


# Ch.8

## Thermodynamic Properties of Mixture



Instructor: Bing Joe Hwang  
(bjh@mail.ntust.edu.tw)

# Outline

<1>  $\left. \begin{array}{l} \bar{H}_i \\ \bar{G}_i \\ \bar{S}_i \end{array} \right\} f(T, P, x_i) \bullet \text{Partial Molar Properties}$

<2>  $\Delta \bar{H}_m, \Delta \bar{G}_m, \Delta \bar{S}_m \bullet \text{Changes of Mixing}$

<3> General equilibrium criteria for multicomponent mixtures

<4> Chemical & phase equilibria

# Thermodynamic description of mixture

~ Pure, Single phase systems

$$d.o.f = 2$$

$(T, P)$  or  $(T, \underline{V}) \Rightarrow$  fix all state variables.

$(T, P, N)$  or  $(T, \underline{V}, N) \Rightarrow$  fix its size

~ Single-phase of C-component systems:

$(T, P, N_1, N_2, \dots, N_C)$  or  $(T, P, \chi_1, \chi_2, \dots, \chi_{C-1})$

e.g.  $\underline{U} = \underline{U}(T, P, N_1, N_2, \dots, N_C)$  or  $\underline{U} = \underline{U}(T, P, \chi_1, \chi_2, \dots, \chi_{C-1})$

# Thermodynamic description of mixture

For a  $c$ -component mixture,

$$\underline{\theta}(T, P, x_1, \dots, x_{c-1}) \stackrel{?}{=} \sum_{i=1}^c x_i \underline{\theta}(T, P)$$

↑  
linear combination

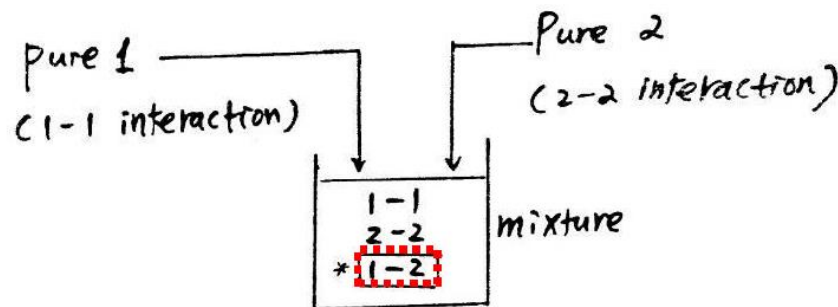
e.g. for a binary system,

$$\Delta_{\text{mix}} \underline{V} = \underline{V}(T, P, x_1) - x_1 \underline{V}_1(T, P) - x_2 \underline{V}_2(T, P)$$

$$\Delta_{\text{mix}} \underline{H} = \underline{H}(T, P, x_1) - x_1 \underline{H}_1(T, P) - x_2 \underline{H}_2(T, P)$$

If the linear combination is valid,

all  $\Delta_{\text{mix}} \theta = 0$ .



# Partial Molar Properties

For any molar property  $\underline{\theta}$  (such as  $\underline{V}$ ,  $\underline{H}$ ,  $\underline{U}$ ...) at fixed  $T$  &  $P$

$$\underline{\theta}_m = N \underline{\theta} = \phi(N_1, N_2, \dots, N_c) \quad (8.1-3)$$

If the no. of moles of each species were doubled,

$$\underline{\theta}_m(T, P, N_1, N_2, \dots, N_c) = \underline{\theta}_m(T, P, 2N_1, \dots, 2N_c)$$

and

$$2N \underline{\theta}_m = \phi(2N_1, 2N_2, \dots, 2N_c) \quad (8.1-4)$$

Eq (8.1-3)  $\times 2 \Rightarrow$

$$2N \underline{\theta}_m = 2\phi(N_1, N_2, \dots, N_c) \quad (8.1-5)$$

$$\phi(2N_1, 2N_2, \dots, 2N_c) = 2\phi(N_1, N_2, \dots, N_c)$$

or

$$\phi(\lambda N_1, \lambda N_2, \dots, \lambda N_c) = \lambda \phi(N_1, N_2, \dots, N_c)$$

↑  
homogeneous function of the first degree in the mole no. of the constituents.

Using Euler's theorem, we obtain

$$\underline{\theta}_m = \sum_{i=1}^c x_i \left[ \frac{\partial(N \underline{\theta}_m)}{\partial N_i} \right]_{T, P, N_{j \neq i}}$$

where  $\left[ \frac{\partial(N \underline{\theta}_m)}{\partial N_i} \right]_{T, P, N_{j \neq i}} \equiv \bar{\theta}_i$  partial molar property

# Partial Molar Properties

i.e.

$$\bar{\theta}_m = \sum_{i=1}^c x_i \bar{\theta}_i$$

Generally,

$$\bar{\theta}_i \neq \theta_i$$

$\bar{\theta}_i$  ← partial molar  
 $\theta_i$  ← pure component  $i$

e.g. partial molar internal energy,

$$\bar{U}_i = \left[ \frac{\partial (N\bar{U})}{\partial N_i} \right]_{T,P,N_j \neq i}$$

&

$$U = \sum x_i \bar{U}_i$$

\* Thermodynamic relationships for partial molar properties,

$$\underline{A} = \underline{U} - T\underline{S} \Rightarrow \bar{A}_i = \bar{U}_i - T\bar{S}_i$$

$$\underline{G} = \underline{H} - T\underline{S} \Rightarrow \bar{G}_i = \bar{H}_i - T\bar{S}_i$$

$$C_{p,i} = \left( \frac{\partial \underline{H}_i}{\partial T} \right)_{P,N} \Rightarrow \bar{C}_{p,i} = \left( \frac{\partial \bar{H}_i}{\partial T} \right)_{P,N_j}$$

\* Property change of Mixing

$$\Delta_{\text{mix}} \theta = \theta_m - \sum N_i \theta_i$$

← Unmixed pure component

$$= \sum N_i \bar{\theta}_i - \sum N_i \theta_i$$

$$= \sum_{i=1}^c N_i [\bar{\theta}_i(T,P,x_i) - \theta_i(T,P)]$$

e.g. Heat of Mixing

$$\Delta_{\text{mix}} H = \sum_{i=1}^c N_i [\bar{H}_i(T,P,x_i) - H_i(T,P)]$$

# Partial Gibbs free energy

$$G = f(T, P, N_1, N_2, \dots, N_c)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, N_j} dT + \left(\frac{\partial G}{\partial P}\right)_{T, N_j} dP +$$

$$+ \sum_{i=1}^c \left(\frac{\partial G}{\partial N_i}\right)_{T, P, N_{j \neq i}} dN_i$$

$$= -S dT + V dP + \sum_{i=1}^c \bar{G}_i dN_i$$

Chemical potential  
 $\mu_i \equiv \bar{G}_i$

Similarly,  $H = f(P, S, N_1, N_2, \dots, N_c)$

$$dH = \left(\frac{\partial H}{\partial P}\right)_{S, N_j} dP + \left(\frac{\partial H}{\partial S}\right)_{P, N_j} dS +$$

$$\sum_{i=1}^c \left(\frac{\partial H}{\partial N_i}\right)_{P, S, N_{j \neq i}} dN_i \quad (8.2-2)$$

$$\bar{H}_i \equiv \left(\frac{\partial H}{\partial N_i}\right)_{T, P, N_{j \neq i}}$$

Since  $H = G + TS$

$$\therefore dH = dG + T ds + S dT$$

$$= -S dT + V dP + \sum \bar{G}_i dN_i + T ds + S dT$$

$$= V dP + T ds + \sum \bar{G}_i dN_i \quad (8.2-3)$$

Comparing Eq (8.2-2) & (8.2-3) yields that

$$\left(\frac{\partial H}{\partial N_i}\right)_{P, S, N_{j \neq i}} = \bar{G}_i = \left(\frac{\partial G}{\partial N_i}\right)_{T, P, N_{j \neq i}}$$

↑  
 $\mu_i$

Similarly,

$$\left(\frac{\partial U}{\partial N_i}\right)_{S, V, N_{j \neq i}} = \left(\frac{\partial A}{\partial N_i}\right)_{T, V, N_{j \neq i}} = \left(\frac{\partial H}{\partial N_i}\right)_{P, S, N_{j \neq i}}$$

$$= \left(\frac{\partial G}{\partial N_i}\right)_{T, P, N_{j \neq i}} = \bar{G}_i \equiv \mu_i$$

# Gibbs-Duhem Eq.

$$N\bar{\theta} = \sum N_i \bar{\theta}_i$$

$$\therefore d(N\bar{\theta}) = \sum N_i d\bar{\theta}_i + \sum \bar{\theta}_i dN_i \quad (8.2-6)$$

Let  $N\bar{\theta} = f(T, P, N_1, N_2, \dots, N_c)$

$$d(N\bar{\theta}) = \left[ \frac{\partial(N\bar{\theta})}{\partial T} \right]_{P, N_j} dT + \left[ \frac{\partial(N\bar{\theta})}{\partial P} \right]_{T, N_j} dP + \sum_{i=1}^c \left[ \frac{\partial(N\bar{\theta})}{\partial N_i} \right]_{T, P, N_{j \neq i}} dN_i$$

$$= N \left( \frac{\partial \bar{\theta}}{\partial T} \right)_{P, N_j} dT + N \left( \frac{\partial \bar{\theta}}{\partial P} \right)_{T, N_j} dP + \sum \bar{\theta}_i dN_i \quad (8.2-7)$$

Comparing Eq (8.2-6) & Eq (8.2-7), we have

$$- N \left( \frac{\partial \bar{\theta}}{\partial T} \right)_{P, N_j} dT - N \left( \frac{\partial \bar{\theta}}{\partial P} \right)_{T, N_j} dP + \sum_{i=1}^c N_i d\bar{\theta}_i = 0$$

$$- \left( \frac{\partial \bar{\theta}}{\partial T} \right)_{P, N_j} dT - \left( \frac{\partial \bar{\theta}}{\partial P} \right)_{T, N_j} dP + \sum_{i=1}^c x_i d\bar{\theta}_i = 0$$

Generalized Gibbs-Duhem Eq.

At constant  $T$  &  $P$ , Gibbs-Duhem eq. becomes,

$$\sum_{i=1}^c (N_i d\bar{\theta}_i)_{T, P} = 0$$

or

$$\sum_{i=1}^c (x_i d\bar{\theta}_i)_{T, P} = 0$$

$$\sum_{i=1}^c N_i \left( \frac{\partial \bar{\theta}_i}{\partial T} \right)_{T, P} = 0$$

↑ any property except mole fraction

$$\sum_{i=1}^c N_i \left( \frac{\partial \bar{\theta}_i}{\partial N_j} \right)_{T, P, N_{k \neq j}} = 0$$

Set  $\theta = G$

Gibbs-Duhem Eq. at const.  $T$  &  $P$  becomes,

$$\sum_{i=1}^c N_i (d\bar{G}_i)_{T, P} = 0$$

$$\sum_{i=1}^c x_i (d\bar{G}_i)_{T, P} = 0$$

$$\sum_{i=1}^c N_i \left( \frac{\partial \bar{G}_i}{\partial T} \right)_{T, P} = 0$$

$$\sum_{i=1}^c N_i \left( \frac{\partial \bar{G}_i}{\partial N_j} \right)_{T, P, N_{k \neq j}} = 0$$



# Thermodynamic Consistency

• Gibbs-Duhem Eq. is a thermodynamic consistency relation.

\*  $\Rightarrow$  the set of  $C+2$  state variables ( $T, P, \bar{G}_1, \dots, \bar{G}_c$ ) in a  $c$ -component system, only " $c-1$ " of these variables are independent.

$$\text{e.g. } d\bar{G}_c = \frac{1}{N_c} \left\{ -SdT + VdP - \sum_{i=1}^{c-1} N_i d\bar{G}_i \right\}$$

• Gibbs-Duhem Eq. is used for testing the consistency of the experimental data.

e.g. ( $T$ - $P$ - $x$ - $y$  data for VLE)

\* Gibbs-Duhem Eq. in terms of mole fraction.

$$\sum_{i=1}^c \chi_i \sum_{j=1}^{c-1} \left( \frac{\partial \bar{G}_i}{\partial \chi_j} \right)_{T,P} d\chi_j = 0$$

For a binary mixture,

$$\sum_{i=1}^2 \chi_i \left( \frac{\partial \bar{G}_i}{\partial \chi_1} \right)_{T,P} d\chi_1 = 0$$

or  $\chi_1 \left( \frac{\partial \bar{G}_1}{\partial \chi_1} \right)_{T,P} + \chi_2 \left( \frac{\partial \bar{G}_2}{\partial \chi_1} \right)_{T,P} = 0$

Let  $\theta \equiv G$

$$\Rightarrow \chi_1 \left( \frac{\partial \bar{G}_1}{\partial \chi_1} \right)_{T,P} + \chi_2 \left( \frac{\partial \bar{G}_2}{\partial \chi_1} \right)_{T,P} = 0$$

Where  $\chi_2 = 1 - \chi_1$   
 $d\chi_2 = -d\chi_1$

# Experimental Determination of Partial Partial Volume and Enthalpy

- Partial molar volumes  $\leftarrow$  mixture density
- Partial molar enthalpy  $\leftarrow$  heat of mixing
- Partial molar Gibbs free energy  $\leftarrow$  equilibrium measurements

For binary mixtures,

$$\begin{aligned} \Delta_{\text{mix}} \underline{V} &= \underline{V}_M - (\chi_1 \underline{V}_1 + \chi_2 \underline{V}_2) \\ &= \chi_1 \bar{V}_1 + \chi_2 \bar{V}_2 - \chi_1 \underline{V}_1 - \chi_2 \underline{V}_2 \\ &= \chi_1 (\bar{V}_1 - \underline{V}_1) + \chi_2 (\bar{V}_2 - \underline{V}_2) \quad (8.6-1) \end{aligned}$$

$$\left. \frac{\partial (\Delta_{\text{mix}} \underline{V})}{\partial \chi_1} \right|_{T,P} = (\bar{V}_1 - \underline{V}_1) + \chi_1 \left( \frac{\partial \bar{V}_1}{\partial \chi_1} \right)_{T,P} - (\bar{V}_2 - \underline{V}_2) + \chi_2 \left( \frac{\partial \bar{V}_2}{\partial \chi_1} \right)_{T,P}$$

Gibbs-Duhem Eq.,  $\bar{\theta}_i = \bar{V}_i$

$$\Rightarrow \chi_1 \left( \frac{\partial \bar{V}_1}{\partial \chi_1} \right)_{T,P} = -\chi_2 \left( \frac{\partial \bar{V}_2}{\partial \chi_1} \right)_{T,P}$$

$$\therefore \left. \frac{\partial (\Delta_{\text{mix}} \underline{V})}{\partial \chi_1} \right|_{T,P} = (\bar{V}_1 - \underline{V}_1) - (\bar{V}_2 - \underline{V}_2) \quad (8.6-3)$$

$$\text{Eq (8.6-1)} - \chi_1 \cdot \text{Eq (8.6-3)} \Rightarrow$$

$$\boxed{\Delta_{\text{mix}} \underline{V} - \chi_1 \left. \frac{\partial (\Delta_{\text{mix}} \underline{V})}{\partial \chi_1} \right|_{T,P} = (\bar{V}_2 - \underline{V}_2)}$$

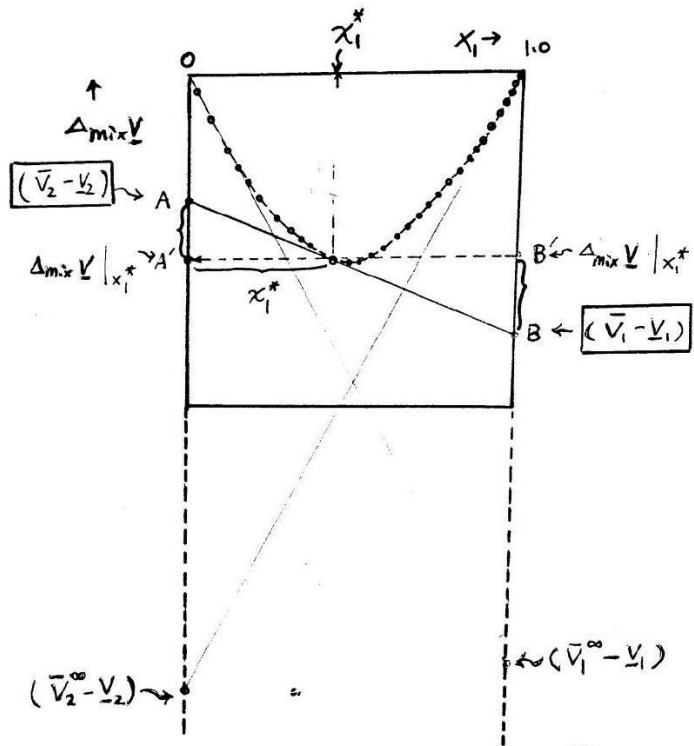
$$\text{Eq (8.6-1)} + \chi_2 \cdot \text{Eq (8.6-3)} \Rightarrow$$

$$\boxed{\Delta_{\text{mix}} \underline{V} + \chi_2 \left. \frac{\partial (\Delta_{\text{mix}} \underline{V})}{\partial \chi_1} \right|_{T,P} = (\bar{V}_1 - \underline{V}_1)}$$

If  $\Delta_{\text{mix}} \underline{V}$  and  $\left. \frac{\partial (\Delta_{\text{mix}} \underline{V})}{\partial \chi_1} \right|_{T,P}$  can be evaluated at  $\chi_1$ , then  $(\bar{V}_1 - \underline{V}_1)$  and  $(\bar{V}_2 - \underline{V}_2)$  are able to be calculated.

pure molar volumes are known

$$\Rightarrow \underline{\bar{V}_1} \ \& \ \underline{\bar{V}_2} \quad *$$



$$\text{slope of } \overline{AB} = \frac{\partial(\Delta_{\text{mix}}V)}{\partial x_1} = -\frac{|\overline{AA'}|}{x_1^*}$$

$$|\overline{AA'}| = -x_1^* \left( \frac{\partial \Delta_{\text{mix}}V}{\partial x_1} \right)_{T,P} \quad \& \quad A' = \Delta_{\text{mix}}V \Big|_{x_1^*}$$

$$\therefore A = A' + |\overline{AA'}| = \Delta_{\text{mix}}V \Big|_{x_1^*} - x_1^* \left( \frac{\partial \Delta_{\text{mix}}V}{\partial x_1} \right)_{T,P} = (\overline{V}_2 - V_2)$$

Similarly,  $B = (\overline{V}_1 - V_1)$

Graphic method is not accurate enough

⇒ analytic method.

fit  $\Delta_{\text{mix}}V = f(x_i)$  ← empirical model

e.g. Redlich-Kister model

$$\Delta_{\text{mix}}V = x_1 x_2 \sum_{i=0}^n a_i (x_1 - x_2)^i$$

Where  $a_i$  are determined from expt'l data. (optimization)

\* Similar models are used for

$$\Delta_{\text{mix}}H, \Delta_{\text{mix}}U, \dots$$

$$\Delta_{\text{mix}}V = x_1 (1-x_1) \sum_{i=1}^n a_i (2x_1 - 1)^i$$

$$\frac{\partial \Delta_{\text{mix}}V}{\partial x_1} \Big|_{T,P} = - \sum_{i=0}^n a_i (2x_1 - 1)^{i+1} + 2x_1 \cdot (1-x_1) \sum_{i=0}^n a_i i (2x_1 - 1)^{i-1}$$

$$\Rightarrow \Delta_{\text{mix}}V - x_1 \frac{\partial(\Delta_{\text{mix}}V)}{\partial x_1} \Big|_{T,P} = \overline{V}_2 - V_2 = x_1^2 \sum a_i [(x_1 - x_2)^i - 2i x_2 (x_1 - x_2)^{i-1}]$$

and

$$\bar{V}_1 - \underline{V}_1 = x_2^2 \sum_{i=0}^n a_i \left[ (x_1 - x_2)^i + 2i x_1 (x_1 - x_2)^{i-1} \right]$$

For example. Water + Methanol system, (298.15K)

$$a_0 = -4.0034 \times 10^{-6}, \quad a_1 = -0.17756 \times 10^{-6}$$

$$a_2 = 0.54139 \times 10^{-6}, \quad a_3 = 0.60481 \times 10^{-6}$$

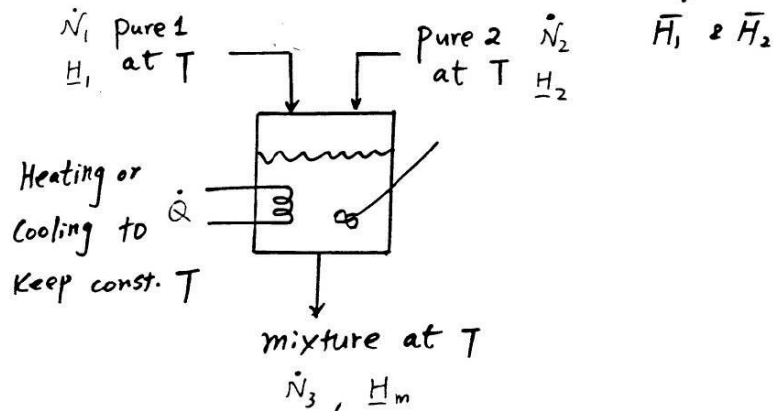
$x_1$	$\bar{V}_1 - \underline{V}_1$	$\bar{V}_1$	$\bar{V}_2 - \underline{V}_2$	$\bar{V}_2$
0	-3.8893	14.180	0	40.722
⋮	⋮	⋮ $\nearrow \bar{V}_1^\infty$	⋮	⋮ $\nearrow \bar{V}_2^\infty$
0.2841	-2.0751	15.994	-0.2773	40.445
⋮	⋮	⋮	⋮	⋮
0.7222	-0.2294	17.840	-2.2363	38.486
⋮	⋮	⋮	⋮	⋮
1.0	0	18.069 $\nwarrow \bar{V}_1^\infty$	-3.0348	37.689 $\nwarrow \bar{V}_2^\infty$
	$\uparrow$ < 0		$\uparrow$ < 0	and $\Delta_{\text{mix}} V < 0$

$\Delta_{\text{mix}} V$ ,  $(\bar{V}_1 - \underline{V}_1)$  &  $(\bar{V}_2 - \underline{V}_2)$  may be negative, positive or positive over part of the comp. range & negative over the rest.

# Heat of Mixing

\* Heat of Mixing,  $\Delta_{mix} H$

Isothermal flow calorimeter  $\Rightarrow \Delta_{mix} H$



M.B.  $\dot{N}_3 = \dot{N}_1 + \dot{N}_2$

E.B.  $\dot{N}_1 \underline{H}_1 + \dot{N}_2 \underline{H}_2 - \dot{N}_3 \underline{H}_m + \dot{Q} = 0$

$$\begin{aligned} \therefore \underline{\dot{Q}} &= [(\dot{N}_1 + \dot{N}_2) \underline{H}_m - \dot{N}_1 \underline{H}_1 - \dot{N}_2 \underline{H}_2] \\ &= \left[ \underline{H}_m - \frac{\dot{N}_1}{\dot{N}_1 + \dot{N}_2} \underline{H}_1 - \frac{\dot{N}_2}{\dot{N}_1 + \dot{N}_2} \underline{H}_2 \right] (\dot{N}_1 + \dot{N}_2) \\ &= [ \underline{H}_m - \chi_1 \underline{H}_1 - \chi_2 \underline{H}_2 ] \cdot (\dot{N}_1 + \dot{N}_2) \\ &= \underline{(\dot{N}_1 + \dot{N}_2) \Delta_{mix} H} \Rightarrow \Delta_{mix} H = \frac{\dot{Q}}{\dot{N}_1 + \dot{N}_2} \end{aligned}$$

The calculations of  $\bar{H}_i$  is analogous to the procedure used for  $\bar{V}_i$

$$\begin{aligned} \Delta_{mix} H - \chi_1 \left( \frac{\partial \Delta_{mix} H}{\partial \chi_1} \right)_{T,P} &= \bar{H}_2 - \underline{H}_2 \\ \Delta_{mix} H + \chi_2 \left( \frac{\partial \Delta_{mix} H}{\partial \chi_1} \right)_{T,P} &= \bar{H}_1 - \underline{H}_1 \end{aligned}$$

In general, for any extensive function  $\Theta$

$$\begin{aligned} \bar{\Theta}_1(T,P,\chi_1) - \underline{\Theta}_1(T,P) &= \Delta_{mix} \underline{\Theta}(T,P,\chi_1) + \chi_2 \left( \frac{\partial \Delta_{mix} \underline{\Theta}}{\partial \chi_1} \right)_{T,P} \\ \bar{\Theta}_2(T,P,\chi_2) - \underline{\Theta}_2(T,P) &= \Delta_{mix} \underline{\Theta}(T,P,\chi_2) - \chi_1 \left( \frac{\partial \Delta_{mix} \underline{\Theta}}{\partial \chi_1} \right)_{T,P} \end{aligned}$$

# Criteria for Phase equilibrium in multicomponent system

For multicomponent systems, the independent variables include  $(T, P, x_1, x_2, \dots, x_{c-1})$  for each phase.

At equilibrium,

$S = \max.$  at const.  $M, U$  &  $V$

$A = \min.$  at const.  $M, T$  &  $V$

$G = \min.$  at const.  $M, T$  &  $P$

\* Two-phase system equilibrium at const  $U$  and  $V$ ,

$$N_i = N_i^I + N_i^{II}$$



$$dS = dS^I + dS^{II}$$

From Eq (6.2-4),

$$dS = \frac{dU}{T} + \frac{P}{T} dV - \frac{1}{T} \sum_{i=1}^c \bar{G}_i dN_i$$

$$\begin{aligned} \text{Since } dU^{II} &= -dU^I \\ dV^{II} &= -dV^I \\ dN_i^{II} &= -dN_i^I \end{aligned}$$

$$\begin{aligned} \Rightarrow dS &= \left( \frac{1}{T^I} - \frac{1}{T^{II}} \right) dU^I + \left( \frac{P^I}{T^I} - \frac{P^{II}}{T^{II}} \right) dV^I - \\ &\quad \sum \left( \frac{\bar{G}_i^I}{T^I} - \frac{\bar{G}_i^{II}}{T^{II}} \right) dN_i^I = 0 \end{aligned}$$

Because  $dU^I, dV^I$  &  $dN_i^I$  are independent,

$$\boxed{\begin{aligned} T^I &= T^{II} \\ P^I &= P^{II} \\ \bar{G}_i^I &= \bar{G}_i^{II} \quad \text{for } i=1, 2, \dots, c \quad (\text{or } \mu_i^I = \mu_i^{II}) \end{aligned}} \quad (8.7-7)$$

\* Phase Equilibrium in a closed system at const.  $T$  &  $P$ .

$$dG = dG^I + dG^{II} = 0$$

$$dG|_{T,P} = \sum_{i=1}^c \bar{G}_i dN_i$$

$$= \sum_{i=1}^c \bar{G}_i^I dN_i^I + \sum_{i=1}^c \bar{G}_i^{II} dN_i^{II}$$

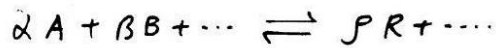
$$= \sum_{i=1}^c (\bar{G}_i^I - \bar{G}_i^{II}) dN_i^I = 0$$

$$\Rightarrow \boxed{\bar{G}_i^I = \bar{G}_i^{II}}$$

For multiphase equilibria,

$$\boxed{\bar{G}_i^I = \bar{G}_i^{II} = \bar{G}_i^{III} = \dots = \bar{G}_i^P}$$

# A notation for chemical reactions



Where  $\alpha, \beta, \dots, \rho, \dots$  are molar stoichiometric coeff.

$$\Rightarrow \underbrace{\rho R + \dots}_{\text{products}} - \underbrace{\alpha A - \beta B - \dots}_{\text{reactants}} = 0$$

or

$$\boxed{\sum \nu_i I = 0}$$

Where

$\nu_i$ : stoichiometric coeff. of species  $I$ .

+ : products

- : reactants

\* Molar extent of reaction,  $\Sigma$  (not conversion)  
 $\uparrow$  mole

$$\boxed{N_i = N_{i0} + \nu_i \Sigma}$$

$\uparrow$  initial no. of moles of species  $i$

or

$$\boxed{\Sigma = \frac{N_i - N_{i0}}{\nu_i}}$$

if  $\Sigma$  and  $N_{i0}$  are given, all  $N_i$  can be computed.

$$dN_i = \nu_i d\Sigma$$

$$\therefore \boxed{\left(\frac{dN_i}{dt}\right)_{\text{rxn}} = \nu_i \left(\frac{d\Sigma}{dt}\right)}$$

$\uparrow$  rate change of the reaction

\* Total no. of moles in a closed system

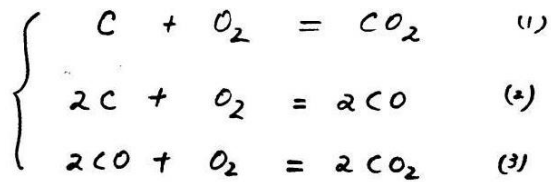
$$N = \sum_{i=1}^c N_i = \sum_{i=1}^c (N_{i0} + \nu_i \Sigma)$$

$$= \sum_{i=1}^c N_{i0} + \Sigma \sum_{i=1}^c \nu_i$$

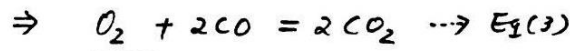
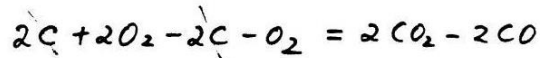
\* Independent Chemical Reactions

: the smallest collection of rxns includes all possible chemical rxns among the species presented.

i.e. No reaction in the set can itself be a linear combination of the others.



$E_1(1) \times 2 - E_1(2) \Rightarrow$  (linear combination)



$\therefore$  Rxns (1), (2) & (3) are not a set of independent rxns.

$\Rightarrow$  Any two of them are formed a set of independent rxns.

\* Linear algebra:

	C	O <sub>2</sub>	CO	CO <sub>2</sub>
[	-1	-1	0	1
-	-2	-1	2	0
]	0	-1	-2	2

• Rank of the matrix is the no. of the rxns that form an independent set.

$$\begin{vmatrix} -1 & -1 & 0 \\ -2 & -1 & 2 \\ 0 & -1 & -2 \end{vmatrix} = \begin{vmatrix} -1 & 0 & 1 \\ -2 & 2 & 0 \\ 0 & -2 & 2 \end{vmatrix} = \begin{vmatrix} -1 & 0 & 1 \\ -1 & 2 & 0 \\ -1 & -2 & 2 \end{vmatrix} = \begin{vmatrix} -1 & -1 & 1 \\ -2 & -1 & 0 \\ 0 & -1 & 2 \end{vmatrix} = 0$$

but

$$\begin{vmatrix} -1 & -1 \\ -2 & -1 \end{vmatrix} = -1 \neq 0, \begin{vmatrix} -2 & -1 \\ 0 & -1 \end{vmatrix} = 2 \neq 0, \begin{vmatrix} 0 & 1 \\ 2 & 0 \end{vmatrix} = -2 \neq 0$$

$\dots \Rightarrow$  Rank = 2 \*

\* For multiple reaction,

$X_j$ : the molar extent of rxn for the  $j$ th independent rxn.

$\nu_{ij}$ : the stoichiometric coeff. for species  $i$  in the  $j$ th rxn

• molar extent of rxn per unit volume,

$$\hat{X}_j = X_j / V$$

$$\begin{aligned} \left(\frac{dN_i}{dt}\right)_{rxn} &= \sum_{j=1}^M \nu_{ij} \frac{d}{dt}(V \hat{X}_j) \\ &= \frac{dV}{dt} \sum_{j=1}^M \nu_{ij} \hat{X}_j + V \sum_{j=1}^M \nu_{ij} \left(\frac{d\hat{X}_j}{dt}\right) \end{aligned}$$

rate of rxn per  $\uparrow$  unit volume





# The heat of reactions

Heat of Reaction,  $\Delta_{rxn} H^\circ$

⇒ Can be calculated from heat of formation information.

e.g.



$$\Delta_{rxn} H^\circ (25^\circ\text{C}, 1.0 \text{ bar}) = 2 \underline{H_{\text{HNO}_3}} (25^\circ\text{C}, 1.0 \text{ bar})$$

$$+ \underline{H_{\text{NO}}} (25^\circ\text{C}, 1.0 \text{ bar}) - 3 \underline{H_{\text{NO}_2}} (25^\circ\text{C}, 1.0 \text{ bar}) - \underline{H_{\text{H}_2\text{O}}} (25^\circ\text{C}, 1.0 \text{ bar})$$

$$= \sum \nu_i \Delta_f H_i^\circ (25^\circ\text{C}, 1.0 \text{ bar})$$

\* enthalpies of atomic species are cancelled due to conservation of atomic species on chemical rxn.

$$\Delta_{rxn} H^\circ (25^\circ\text{C}, 1.0 \text{ bar}) = \sum_i \nu_i \Delta_f H_i^\circ (25^\circ\text{C}, 1.0 \text{ bar})$$

$$\Delta_{rxn} G^\circ (25^\circ\text{C}, 1.0 \text{ bar}) = \sum_i \nu_i \Delta_f G_i^\circ (25^\circ\text{C}, 1.0 \text{ bar})$$

Standard state:  $p = 1 \text{ bar}$  and temp.  $T$

\* Standard heat of reaction at temp.  $T$ ,  $\Delta_{rxn} H^\circ(T)$

$$\begin{cases} \Delta_{rxn} H^\circ(T, 1.0 \text{ bar}) = \sum_i \nu_i \Delta_f H_i^\circ(T, 1.0 \text{ bar}) \\ \Delta_{rxn} G^\circ(T, 1.0 \text{ bar}) = \sum_i \nu_i \Delta_f G_i^\circ(T, 1.0 \text{ bar}) \end{cases}$$

$$\underline{H_i^\circ(T, p)} = \underline{H_i^\circ(T_0, p)} + \int_{T_0}^T C_{p,i}^\circ dT$$

↑  
at  $25^\circ\text{C}, 1.0 \text{ bar}$   
Tabulated values

$$\Delta_{rxn} H_i^\circ(T, 1.0 \text{ bar}) = \sum_i \nu_i \Delta_f H_i^\circ(25^\circ\text{C}, 1.0 \text{ bar})$$

$$+ \sum_i \nu_i \int_{298}^T C_{p,i}^\circ dT$$

$$= \Delta_{rxn} H^\circ(25^\circ\text{C}, 1.0 \text{ bar})$$

$$+ \sum_i \nu_i \int_{298}^T C_{p,i}^\circ dT$$

\* Standard heat of combustion,  $\Delta_c H^\circ(T)$

$\Delta_c H^\circ(25^\circ\text{C}, 1.0 \text{ bar})$  are listed in Appendix A.V.

↳ Can also give  $\Delta_{\text{rxn}} H^\circ$ .

$$\underline{\Delta_{\text{rxn}} H^\circ(25^\circ\text{C}, 1.0 \text{ bar}) = -\sum \nu_i \Delta_c H^\circ_i(25^\circ\text{C}, 1.0 \text{ bar})}$$

2

$$\underline{\Delta_{\text{rxn}} H^\circ(T, 1.0 \text{ bar}) = \Delta_{\text{rxn}} H^\circ(25^\circ\text{C}, 1.0 \text{ bar})}$$

$$\underline{+ \int_{298}^T \sum \nu_i c_{p,i}^\circ dT}$$

# Chemical Equilibrium & Phase Equilibrium

For a single chemical rxn occurring in a single phase,

$$G = \sum_{i=1}^C N_i \bar{G}_i = \sum_{i=1}^C (N_{i,0} + \nu_i \bar{X}) \bar{G}_i$$

↑  
Variable

Equilibrium criterion is given by

$$\left( \frac{\partial G}{\partial X} \right)_{T,P} = 0$$

$$\therefore \boxed{0 = \sum_{i=1}^C \nu_i \bar{G}_i}$$

The case of multiple rxns (M) in a closed single-phase

$$N_i = N_{i,0} + \sum_{j=1}^M \nu_{ij} X_j$$

$$\begin{aligned} G &= \sum_{i=1}^C N_i \bar{G}_i = \sum_{i=1}^C (N_{i,0} + \sum_{j=1}^M \nu_{ij} X_j) \bar{G}_i \\ &= \sum_{i=1}^C N_{i,0} \bar{G}_i + \sum_{i=1}^C \sum_{j=1}^M \nu_{ij} X_j \bar{G}_i \end{aligned}$$

Chemical equilibrium at const. T & P

$$\Rightarrow \underline{G_{\min.}} \text{ or } \underline{dG = 0}$$

$$\therefore \left( \frac{\partial G}{\partial X_j} \right)_{T,P, X_{i \neq j}} = 0, \quad j = 1, 2, \dots, M$$

$$\Rightarrow \left( \frac{\partial G}{\partial X_j} \right)_{T,P, X_{i \neq j}} = 0 = \sum_{i=1}^C \nu_{ij} \bar{G}_i + \sum_{i=1}^C N_i \underbrace{\left( \frac{\partial \bar{G}_i}{\partial X_j} \right)_{T,P, X_{i \neq j}}}_{\substack{0 \text{ Gibbs-Duhem} \\ \text{Eq.}}}$$

⇒ The equilibrium criterion is

$$\boxed{\sum_{i=1}^C \nu_{ij} \bar{G}_i = 0} \quad - (8.8-4), \quad j = 1, 2, \dots, M$$

# Combined Chem. Equilibrium and Phase Equilibrium

Eq (8.7-7) and Eq (8.8-4) have to be simultaneously satisfied for all species and all rxns in all phases.

Proof:

$$\min G = \sum_{k=1}^P \left( \sum_{i=1}^C N_i^k \bar{G}_i^k \right)$$

Subject to Constraints

$$\sum_{k=1}^P N_i^k = N_{i,0} + \sum_{j=1}^M \nu_{ij} X_j \quad (8.8-11)$$

mole balances for each comp.  $i$

\* The criteria for a combined phase and chemical equilibrium are Eq (8.8-11), Eq (8.8-15) & Eq (8.8-18).

Lagrange multipliers method.

$$G = \sum_{k=1}^P \sum_{i=1}^C N_i^k \bar{G}_i^k + \sum_{i=1}^C \alpha_i \left\{ \sum_{k=1}^P N_i^k - N_{i,0} - \sum_{j=1}^M \nu_{ij} X_j \right\}$$

↑  
Lagrange multipliers  
(determined latter)

Independent variables:  $X_1, X_2, \dots, X_M, N_i^I, N_i^{II}, \dots, N_i^P, \alpha_1, \alpha_2, \dots, \alpha_C$

$$\left( \frac{\partial G}{\partial N_i^I} \right) = \bar{G}_i^I + \sum_{k=1}^P \sum_{l=1}^C N_l^k \left( \frac{\partial \bar{G}_l^k}{\partial N_i^I} \right) + \alpha_i$$

$$= \bar{G}_i^I + \alpha_i = 0 \quad \uparrow \text{0. G-D eq.}$$

$$\therefore -\alpha_i = \bar{G}_i^I, \quad i=1, 2, \dots, C$$

$$\Rightarrow \bar{G}_i^I = \bar{G}_i^{II} = \dots = \bar{G}_i^P = -\alpha_i \quad (8.8-15)$$

$$\left( \frac{\partial G}{\partial X_j} \right) = 0 = \sum_{k=1}^P \sum_{i=1}^C N_i^k \left( \frac{\partial \bar{G}_i^k}{\partial X_j} \right)_{k+j} - \sum_{i=1}^C \alpha_i \nu_{ij}$$

0, G-D eq.

$$\sum_{i=1}^C \nu_{ij} \bar{G}_i^k = 0 \quad \begin{matrix} k=I, II, \dots, P \\ j=1, 2, \dots, M \end{matrix} \quad (8.8-18)$$

# The specification of equilibrium thermodynamic state of Multicomponent and multiphase Systems: Gibbs Phase Rules

For a  $C$ -component single-phase system.

independent variables:  $(T, P, x_1, x_2, \dots, x_{C-1})$

$\Downarrow$   
 $(C+1)$  d.o.f (unknows)

- No. of comp. :  $C$
- No. of phases :  $P$
- no. of rxns :  $M$

Total variables:  $P(C+1)$

No. of relations:

* $T^I = T^II \dots = T^P$	$P-1$	$\frac{(2+C)(P-1)+M}{}$
* $p^I = p^II \dots = p^P$	$P-1$	
* $\bar{G}_i^I = \bar{G}_i^II \dots = \bar{G}_i^P$ $i=1, 2, \dots, C$	$C(P-1)$	
* $\sum_{i=1}^C \nu_{ij} \bar{G}_i = 0$ $j=1, 2, \dots, M$	$M$	

$$F = P(C+1) - (2+C)(P-1) - M$$

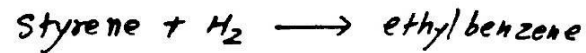
$$= C - M - P + 2$$

(8.9-6)

Gibbs phase rule

Independent variables: thermodynamic properties of the "individual phase"; not those of composite multiphase system.

Example 8.9-1



① Single-phase rxn

$$C=3$$

$$M=1$$

$$P=1$$

$$\rightarrow F = \overset{C}{3} - \overset{M}{1} - \overset{P}{1} + 2 = 3$$

② Two-phase rxn

$$C=3$$

$$M=1$$

$$P=2$$

$$\rightarrow F = 3 - 1 - 2 + 2 = 2$$

\* Fix the relative amounts of each of the phases  
 in equilibrium  $\Rightarrow \underline{\underline{\chi^I, \chi^{II}, \dots, \chi^P}} \leftarrow P$ 's unknowns  
 $\uparrow$   
 mass fraction of the  $i$ th phase.

$\Rightarrow$  need " $P$ " equations

$$P \text{ Eqs. } \left\{ \begin{array}{l} 1 = \chi^I + \chi^{II} + \chi^{III} + \dots + \chi^P \\ \hat{V} = \chi^I \hat{V}^I + \chi^{II} \hat{V}^{II} + \dots + \chi^P \hat{V}^P \\ \hat{S} = \chi^I \hat{S}^I + \chi^{II} \hat{S}^{II} + \dots + \chi^P \hat{S}^P \\ \vdots \end{array} \right\} (P-1) \text{ Eqs.}$$

Where specific volumes, entropies, ... for  
 each phase have been known from  
EOS or experiments.