Chemical Engineering Thermodynamics
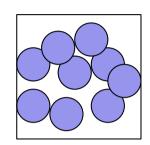
Solution Thermodynamics:

Theory and Derivation

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Single component system !

Example: Steam Line

We know that for a single component system, the most common thermodynamic variables are……

T and P

By now, we know how to determine T^{sat}, P^{sat},
H (liquid and ideal/non-ideal gas),
V (liquid and ideal/non-ideal gas) and ΔH^{vap}.
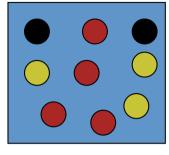
Ok….we also learned about mixture before!!!

$$H = \sum_i y_i H_i \qquad \text{etc.}$$

………we will see that this equation is only valid for ideal mixture!!!

Consider the following systems,

$$A \qquad\qquad B$$

Both systems at the sameT, P and n but with different compositions. Assuming an ideal mixture,

$$(H)_A = \sum y_{iA} H_i \qquad\qquad (H)_B = \sum y_{iB} H_i$$
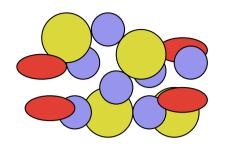
$$y_{iA} \neq y_{iB}$$

so

$$(H)_A \neq (H)_B$$

So we have new thermodynamic variables
for
multicomponent system…………

Composition!!

(x_1, x_2, x_3) or (y_1, y_2, y_3)

BUT typical chemical processes involve
a multicomponent system
whereby we can't assume ideal
mixture or ideal solution
behavior

Consider mixing 1000 cm^3 methanol and 1000 cm^3 water at 25°C.

1000 cm^3 MeOH + 1000 cm^3 H$_2$O

$\neq$ 2000 cm^3 solution !!!!!

In fact,

1000 cm^3 MeOH + 1000 cm^3 H$_2$O

= 1970 cm^3 solution

Discuss with a person next to you why
the volume of the solution is less than 2000 cm^3?

Let's determine the density of the solution

Assume ideal solution

$$\rho = \frac{1}{V} = \frac{1}{\sum x_i V_i}$$

From above eqn, the calculated solution molar density is 0.0396 mol/cm³

The actual molar density is 0.0410 mol/cm³ that could be calculated from

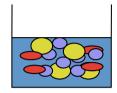$$\rho = \frac{1}{V} = \frac{1}{\sum x_i \overline{V}_i}$$

→ Partial Properties

We just introduced a new thermodynamic property for a multicomponent system……

Partial properties!!

11.1 Fundamental Property Relation
(for variable composition mixture)

Definition of Chemical Potential

Consider the following system,

      - Open system and multicomponent
      - Single phase at T and P
      - Variable composition (n_1, n_2, n_3 etc)

So Gibbs energy (G) could be written as a function of T, P, n_1, n_2, n_3 etc.

$$(nG) = g\left(P, T, n_1, n_2 ... n_i\right)$$

Apply partial differentiation and FPR (Chapter 6),

$$d(nG) = \left[\frac{\partial(nG)}{\partial P}\right]_{T,n} dP + \left[\frac{\partial(nG)}{\partial T}\right]_{P,n} dT + \sum_i \left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j} dn_i$$

$$d(nG) = nVdP - nSdT + \sum_i \left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j} dn_i$$

Let's define $\quad \mu_i = \left[\dfrac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j} \quad \equiv$ Chemical potential for species i in the mixture

This equation forms the basis for the definition of partial properties.

So,

$$d(nG) = nVdP - nSdT + \sum_i \mu_i dn_i \qquad (11.2)$$

How do we determine the phase of
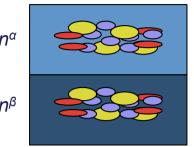a multicomponent system?

If it is two phases, how do we determine
the composition of each phase?

Before answering these, we need to establish
the concept of phase equilibria for
multicomponent system.

n^α

n^β

Consider the following system,

     - Closed system and multicomponent
     - Two phases in equilibrium.
     - Mass transfer occurs if the equilibrium is disturbed.

Each phase (α and β) is actually an open system, so eqn 11.2 becomes,

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

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

Add the two equations for a VL system (α is replaced by v and β is replaced by l).

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

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

For system in equilibrium,

$$(nV)dP - (nS)dT = (nV)dP - (nS)dT + \sum_i \mu_i^v dn_i^v + \sum_i \mu_i^l dn_i^l$$

So, $\qquad \sum_i \mu_i^v dn_i^v + \sum_i \mu_i^l dn_i^l = 0 \qquad$ also $\quad dn_i^l = -dn_i^v$

$$\sum_i \mu_i^v dn_i^v - \sum_i \mu_i^l dn_i^v = \sum_i (\mu_i^v - \mu_i^l) dn_i^v = 0$$

$$\mu_i^v - \mu_i^l = 0 \qquad\qquad \mu_i^v = \mu_i^l$$

If apply to system with π phases (i.e. more than two phases)
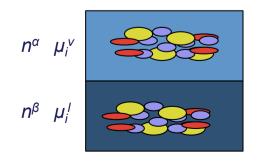
$$\mu_i^v = \mu_i^l = \mu_i^\alpha = \mu_i^\beta = \ldots\ldots\ldots = \mu_i^\pi \qquad (11.6)$$

This is the criteria for phase equilibrium for multicomponent system.

Criteria for Phase Equilibrium for Multicomponent System

Multiple phase at the same
T and P are in equilibrium
when the chemical potential (μ_i) of
each species is the same in
all phases

$n^\alpha \quad \mu_i^v$

$n^\beta \quad \mu_i^l$

$$\mu_i^v = \mu_i^l$$

11.3 PARTIAL PROPERTIES

Based on the definition of μ_i , let's define a partial molar property as follows,

$$\bar{M}_i = \left[\frac{\partial (nM)}{\partial n_i} \right]_{P,T,n_j} \qquad (11.7)$$

Where $M \equiv V, U, H, S, G$ etc.

This is a partial property of individual species as they exist in a solution or mixture.

This property is different from a pure species property primarily due to molecular interaction of different species in the solution or mixture

Hence, the chemical potential of species *i* (μ_i) is known also as partial property of Gibbs energy for species *i*.

$$\mu_i = \left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j} = \overline{G}_i \qquad (11.8)$$

Example 11.1

This example explains the physical and mathematical interpretation of partial molar volume equation.

Let's familiar with symbols in solution thermodynamics,

Symbol	Type of property	Example
M_i	Pure-species properties	$U_i\ H_i\ S_i\ G_i$
$\overline{M}_i$	Partial properties	$\overline{U}_i\ \overline{H}_i\ \overline{S}_i\ \overline{G}_i$
M	Solution or mixture properties	$U\ H\ S\ G$

In general, for a homogenous mixture,

$$nM = M(T, P, n_1, n_2, n_3.....)$$

$$d(nM) = \left[\frac{\partial(nM)}{\partial P}\right]_{T,n} dP + \left[\frac{\partial(nM)}{\partial T}\right]_{P,n} dT + \sum_i \left[\frac{\partial(nM)}{\partial n_i}\right]_{P,T,n_j} dn_i$$

Could also be written as,

$$d(nM) = \left[\frac{n\partial M}{\partial P}\right]_{T,x} dP + \left[\frac{n\partial M}{\partial T}\right]_{P,x} dT + \sum_i \bar{M}_i dn_i \qquad (11.9)$$

i.e. constant composition

where $d(nM) = ndM + Mdn$

Also, $x_i = \dfrac{n_i}{n}$ $n_i = x_i n$ so, $dn_i = x_i dn + ndx_i$

Substitute into (11.9)

$$ndM + Mdn = \left[\frac{n\partial M}{\partial P}\right]_{T,x} dP + \left[\frac{n\partial M}{\partial T}\right]_{P,x} dT + \sum_i \bar{M}_i (x_i dn + ndx_i n_i)$$

Rearrange,

$$\left[dM - \left(\frac{\partial M}{\partial P} \right)_{T,x} dP - \left(\frac{\partial M}{\partial T} \right)_{P,x} dT - \sum_i \bar{M}_i dx_i \right] n + \left[M - \sum_i \bar{M}_i x_i \right] dn = 0$$

This is equal to 0 if both terms in the brackets are zeros, so for the 1st bracket,

$$dM = \left(\frac{\partial M}{\partial P} \right)_{T,x} dP + \left(\frac{\partial M}{\partial T} \right)_{P,x} dT + \sum_i \bar{M}_i dx_i \qquad (11.10)$$

And the 2nd bracket,

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

note: (11.10) similar to (11.9) for $n = 1$

$$M = \sum_i x_i \bar{M}_i \qquad (11.11)$$

or

$$nM = \sum_i n_i \bar{M}_i \qquad (11.12)$$

Eqns 11.11 and 11.12 show that the calculation of mixture properties of constituent species from partial properties is by a simple summability relation!

Eqn 11.11 can be further expanded to give,

$$M = \sum_i x_i \bar{M}_i \qquad \rightarrow \qquad dM = \sum_i x_i d\bar{M}_i + \sum_i \bar{M}_i dx_i$$

Substitute into 11.10, ,

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

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

$$\left(\frac{\partial M}{\partial P}\right)_{T,x} dP + \left(\frac{\partial M}{\partial T}\right)_{P,x} dT - \sum_i x_i d\bar{M}_i = 0 \qquad (11.13)$$

Eqn 11.13 is a Gibbs/Duhem Eqn that must be satisfied for any a changes in P,T and $\bar{M}_i$ in a homogeneous phase.

This eqn shows that the partial properties of species making up a solution are dependent on one another.

Partial Properties in Binary Solutions
(two-component system: *i =1, 2)*

Here we will derive an eqn for partial property of a species in binary mixtures as in term of solution property (express a function of composition at constant T and P).

From eqn 11.11

$$M = x_1\bar{M}_1 + x_2\bar{M}_2$$

$$dM = x_1 d\bar{M}_1 + \bar{M}_1 dx_1 + x_2 d\bar{M}_2 + \bar{M}_2 dx_2$$

$$dM = x_1 d\bar{M}_1 + \bar{M}_1 dx_1 + x_2 d\bar{M}_2 - \bar{M}_2 dx_1$$

From eqn 11.13 at constant T and P,

$$\left(\frac{\partial M}{\partial P}\right)_{T,x} dP + \left(\frac{\partial M}{\partial T}\right)_{P,x} dT - \sum_i x_i d\bar{M}_i = 0 \qquad (11.13)$$

$$x_1 d\bar{M}_1 + x_2 d\bar{M}_2 = 0$$

So,
$$dM = \bar{M}_1 dx_1 - \bar{M}_2 dx_1 \qquad \frac{dM}{dx_1} = \bar{M}_1 - \bar{M}_2$$

Hence, we could show that,

$$\bar{M}_1 = M + x_2 \frac{dM}{dx_1} \quad (11.15) \qquad \bar{M}_2 = M - x_1 \frac{dM}{dx_1} \qquad (11.16)$$

Example 11.4 shows the application of eqn 11.15 and 11.16

Parallel Relation Between
Eqn for Constant Composition and
Partial Properties

Eqn for Constant Composition   **Eqn for Partial Properties**

$$H = U + PV$$

Similarly we can write $\rightarrow$

$$\overline{H}_i = \overline{U}_i + P\overline{V}_i$$

$$dG = VdP - SdT$$

$\rightarrow$

$$d\overline{G}_i = \overline{V}_i dP - \overline{S}_i dT$$

Ideal-Gas Mixture

Molar Volume of Ideal-Gas Mixture

Consider,

System A contain species 1 at T,P

System B contain species 2 at T,P

System C contain mixture 1 and 2 at T,P

$$\left(V^{ig}\right)_A = \frac{RT}{P} = V_1^{ig}$$

$$\left(V^{ig}\right)_B = \frac{RT}{P} = V_2^{ig}$$

$$\left(V^{ig}\right)_C = \frac{RT}{P} = V^{ig}$$

Partial Molar Volume of Species i in an Ideal-Gas Mixture

Application of partial properties to

molar volume,

$$\overline{V}_i^{ig} = \left[\frac{\partial(nV^{ig})}{\partial n_i}\right]_{T,P,n_j} = \left[\frac{\partial(n\frac{RT}{P})}{\partial n_i}\right]_{T,P,n_j} = \frac{RT}{P}\left(\frac{\partial n}{\partial n_i}\right)_{n_j} = \frac{RT}{P}$$

The last equality infers an independent of composition!!!

So for Ideal-Gas Mixture

$$V^{ig}(T,P) = V_i^{ig}(T,P) = \overline{V}_i^{ig}(T,P)$$

Partial Pressure of Species *i* in an Ideal-Gas Mixture

The pressure that a species *i* would exert if it alone occupied the molar volume of the mixture

$$P_i V^{T,ig} = n_i RT$$

Divide by ideal gas for mixture, $PV^{T,ig} = n_T RT$,

So,

$$\frac{P_i}{P} = \frac{n_i}{n_T} = y_i$$

$$p_i = y_i P = \frac{y_i RT}{V^{ig}}$$

Partial Molar Properties of Species *i* in an Ideal-Gas Mixture

Gibb's Theorem,

A partial properties (other than partial molar volume) of a constituent species in an ideal-gas mixture is equal to the corresponding molar property of the species as a pure ideal gas at the mixture temperature but at a pressure equal to its partial pressure in the mixture.

$$\overline{M}_i^{ig}(T,P) = M_i^{ig}(T,p_i)$$

Apply this theory to Enthalpy, Internal Energy and Heat Capacity

$$\overline{H}_i^{ig}(T,P) = H_i^{ig}(T,p_i) = H_i^{ig}(T,P)$$

$$\overline{H}_i^{ig} = H_i^{ig}$$

Since H^{ig} is independent of pressure

Similarly,

$$\overline{U}_i^{ig} = U_i^{ig} \qquad \overline{C}_{pi}^{ig} = C_{p,i}^{ig} \qquad \overline{C}_{vi}^{ig} = C_{v,i}^{ig}$$

U^{ig}, C_p^{ig} and C_v^{ig} are also independent of pressure

So for ideal-gas mixture,

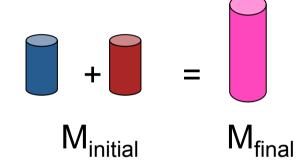$$H^{ig} = \sum y_i H_i^{ig} \qquad U^{ig} = \sum y_i U_i^{ig} \qquad C_P^{ig} = \sum y_i C_{P,i}^{ig} \quad \text{etc}$$

Property Change of Mixing
for ideal gas mixture (ΔH^{ig} and ΔU^{ig})

$$\Delta M_{mix}^{ig} = M_{final} - M_{initial} = M^{ig} - \sum_i y_i M_i^{ig}$$

$$but \quad M^{ig} = \sum_i y_i M_i^{ig}$$

$$so$$

$$\Delta M_{mix}^{ig} = 0 \quad for \; M = H, U$$

$M_{initial}$ + = M_{final}

Note: Both initial and final conditions (T,P) are the same.

For example,

Enthalpy change of mixing for ideal gas mixture,

$$\Delta H_{mix}^{ig} = 0$$

Property Change of Mixing
for ideal gas mixture (ΔV^{ig})

$$\Delta V_{mix}^{ig} = V_{final} - V_{initial} = V^{ig} - \sum y_i V_i^{ig} = V^{ig} - V_i^{ig} \sum_i y_i$$

$note:$ $V^{ig} = V_i^{ig} = V_j^{ig}$

so

$$\Delta V_{mix}^{ig} = 0$$

Note: Both initial and final conditions (T,P) are the same.

Partial Molar Entropy of Species *i* in an Ideal-Gas Mixture

S^{ig} is dependent of pressure,

$$dS_i^{ig} = C_{Pi}^{ig} \frac{dT}{T} - R\frac{dP}{P} \qquad (6.24)$$

For isothermal mixing,

$$dS_i^{ig} = -R\frac{dP}{P}$$

Integrate from p_i to P,

$$S_i^{ig}(T,P) - S_i^{ig}(T,p_i) = -R\ln\frac{P}{p_i} = -R\ln\frac{1}{y_i}$$

$$S_i^{ig}(T,p_i) = S_i^{ig}(T,P) - R\ln y_i$$

From Gibbs Theorem,

$$\overline{S}_i^{ig}(T,P) = S_i^{ig}(T,p_i) = S_i^{ig}(T,P) - R\ln y_i$$

Property Change of Mixing
for ideal gas mixture ΔS^{ig}

Hence, for ideal-gas mixture,

$$S^{ig}(T,P) = \sum y_i S_i^{ig}(T,p_i) = \sum_k y_i \left(S_i^{ig}(T,P) - \mathrm{R}\ln y_i \right)$$

$$S^{ig}(T,P) = \sum y_i S_i^{ig} - \mathrm{R}\sum y_i \ln y_i \qquad (11.26)$$

So *entropy* change of mixing for ideal gas mixture,

$$\Delta S_{mix}^{ig} = S^{ig}(T,P) - \sum y_i S_i^{ig}$$

$$= -R\sum y_i \ln y_i$$

$$= R\sum y_i \ln \frac{1}{y_i}$$

Partial Molar Gibbs Energy of Species *i* in an Ideal-Gas Mixture

By parallel relation,

$$G^{ig} = H^{ig} - TS^{ig}$$

$$\overline{G}_i^{ig} = \overline{H}_i^{ig} - T\overline{S}_i^{ig}$$

So,

$$\overline{G}_i^{ig} = \overline{H}_i^{ig} - T(S_i^{ig} - R\ln y_i) = H_i^{ig} - T(S_i^{ig} - R\ln y_i) = G_i^{ig} + RT\ln y_i$$

So for ideal-gas mixture,

$$G^{ig} = \sum y_i \overline{G}_i^{ig}$$

$$G^{ig} = \sum y_i G_i^{ig} + RT\sum y_i \ln y_i$$

Property Change of Mixing
for ideal gas mixture (ΔG^{ig})

$$\Delta G_{mix}^{ig} = G^{ig} - \sum_i y_i G_i^{ig}$$
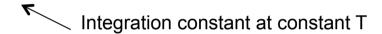
$$= RT \sum_i y_i \ln y_i$$

In terms of variables (T,P) for Gibbs Energy ,

$$dG_i^{ig} = V_i^{ig} dP - S_i^{ig} d\cancel{T} = \frac{RT}{P} dP = RTd \ln P \qquad \text{(for constant T)}$$

Integrate

$$G_i^{ig} = \Gamma_i(T) + RT \ln P \qquad (11.28)$$

Integration constant at constant T

so

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

$$\overline{G}_i^{ig} = \Gamma_i(T) + RT \ln y_i P \qquad (11.29)$$

Hence for ideal-gas mixture,

$$G^{ig} = \sum y_i \overline{G}_i^{ig} = \sum y_i \Gamma_i(T) + RT \sum y_i \ln(y_i P) \qquad (11.30)$$

Summary of Property Change of Mixing for Ideal-Gas Mixture

$$\Delta M_{mix}^{ig} = M_{final} - M_{initial} = M^{ig} - \sum y_i M_i^{ig}$$

$$\Delta H_{mix}^{ig} = 0$$

$$\Delta U_{mix}^{ig} = 0$$

$$\Delta V_{mix}^{ig} = 0$$

$$\Delta S_{mix}^{ig} = R \sum y_i \ln \frac{1}{y_i}$$

$$\Delta G_{mix}^{ig} = RT \sum y_i \ln y_i$$

Fugacity and Fugacity Coefficient:

Pure Species

Fugacity of Pure Species

The concept of fugacity is introduced when we want to apply an eqn similar to 11.28 (ideal gas) to a real fluid (liquid or gas).

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

This is done by replacing *P* with a property specific to a particular species called fugacity.

$$G_i = \Gamma_i(T) + RT \ln f_i \qquad\qquad (11.31)$$

$f_i \equiv$ fugacity of pure species i (with unit of pressure)

i.e. f_i is a pseudopressure.

note : for a gas under an ideal gas condition, $f_i = P$

Residual Gibb Energy and Fugacity Coefficient of Pure Species

Eqn $(11.31) -$ Eqn (11.28),

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

$$G_i^R = RT \ln \frac{f_i}{P} \qquad\qquad (11.33)$$

let's us defined ϕ_i as a fugacity coefficient for species i as follows,

$$\phi_i = \frac{f_i}{P} \qquad \text{, a dimensionless quantity}$$

So for ideal gas, ϕ_i is 1

Determination of Fugacity Coefficient ϕ_i

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

or

$$\ln \phi_i = \frac{G_i^R}{RT}$$

$$\frac{G^R}{RT} = \int \frac{(Z-1)}{P} dP$$

Combine with Eqn 6.49 , $\dfrac{G_i^R}{RT} = \displaystyle\int_0^P (Z_i - 1) \dfrac{dP}{P}$

$$\ln \phi_i = \int_0^P (Z_i - 1) \frac{dP}{P} \qquad (11.35)$$

Fugacity Coefficient of
Pure Species from Virial Eqn

The 2-term Virial Equation for Z_i :
$$Z_i - 1 = \frac{B\,P}{RT}$$

$$\ln\phi_i = \int_0^P (Z_i - 1)\frac{dP}{P}$$

Substitute,

$$\ln\phi_i = \int_0^P \left(\frac{B\,P}{RT}\right)\frac{dP}{P} = \frac{B}{RT}\int_0^P dP = \frac{B\,P}{RT}$$

$$\phi_i = exp\left[\frac{B\,P}{RT}\right]$$

$Note : B = B_{ii}$

Alternatively for the 2-term Virial Equation for Z_i :

$$Z_i - 1 = \frac{B\,P}{RT} = \frac{BP_c}{RT_c}\frac{P_r}{T_r} = \hat{B}\frac{P_r}{T_r}\quad \frac{P_r}{T_r} = (B^0 + \omega B^1)\frac{P_r}{T_r}$$

$$\ln\phi_i = \int_0^P (Z_i - 1)\frac{dP}{P} = \int_0^{P_r} (Z_i - 1)\frac{dP_r}{P_r}$$

$$\ln\phi_i = \int_0^{P_r} \frac{(B^0 + \omega B^1)}{T_r}dP_r = (B^0 + \omega B^1)\frac{P_r}{T_r}$$

$$\phi_i = \exp\left[\frac{P_r}{T_r}(B^0 + \omega B^1)\right]$$

for B^0 and B^1, see eqn 3.65 and 3.66

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \quad \text{and} \quad B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

Fugacity Coefficient of Pure Species from Generic Cubic EOS

Combined eqn 11.33 with 6.66b (and apply for species i),

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

$$\frac{G_i^R}{RT} = Z_i - 1 - \ln(Z_i - \beta_i) - q_i I_i \qquad (6.66b)$$

We get,

$$\ln \phi_i = Z_i - 1 - \ln(Z_i - \beta_i) - q_i I_i \qquad (11.37)$$

Fugacity Coefficient of
Pure Species from Generalized Correlation

Lee/Kesler correlation,

$$\ln \phi_i = \int_0^P (Z_i - 1)\frac{dP}{P}$$

for $P = P_c P_r$ $\quad$ $dP = P_c dP_r$

$$\ln \phi_i = \int_0^{P_r} (Z - 1)\frac{P_c dP_r}{P_c P_r} = \int_0^{P_r} (Z - 1)\frac{dP_r}{P_r} = \int_0^{P_r} (Z^0 + \omega Z^1 - 1)\frac{dP_r}{P_r}$$

$$\ln \phi_i = \int_0^{P_r} (Z^0 - 1)\frac{dP_r}{P_r} + \omega \int_0^{P_r} Z^1 \frac{dP_r}{P_r}$$

$$\ln \phi_i = \ln \phi_i^0 + \omega \ln \phi_i^1$$

$$\ln \phi_i = \ln \phi_i^0 + \omega \ln \phi_i^1$$

$$\phi_i = \phi_i^0 (\phi_i^1)^\omega$$

Values for ϕ_i^0 and ϕ_i^1 are found from Table E13-E16

Vapor/Liquid Equilibrium for Pure Species

From chapter 6 we know that criteria for VLE for

pure species is $G^v = G^l$ or $G^v - G^l = 0$

Let's apply eqn 11.31 for each phase.

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

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

By difference,

$$G_i^v - G_i^l = RT \ln \frac{f_i^v}{f_i^l} = 0$$

$$\ln \frac{f_i^v}{f_i^l} = 0 \qquad \frac{f_i^v}{f_i^l} = 1 \qquad f_i^v = f_i^l = f_i^{sat}$$

Also

$$\phi_i^{sat} = \frac{f_i^{sat}}{P_i^{sat}} \qquad\qquad \phi_i^v = \phi_i^l = \phi_i^{sat}$$

Another phase equilibrium criteria for pure species!

Fugacity of Pure Liquid

Only for the fugacity of pure liquid at P and T. Easily calculated
by the Poynting factor equation as derived below,

$$f_i^l(P) = \frac{f_i^l(P_i^{sat})}{f_i^v(P_i^{sat})} \frac{f_i^v(P_i^{sat})}{P_i^{sat}} \frac{f_i^l(P)}{f_i^l(P_i^{sat})} P_i^{sat} = (1)(\phi_i^{sat}) \frac{f_i^l(P)}{f_i^l(P_i^{sat})} P_i^{sat} = \phi_i^{sat} P_i^{sat} \frac{f_i^l(P)}{f_i^l(P_i^{sat})}$$ (A)

Also

$$G_i^l - G_i^{l,sat} = RT \ln f_i^l - RT \ln f_i^{l,sat} = RT \ln \frac{f_i^l}{f_i^{l,sat}}$$ (B)

also at constant T,

$$dG_i = V_i dP$$ and we integrate from sat liquid to compressed liquid,

$$G_i^l - G_i^{l,sat} = \int_{P_i^{sat}}^{P} V_i^l dP$$ (C)

Combine (B) and (C),

$$RT \ln \frac{f_i^l}{f_i^{l,sat}} = \int_{P_i^{sat}}^{P} V_i^l \, dP \qquad \text{rearrange,} \qquad \frac{f_i^l}{f_i^{l,sat}} = \exp \frac{1}{RT} \int_{P_i^{sat}}^{P} V_i^l \, dP$$

subs into (A),

$$f_i^l = \phi_i^{sat} P_i^{sat} \exp \frac{1}{RT} \int_{P_i^{sat}}^{P} V_i^l \, dP = \phi_i^{sat} P_i^{sat} \exp \frac{V_i^l}{RT} \int_{P_i^{sat}}^{P} dP$$

note : V_i^l is approximately constant and is evaluated at sat liquid, therefore:

$$f_i^l = \phi_i^{sat} P_i^{sat} \exp \frac{V_i^l (P - P_i^{sat})}{RT} \qquad (11.44) \quad \text{fugacity of pure liquid } i$$

The exponential is known as a Poynting factor

Fugacity
for Species *i* in Solution $(\hat{f}_i)$

Revisit, for an ideal gas mixture,

$$\mu_i^{ig} = \overline{G_i}^{ig} = \Gamma_i(T) + RT \ln(y_i P) \qquad (11.29)$$

Parallel to the definition of fugacity for pure species,
the introduction of fugacity for solution is done by
replacing $y_i P$ in Eqn 11.29 with fugacity for species in solution $(\hat{f}_i)$

So, for a real mixture or solution,

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

$\hat{f}_i \equiv$ fugacity of species i in mixture or solution.

at VLE

$$\mu_i^l = \mu_i^v$$

$$\Gamma_i(T) + RT \ln \hat{f}_i^l = \Gamma_i(T) + RT \ln \hat{f}_i^v$$

So

$$\hat{f}_i^l = \hat{f}_i^v$$ Criteria of VLE for multicomponent system !!

Also, $\quad nG^R = nG - nG^{ig}$

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

$$\bar{G}_i^R = \bar{G}_i - \bar{G}_i^{ig}$$

$$= \mu_i - \mu_i^{ig}$$

$$= RT\ln\hat{f}_i - RT\ln y_i P$$

$$= RT\ln\frac{\hat{f}_i}{y_i P}$$

$$= RT\ln\hat{\phi}_i \qquad\qquad (11.51)$$

where
$$\hat{\phi}_i = \frac{\hat{f}_i}{y_i P}$$

$$\hat{\phi}_i = \frac{\hat{f}_i}{y_i P}$$ fugacity coefficient* of species i in solution or mixture.

$$\hat{f}_i = \hat{\phi}_i y_i P$$

*mostly applied to gas mixture

Calculation of Fugacity Coefficient of Species i in Solution $(\hat{\phi}_i)$

Application of Fundamental
Residual-Property Relation........

$$d\left(\frac{nG}{RT}\right) = \frac{1}{RT}d(nG) - \frac{nG}{RT^2}dT$$

$$d\left(\frac{nG}{RT}\right) = \frac{1}{RT}\left((nV)dP - (nS)dT + \sum \bar{G}_i dn_i\right) - \frac{n(H-TS)}{RT^2}dT$$

$$d\left(\frac{nG}{RT}\right) = \frac{nVdP}{RT} - \frac{nS}{RT}dT + \sum \frac{\bar{G}_i dn_i}{RT} - \frac{nH}{RT^2}dT + \frac{nS}{RT}dT$$

$$d\left(\frac{nG}{RT}\right) = \frac{nVdP}{RT} - \frac{nH}{RT^2}dT + \sum \frac{\bar{G}_i}{RT}dn_i \qquad (11.54)$$

for ideal gas,

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

(11.54 - 11.54ig)

$$d\left(\frac{nG^R}{RT}\right) = \frac{nV^R dP}{RT} - \frac{nH^R}{RT^2}dT + \sum \frac{\bar{G}_i^R}{RT}dn_i \quad (11.55)$$

substitute (11.51),

$$d\left(\frac{nG^R}{RT}\right) = \frac{nV^R}{RT}dP - \frac{nH^R}{RT^2}dT + \sum \ln \hat{\phi}_i dn_i \quad (11.56)$$

So,

$$\ln \hat{\phi}_i = \left[\frac{\partial(nG^R/RT)}{\partial n_i}\right]_{P,T,n_j} \quad (11.59)$$

Note:

$\ln \hat{\phi}_i$ is a partial property of G^R/RT

$$\frac{G^R}{RT} = \int \frac{(Z-1)}{P} dP$$

Combine with eqn 6.49 and 11.59 becomes,

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

$$= \int_0^P \left[\frac{\partial nZ}{\partial n_i} - \frac{\partial n}{\partial n_i} \right]_{P,T,n_j} \frac{dP}{P}$$

$$= \int_0^P \left(\left[\frac{\partial nZ}{\partial n_i} \right]_{P,T,n_j} - \overset{1}{\cancel{\left[\frac{\partial n}{\partial n_i} \right]_{P,T,n_j}}} \right) \frac{dP}{P}$$

$$\ln \hat{\phi}_i = \int_0^P \left(\bar{Z}_i - 1 \right) \frac{dP}{P} \qquad (11.60)$$

Using Two-term Virial EOS

$$Z = 1 + \frac{BP}{RT} \qquad\qquad nZ = n + \frac{nBP}{RT}$$

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

$$\longleftrightarrow$$

Substitute into eqn 11.60

$$\ln \hat{\phi}_1 = \int_0^P \left(1 + \frac{P}{RT}\left[\frac{\partial(nB)}{\partial n_1} \right]_{T,n_2} - 1 \right) \frac{dP}{P} = \frac{1}{RT} \int_0^P \left(\left[\frac{\partial(nB)}{\partial n_1} \right]_{T,n_2} \right) dP$$

$$\ln \hat{\phi}_1 = \frac{1}{RT}\left[\frac{\partial(nB)}{\partial n_1} \right]_{T,n_2} P = \frac{P}{RT}\left[\frac{\partial(nB)}{\partial n_1} \right]_{T,n_2}$$

How to evaluate?

For mixture,

$$B = \sum_i \sum_j y_i y_j B_{ij}$$

Consider a binary system (species 1 and 2),

$$B = y_1 y_1 B_{11} + y_1 y_2 B_{12} + y_2 y_1 B_{21} + y_2 y_2 B_{22}$$

$$B = y_1^2 B_{11} + 2 y_1 y_2 B_{12} + y_2^2 B_{22}$$

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

Rearrange further,

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

where $\quad \delta_{12} = 2 B_{12} - B_{11} - B_{22}$

Multiply by n (note: $y_i = n_i / n$),

$$nB = n_1 B_{11} + n_2 B_{22} + n_1 \frac{n_2}{n} \delta_{12}$$

$$nB = n_1B_{11} + n_2B_{22} + n_1\frac{n_2}{n}\delta_{12}$$

$$\left[\frac{\partial(nB)}{\partial n_1}\right]_{T,n_2} = B_{11} + 0 + n_2\delta_{12}\left(\frac{\partial\frac{n_1}{n}}{\partial n_1}\right) \qquad \text{note: } \partial\frac{u}{v} = \frac{v\partial u - u\partial v}{v^2}$$

$$= B_{11} + n_2\left(\frac{\frac{n\partial n_1 - n_1 dn}{n^2}}{\partial n_1}\right)\delta_{12} = B_{11} + n_2\left(\frac{1}{n} - \frac{n_1\partial n}{n^2\partial n_1}\right)\delta_{12}$$

$$= B_{11} + \left(\frac{n_2}{n} - \frac{n_2 n_1\partial n}{n^2\partial n_1}\right)\delta_{12} = B_{11} + \left(y_2 - y_2 y_1\frac{\partial n}{\partial n_1}\right)\delta_{12}$$

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

note,

$$B_{11} = B_1 \quad B_{22} = B_2$$

$$B_{12} = \frac{RT_{c12}}{P_{c12}}\left(B^0 + \omega_{12}B^1\right)$$

Interaction parameter
(=0 if no data provided)

$$\omega_{12} = \frac{\omega_1 + \omega_2}{2} \qquad T_{c12} = (T_{c1}T_{c2})^{1/2}(1 - k_{12})$$

$$P_{c12} = \frac{Z_{c12}RT_{c12}}{V_{c12}} \qquad V_{c12} = \left(\frac{V_{c1}^{1/3} + V_{c2}^{1/3}}{2}\right)^3 \qquad Z_{c12} = \frac{Z_{c1} + Z_{c2}}{2}$$

So,

$$\ln \hat{\phi}_1 = \frac{P}{RT} \left[\frac{\partial(nB)}{\partial n_1} \right]_{T,n_2} = \frac{P}{RT} \left(B_{11} + y_2^2 \delta_{12} \right)$$

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

similarly

$$\ln \hat{\phi}_2 = \frac{P}{RT} \left(B_{22} + y_1^2 \delta_{12} \right)$$

In general, for multicomponent gas mixture,

$$\ln \hat{\phi}_k = \frac{P}{RT}\left(B_{kk} + \frac{1}{2}\sum_i\sum_l y_i y_l (2\delta_{ik} - \delta_{il})\right)$$

where,

$$\delta_{ik} = 2B_{ik} - B_{ii} - B_{kk} \quad \text{and} \quad \delta_{il} = 2B_{il} - B_{ii} - B_{ll}$$

$$\delta_{ii} = \delta_{ll} = 0 \quad \text{and} \quad \delta_{ik} = \delta_{ki}$$

$$B_{ij} = \frac{RT_{cij}}{P_{cij}}\left(B^0 + \omega_{ij}B^1\right) \quad \omega_{ij} = \frac{\omega_i + \omega_j}{2} \quad T_{cij} = (T_{ci}T_{cj})^{1/2}(1 - k_{ij})$$

$$P_{cij} = \frac{Z_{cij}RT_{cij}}{V_{cij}} \quad V_{cij} = \left(\frac{V_{ci}^{1/3} + V_{cj}^{1/3}}{2}\right)^3 \quad Z_{cij} = \frac{Z_{ci} + Z_{cj}}{2}$$

Using Generic Cubic EOS

$$\ln\hat{\phi}_i = \frac{b_i}{b}\left(Z-1\right) - \ln(Z-\beta) - \overline{q}_i I$$

Refer to chapter 14 if you interested in the details.

(Out of scope for this class)

Ideal-Solution

We know for an ideal-gas mixture, $\qquad \mu_i^{ig} = \overline{G}_i^{ig} = G_i^{ig}(T,P) + RT \ln y_i$

No intermolecular forces/interaction
and negligible particle volume (compare to molar volume).
Only for an ideal gas mixture.

For an ideal solution, we define $\quad \mu_i^{id} = \overline{G}_i^{id} = G_i(T,P) + RT \ln x_i$

There exist intermolecular interaction but the various molecules
have similar size, structure and intermolecular forces.
Applicable for real gas mixture and liquid solution.
However, application is most often to liquid solution.

So for an ideal solution, $G^{id} = \sum x_i \overline{G}_i^{id} = \sum x_i G_i + RT \sum x_i \ln x_i$

Entropy for Ideal Solution

Substitute $\mu_i = \bar{G}_i$ into Eqn 11.3,

$$dG = VdP - SdT + \sum_i \bar{G}_i dx_i$$

Apply criterion of exactness,

$$\bar{S}_i = \left[\frac{\partial(nS)}{\partial x_i} \right]_{P,T,x} = -\left(\frac{\partial \bar{G}_i}{\partial T} \right)_{P,x}$$

For ideal solution,

$$\bar{S}_i^{id} = -\left(\frac{\partial \bar{G}_i^{id}}{\partial T} \right)_{P,x} = -\left(\frac{\partial(G_i(T,P) + RT \ln x_i)}{\partial T} \right)_{P,x}$$

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

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

Enthalpy for Ideal Solution

$$\bar{H}_i^{id} = \bar{G}_i^{id} + T\bar{S}_i^{id}$$

$$\bar{H}_i^{id} = G_i + RT \ln x_i + T(S_i - R \ln x_i)$$

$$= G_i + TS_i$$

$$= H_i$$

So for ideal solution,

$$H = \sum_i x_i H_i$$

Molar Volume for Ideal Solution

$$dG = VdP - SdT + \sum_i \bar{G}_i dx_i$$

Apply criterion of exactness,

$$\left(\frac{\partial \bar{G}_i}{\partial P} \right)_{T,x} = \left[\frac{\partial V}{\partial x_i} \right]_{P,T,x} = \bar{V}_i$$

For ideal solution,

$$\bar{V}_i^{id} = \left(\frac{\partial \bar{G}_i^{id}}{\partial P} \right)_{T,x} = -\left(\frac{\partial (G_i(T,P) + RT \ln x_i)}{\partial P} \right)_{T,x}$$

$$\bar{V}_i^{id} = \left[\frac{\partial G_i(T,P)}{\partial P} \right]_{T,x} = V_i$$

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

Non-Ideal Solution

Excess Property (M^E)

In previous discussion, the real solution is evaluated with reference to ideal gas mixture by using the definition of residual property. Hence the following equation is generally and easily apply for a gas mixture.

$$\hat{\phi}_i = \frac{\hat{f}_i}{y_i P}$$

Real liquid solution is, however, much more convenient to be evaluated with reference to its departure from an ideal solution (not ideal-gas) behavior.

Hence, we define an excess property as,

The difference between actual property of a solution and the property of an ideal solution at the same T, P and x_i

$$M^E = M - M^{id}$$

So,

$$M = M^E + M^{id}$$

for example: $H = H^E + H^{id}$

Now, let's apply this definition to Gibb's Energy.

$$G^E = G - G^{id}$$

$$nG^E = nG - nG^{id}$$

$$\left[\frac{\partial\left(nG^E\right)}{\partial n_i}\right]_{P,T,n_j} = \left[\frac{\partial\left(nG\right)}{\partial n_i}\right]_{P,T,n_j} - \left[\frac{\partial\left(nG^{id}\right)}{\partial n_i}\right]_{P,T,n_j}$$

$$\overline{G}_i^E = \overline{G}_i - \overline{G}_i^{id}$$

from 11.46, $\overline{G}_i = \Gamma_i(T) + RT \ln \hat{f}_i$

also we know, $\overline{G}_i^{id} = G_i + RT \ln x_i$

$$= \Gamma_i(T) + RT \ln f_i + RT \ln x_i$$

so,

$$\overline{G}_i^E = \Gamma_i(T) + RT \ln \hat{f}_i - (\Gamma_i(T) + RT \ln f_i + RT \ln x_i)$$

$$\overline{G}_i^E = RT \ln \hat{f}_i - RT \ln f_i - RT \ln x_i$$

$$\overline{G}_i^E = RT(\ln \frac{\hat{f}_i}{x_i f_i})$$

Activity Coefficient of Species i in Solution γ_i

The previous equation could be written as,

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

where

$$\gamma_i = \frac{\hat{f}_i}{x_i f_i}$$ an activity coefficient of species *i*

or

$$\hat{f}_i = \gamma_i x_i f_i$$

For a liquid solution!

Ideal Solution
(Lewis/Randall rule)

For ideal solution,

$$\bar{G}_i^E = 0$$

so

$$RT(\ln \frac{\hat{f}_i^{id}}{x_i f_i}) = RT(\ln \gamma_i) = 0$$

therefore,

$$\gamma_i = \frac{\hat{f}_i^{id}}{x_i f_i} = 1$$

$$\hat{f}_i^{id} = x_i f_i \qquad \text{Lewis/Randall rule}$$

also divide by Px_i

$$\frac{\hat{f}_i^{id}}{Px_i} = \frac{x_i f}{Px_i}$$

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

Fundamental Excess-Property Relation

$$d\left(\frac{nG}{RT}\right) = \frac{1}{RT}\,d(nG) - \frac{nG}{RT^2}\,dT$$

$$d\left(\frac{nG}{RT}\right) = \frac{1}{RT}\left((nV)dP - (nS)dT + \sum \bar{G}_i dn_i\right) - \frac{n(H-TS)}{RT^2}\,dT$$

$$d\left(\frac{nG}{RT}\right) = \frac{nVdP}{RT} - \frac{nSdT}{RT} + \sum \frac{\bar{G}_i dn_i}{RT} - \frac{nH}{RT^2}\,dT + \frac{nS}{RT}\,dT$$

$$d\left(\frac{nG}{RT}\right) = \frac{nVdP}{RT} - \frac{nH}{RT^2}\,dT + \sum \frac{\bar{G}_i}{RT}dn_i \qquad (11.54)$$

for ideal solution,

$$d\left(\frac{nG^{id}}{RT}\right) = \frac{nV^{id}dP}{RT} - \frac{nH^{id}}{RT^2}\,dT + \sum \frac{\bar{G}_i^{id}}{RT}dn_i \qquad (11.54\text{id})$$

Fundamental Excess-Property Relation

(11.54) - (11.54id)

$$d\left(\frac{nG^E}{RT}\right) = \frac{nV^E dP}{RT} - \frac{nH^E}{RT^2}dT + \sum \frac{\bar{G}_i^E}{RT}dn_i \quad (11.89)$$

$$d\left(\frac{nG^E}{RT}\right) = \frac{nV^E dP}{RT} - \frac{nH^E}{RT^2}dT + \sum \ln \gamma_i dn_i \quad (11.93)$$

So,

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

Therefore,

$\ln \gamma_i$ is a partial property of G^E/RT

Consider a multicomponent system in VLE, the fugacity of species *i* for each phase,
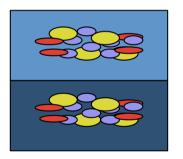
For vapor mixture

$$\hat{f}_i^v = \hat{\phi}_i y_i P$$

For liquid solution

$$\hat{f}_i^l = \gamma_i x_i f_i$$

VLE criteria,

$$\hat{f}_i^v = \hat{f}_i^l$$

so

$$\hat{\phi}_i y_i P = \gamma_i x_i f_i$$

This is the VLE relation that relates the composition of vapor phase and that of liquid phase. See Chapter 10 for application of this relation. Chapter 12 for correlation for γ_i