γ_i => Can be obtained by experiment

- γ_i : from VLE data
- V^E, H^E : from mixing experiment

$\ln\gamma_i$: partial property of $\frac{G^E}{RT}$, $\therefore \ln\gamma_i = \frac{\overline{G}^E}{RT}$

$$\therefore \frac{\overline{V}_i^E}{RT} = \left(\frac{\partial \ln\gamma_i}{\partial P}\right)_{T,x} \quad (11.97), \qquad -\frac{\overline{H}_i^E}{RT^2} = \left(\frac{\partial \ln\gamma_i}{\partial T}\right)_{P,x} \quad (11.98)$$

=> Effect of T, D on the γ_i

From the summability eqn $M = \sum x_i \overline{M}_i$

$$\frac{G^E}{RT} = \sum_i x_i \ln\gamma_i \quad (11.99)$$

From Gibbs/Duhem eqn (at const T, P) $\sum x_i d\overline{M}_i = 0$

$$\sum_i x_i d\ln\gamma_i = 0$$