Chapter 11 Solution Thermodynamics: Theory

- Chapter 6: constant composition fluids.
- Most commonly in chemical engineering application "multi component mixtures" of gases or liquids undergo (composition change). Mixing process, separation, mass transfer process or chemical reactions.
- Objectives:
 - 1. To develop a fundamental property relation for homogenous solution of variable compositions.
 - 2. Introduce new properties known as Partial Properties.
 - 3. Ideal gas mixtures and ideal solution concept.
 - 4. Fugacity property.

11.1 Fundamental Property Relation

The Chemical Potential of species i in the mixtures,

$$\mu_{i} \equiv \left[\partial(nG) / \partial n_{i} \right]_{P,T,n_{i}}$$
(11.1)

The derivative of nG with respect to the number of moles of species i.

Fundamental of Gibbs energy for closed system	
d(nG) = (nV) dp - (nS) dT	(6.6)

For open system it becomes, $d(nG) = (nV) dp - (nS) dT + \sum \mu_i dn_i$ (11.2)

11.2 **Chemical Potential as a Criterion for Phase Equilibrium**

• Write equation 10.2 for each phase in this closed system.



• Total change in the Gibbs free energy of this closed system is given by summation

$$d(nG) = (nV) dp - (nS) dT + \sum \mu_i^{\alpha} dn_i^{\alpha} + \sum \mu_i^{\beta} dn_i^{\beta}$$

- But for closed system, eq'n 6.6 applies d(nG) = (nV) dp - (nS) dT
- Then at equilibrium,

$$\sum \mu_i^{\alpha} dn_i^{\alpha} + \sum \mu_i^{\beta} dn_i^{\beta} = 0$$

• Since $dn_i^{\alpha} = -dn_i^{\beta}$

• Then
$$\sum (\mu_i^{\alpha} - \mu_i^{\beta}) dn_i^{\alpha} = 0$$

$$\mu_i^{\alpha} = \mu_i^{\beta}$$
 (i=1,2,....,N)
Criteria of phase equilibrium.

• More than 2 phases,

$$\mu_i^{\alpha} = \mu_i^{\beta} = \dots = \mu_i^{\pi}$$
 (i=1,2,....,N) (11.6)

Thus, multiple phases at the same T and P are in equilibrium when the chemical potential of each species is the same in all phases.

11.2 **Partial Properties**

$$\mathbf{M}_{i} \equiv \left[\partial(\mathbf{n}\mathbf{M}) / \partial \mathbf{n}_{i}\right]_{\mathbf{P},\mathbf{T},\mathbf{n}_{j}}$$
(11.7)

Partial molar property of species i in solution U_i , H_i , S_i , G_i ,etc.

It is a <u>response function</u>, representing the change of total property nM due to the addition of a differential amount of species i to a finite amount of solution at constant T and P.

Equations relating molar and Partial properties:

A-
$$M = \sum x_i M_i$$
(11.11)
$$nM = \sum n_i M_i$$
(11.12)

"Summability Relations"

B- Gibbs/Duhem equation

$$(\partial M / \partial P)_{T,x} dP + (\partial M / \partial T)_{P,x} dT - \sum x_i dM_i = 0$$
(11.13)

At constant T and P

$$\sum \mathbf{x}_i \, \mathbf{d}^{-} \mathbf{M}_i = 0 \tag{11.14}$$

• In summary,

M, Solution Properties.

⁻M_i, Partial Properties.

- M_i, Pure-species Properties.
- Binary Solution: Writing Summability equation for 2 components

 $M_1 = M + x_2 \, dM/dx_1$ (11.15) $M_2 = M + x_1 \, dM/dx_1$ (11.16) Ex. 11.2: Describe a graphical interpretation of equations 11.15 and 11.16



Figure 11.1: (*a*) Graphical construction of Example 11.2. (*b*) Infinite-dilution values of partial properties.

- Draw a tangent of the curve M vs x.
- From taking two slopes of this line, (Large triangle): $dM/dx_1 = M - I_2 / x_1 - 0$ (Small triangle): $dM/dx_1 = I_1 - I_2 / 1 - 0 = I_1 - I_2$ Then solve these two equations.

 $I_1 = M_1$, $I_2 = M_2$ The tangent intercepts gives directly the partial properties.

- The intercepts shift as point tangency moves along the curve and the <u>limiting</u> <u>value</u> are indicated by fig 11.1 (b).
- At pure species 2 [(x₁=0), (x₂=1)] Subs. in 11.16, M₂ = M₂
 The molar property = partial property.

The opposite intercept gives $M_1 = M_1$ (Partial property of species 1 when it is present at infinite dilution)

Similar at pure species 1 [(x₁=1), (x₂=0)]
 Subs. in 11.16, M₁ = M₁
 The molar property = partial property.

The opposite intercept gives $M_2 = M_2$ (Partial property of species 2 when it is present at infinite dilution)

Ex. 11.3

The need arises in a laboratory for 2,000 cm³ of an antifreeze solution consisting of 30-mol-% methanol in water. What volumes of pure methanol and of pure water at 25°C must be mixed to form the 2,000 cm³ of antifreeze, also at 25°C? Partial molar volumes for methanol and water in a 30-mol-% methanol solution and their pure-species molar volumes, both at 25°C, are:

Methanol(1):	$V_1 = 38.632 \text{ cm}^3 \text{ mol}^{-1}$	$V_1 = 40.727 \text{ cm}^3 \text{ mol}^{-1}$
Water(2):	$\bar{V}_2 = 17.765 \text{ cm}^3 \text{ mol}^{-1}$	$V_2 = 18.068 \text{ cm}^3 \text{ mol}^{-1}$

Solution 11.3

Equation (11.11) is written for the molar volume of the binary antifreeze solution, and known values are substituted for the mole fractions and partial volumes:

 $V = x_1 \bar{V}_1 + x_2 \bar{V}_2 = (0.3)(38.632) + (0.7)(17.765) = 24.025 \text{ cm}^3 \text{ mol}^{-1}$

Because the required total volume of solution is $V^t = 2,000 \text{ cm}^3$, the total number of moles required is:

$$n = \frac{V'}{V} = \frac{2,000}{24,025} = 83.246 \text{ mol}$$

Of this, 30% is methanol, and 70% is water:

 $n_1 = (0.3)(83.246) = 24.974$ $n_2 = (0.7)(83.246) = 58.272 \text{ mol}$

The volume of each pure species is $V_i^t = n_i V_i$; thus,

$$V_1^t = (24.974)(40.727) = 1,017$$
 $V_2^t = (58.272)(18.068) = 1,053 \text{ cm}^2$

Note that the simple sum of the initial volumes = $2,070 \text{ cm}^3$. A volume more than <u>3% larger</u> than that of solution formed (2000cm³).





- Plot V curve from the known values. (V₁= 40.727, V₂= 18.068, V $_{(a)x_1=0.3} = 24.025$)
- Draw tangent line to the V curve @x₁=0.3 Obtain values V₁, V₂
- Now construct V_1 , V_2 by the same method. (Or substitute in a given equation as in ex. 11.4)
- From intercept at $x_1=0 \rightarrow -V_1^{\infty}$ From intercept at $x_1=1 \rightarrow -V_2^{\infty}$
- Note that V_1 curve becomes horizontal (slope = 0) ($dV_1 / dx_1 = 0$) at $x_1 = 1$ And V_2 curve becomes horizontal (slope = 0) ($dV_2 / dx_1 = 0$) at $x_1 = 0$ This is required by Gibbs/Duhem equation $\sum x_i dM_i = 0$ (11.14)

It becomes $x_1 d^{-}V_1 + x_2 d^{-}V_2 = 0$ Divide by dx1 and arrange, $d^{-}V_1/dx_1 = -x_2/x_1 d^{-}V_2/dx_1$

- The results show: dV_1/dx_1 and dV_2/dx_1 must be of opposite signs.
- Read <u>Ex.11.4</u>

Plot values of V_1 , V_2 and V for the binary solution methanol(1)/water(2) at 25°c as function of x_1 .

11.4 Ideal Gas Mixtures

$$\implies m_{i}^{i2}(T \circ P) = m_{i}^{i2}(T \circ P_{i})$$
 (11.21)
But $m_{i}^{i2} \neq v_{i}^{i2}$

* For Properties indep. of Pressure, such as
$$(H - U)$$

 $H^{ij} = H_{i}^{ij}$ (11.22)
 $H^{ij} = \sum_{j=1}^{ij} H_{i}^{ij}$ (11.23)
 $H^{ij} - \sum_{j=1}^{ij} H_{i}^{ij} = 0$
Enchalpy change of mixing
* For Property def. on Pressure at Embropy²²
 $\overline{S}_{i}^{ij}(\overline{T}CP) = \widehat{S}_{i}^{ij}(\overline{T},P) - R \ln \vartheta_{i}^{ij}$
or
 $\overline{S}_{i}^{ij} = S_{i}^{ij} - R \ln \vartheta_{i}^{ij}$ (11.24)
By the summability eq'n $M = \Sigma \vartheta_{i} M_{i}^{ij}$ or $S^{ij} = \Sigma \vartheta_{i} S_{i}^{ij}$
 $\overline{S}_{i}^{ij} = \Sigma \vartheta_{i}^{ij} - R \Sigma \vartheta_{i} M_{i}^{ij}$ (11.26)
Earrowse, $S^{ij} - \Sigma \vartheta_{i}^{ij} S_{i}^{ij} = R \Sigma \vartheta_{i} \ln \vartheta_{i}^{ij}$ Gmeropy change for $\overline{M} \Sigma \vartheta_{i}^{ij}$

Problem 11.2

11.2

$$\frac{M_{A}}{partia} \frac{Ar}{2sord} \quad fix \qquad Ar \\
\frac{M_{A}}{partia} \frac{Ar}{2sord} \quad fix \qquad Ar \\
\frac{M_{A}}{partia} \frac{Ar}{2sord} \quad fix \qquad Ar \\
M_{A} \approx diadeticg \\
N_{A} \leq R \quad ideal detes \\
C_{M_{A}} - S_{R} \quad C_{M_{A}} = \frac{3}{2}R \\
\frac{for \ closed \ systemm , \ adjadatic ; fixed volume \ systemm \\
\hline
\Delta U = 0$$
for ideal des $\Delta U = C_{V} \Delta T$

$$\frac{ArT}{m} \quad SO = 0 \quad DU = C_{V} \Delta T \\
= \frac{N_{A}}{N_{A}} \frac{C_{V}}{C_{V}} (T - T_{A}) + \frac{N_{A}}{C_{M_{A}}} \frac{C_{V}}{C_{V}} (T - T_{A}) = 0 \\
\frac{Golve \ for \ T}{P} \quad M_{A} = \frac{N_{A}}{R_{A}} \quad M_{A} = \frac{N_{A}}{R_{A}} \\
= \frac{n^{L}RT}{\frac{RT}{R}} = \frac{N_{M_{A}}RT_{RL}}{\frac{N_{A}}{R_{A}}} = \frac{N_{A}R}{R_{A}} \\
= \frac{n^{L}RT}{\frac{RT}{R}} = \frac{N_{M_{A}}RT_{RL}}{\frac{N_{A}}{R_{A}}} = \frac{N_{A}R}{R_{A}} \\
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= \frac{n^{L}RT}{\frac{R}{R}} = \frac{N_{M_{A}}RT_{RL}}{\frac{R}{R}} = \frac{N_{A}R}{R} \\
= \frac{N}{R} = \frac{N}{R} \\
= \frac{N}{R} = \frac{N}{R} \\
= \frac{N}{R} \\$$

New Calculate Energy by two step Pach;
(D) Bring individual ges to mixture TXP
(D) mix genes (D) mix. TXP.

$$\frac{1}{\Delta S} = \Delta S_{M_{1}} + \Delta S_$$

* Application of equili. Criteria is Facilated by the use of Er Fugacity" * The origine of fugacity concept comes from egn 11.27 $G^{\prime 2} = \Gamma(T) + RT \ln P$ Validonly for Pure species i in the ideal-gas state. * For Real Fluid, write an analoge eq'n: $G_{i} = f_{i}(T) + RT \ln f_{i}$ (11.30) * Fugacity (F) : is a thermodynamic function used in Place of Partial Pressure in rxns involving real Joses & mixtures. * subtract 11.27 from 11.30 $G_{i} - G_{i}^{i} = RT \ln \frac{F_{i}}{P}$ $G_{i}^{R} = F_{i} \log \operatorname{city} \operatorname{coeff}.$ $G_{i} = F_{i} \operatorname{coeff}.$ $G_{i} = F_{i} \operatorname{coeff}.$ $(\operatorname{dimensionless})$

11.5 Fugacity and Fugacity Coefficient: Pure Species

* Fugacity:
Fugacity:
Fugacity Determination:

$$f'^2 = P (11.32)$$

Fugacity Determination:
(*) PVT Data
 $\ln \phi_i = \int_0^P (2; -1) \frac{dP}{P} (come 7) (11.35)$
(*) Cubic eques
 $\ln \phi_i = 2; -1 - \ln (2; -\beta_i) - \gamma_i T_i (11.17)$
(*) Let come core for the fugacity coeff. (Jeves)
 $\ln p_i = 2; -1 - \ln (2; -\beta_i) - \gamma_i T_i (11.17)$
(*) Inthe come core for the fugacity coeff. (Jeves)
 $\ln p_i = 2; -1 - \ln (2; -\beta_i) - \gamma_i T_i (11.17)$
(*) Inthe come core of h^2
 $\ln p_i = 2; -1 - \ln (2; -\beta_i) - \gamma_i T_i (11.17)$
(*) Inthe come core of h^2
 $\ln p_i = 2; -1 - \ln (2; -\beta_i) - \gamma_i T_i (11.17)$
(*) Let Kenner come of h^2
 $\ln p_i = 2; -1 - \ln (2; -\beta_i) - \gamma_i T_i (11.17)$
(*) Let Kenner come of h^2
 $\ln \phi = \frac{P}{T_p} - \frac{P}{T_p} (6^0 + w 8^1)$
 $\int \frac{1}{\sqrt{1 + c}} \frac{P}{T_p} = \frac{P}{T_p} (6^0 + w 8^1)$
 $\int \frac{1}{\sqrt{1 + c}} \frac{P}{T_p} = \frac{P}{T_p} (6^0 + w 8^1)$
 $\int \frac{1}{\sqrt{1 + c}} \frac{P}{T_p} \frac{P}{T_p} = \frac{P}{T_p} (6^0 + w 8^1)$
 $\int \frac{1}{\sqrt{1 + c}} \frac{P}{T_p} \frac{P}{T_p}$

Hit Calc.
$$\phi$$
 and f bar by the Rt $\frac{1}{24}$ of state is Compare
with volues office from a suitable gene carr.
© Acetylene @ 325K & 15 har
here APP. B , for a cecylare
 $T_{c} = 3\pi 8.3 k$ $P_{c} = 61.39 har$ $w = 0.187$
 $T_{r} = \frac{T}{T_{c}} = 1.054$ $P_{r} = \frac{P}{P_{c}} = 0.244$
 $P = \mathcal{R} \frac{V_{r}}{T_{r}} (3.50) \Rightarrow P = 0.02$
 $q = \frac{WalTD}{32 T_{r}} (3.50)$ from back 3.1
 $T = \frac{q}{2} \frac{Q}{2} \frac{V_{r}}{T_{r}} = \frac{1}{2} \frac{Q}{2} \frac{Q}{2} \frac{W}{T_{r}} = \frac{Q}$

Continue iteration till Z = 0.925

(P * 1 From (6.626) . I = In (2+6B) $\Rightarrow \phi_i = exp[$ = exp[0.925 - 1 - ln(0.925 - 0.02) - (4.559)(-= 0.93] $P_{i} = \Phi_{i}P_{i} = (0.93)(15) = 13.95$

Generalized Correlation

second Parto @ 15 box -> we by gen. corr. vie Virial e from APPB for Acetylere Te= 308.3 K Pe= 61.39 ber w = 0.187 $P_{\mathbf{F}} = \frac{P}{P_{c}} = 0.244$ $T_r = \frac{T}{T_r} = 1.054$ B = 6.083 - 0.422 (3.61) = 0.083 - 0.422 = -0.3049 (1.054)1.6 $\dot{B} = 0.139 - \frac{0.172}{T_r^{4.2}}$ (3.62) = 0.001 $\varphi = exp\left[\frac{P_r}{T} \left(B^6 + wB\right)\right] \qquad (11.65)$ 0.932 F. = \$P; = (0.932) (15) = 13.98

VaPor - liquid Equilibrium For Pure species: $G'_{i} = \int_{i}^{v} (T) + R T \ln R^{V} (11.38 a)$ G; = (; (T) + RT INF. (11.386) By Liffrence $G_{i}^{*} - G_{j}^{L} = RT \ln \frac{F_{i}}{F^{L}}$ ~ G. - G. = 0 (6.66) = $F_i^{V} = F_i^{V} = F_i^{Sat}$ (11.38) $\Phi_i^{Sat} = \frac{F_i^{Sat}}{P_i^{Sat}}$ (1) \$ = \$ = \$ at (11.24) "I value of said lig. or said vapor. > For a fure species Coexisting liquid & vapor phares are in equilibrium when they have the same T &P and (Fuzacing). Fugacity of Pure liquids D sugaring coeff. of said vapor \$ at = \$ - Integral of (11.34) Ind; = f(2;-1) df - (11.40) Find Fig = \$ sat prat DAS poor P, state said lig. -> Compressed lig. From engerity chunge conditing from $\frac{F_i}{F_i} = \frac{V_i^L (P - P_i^{-Sac})}{R T}$ $= F_{i}^{sat} = \phi_{i}^{sat} p_{i}^{sat} \xrightarrow{Po y_{kt} ing factor}$ $= \int F_{i} = \phi_{i}^{sat} p_{i}^{sat} \xrightarrow{Po y_{kt} ing factor}$ $= \int \left(F_{i} = \phi_{i}^{sat} p_{i}^{sat} + p_{i}^{s$ (Ex 11.5)

EX. 11.5 H20 @ T= 300°C Pup to logooo kPa (100 ber) Calc. volves of f; and of from Laba in steam tables & plot VSP. Sol'n: الفرفي مذال فوال المعاني ال * write enja 11.34 twice, For a state at Pressure P G:= F. (+) + R T Jaf: & For a low Premure ref. state G. = F. (7) + R7 In F. * The difference In Fin = 1 (G; -G;) * " by definition G; = H; - TSi $\ln \frac{f}{f^{\star}} = \frac{1}{RT} \left[\frac{H-H_{1}^{\star}}{T} - (S_{1} - S_{1}^{\star}) \right] \qquad (A)$ * From sbeam tables @ 300°C, lowert Pressure, IKPa (F-2) :. for Practical reasons can be orsumed IDEAL GAS where $\vec{F} = P^* = 1$ KPa (As we said for ideal gos $\vec{F}^2 = P$) and H* = 3,076.8 J S; = 10.345 J * For the state of superheated steam @ 300°C for various Pressures from IKPa to the Sola Pressure of 8,592.7 KA apply eq' Q. (all 1) P.721 T=300 is F.1 (1) لعد المانتروسة معدد عندى (١٩). For example, @ P= 4000 kpa & 300°C (F.2) P.711 H;=2,962 5/2 S;=6.3642 3/2K 3002 said Press. Superheated Huid

To inversion in gin (b) (correct for units
$$R=3034$$
 $\frac{1}{2}$)
Bule 1/2 by more (18.015)
In $\frac{1}{5^{4}} = 18.015$
 $\frac{1}{5^{4}} = 18.015$
 $\frac{1}{5^{4}} = 37611.20$
 $\frac{1}{5^{4}} = 37621.20$
 $\frac{1}{5^{4}} = \frac{1}{5^{4}} = \frac{1}{5^{4}$



Comments on fig. 11.3:

- f_i starts at the origin.
- Deviation from ideality (dashed line) increases as pressure increase.
- At Pi^{sat} there is discontinuity in f_i curve slope.
- Fugacity of liquid water at 300°c is weak function of pressure. (Characteristics of liquids at temp. well below T_c).
- ϕ_i decreases from unity steadily from its zero pressure value as the pressure raises.
- Then decrease rapidly in the liquid region as a result of fugacity behavior.



11.6 Fugacity and Fugacity Coefficient: Species in Solution

11.8 The Ideal Solution

* Similar to ideal ges mixtures. (change iz by id) (N.8) * Replace Residual Properties / by Excens properties (E) (sec. 11.9)