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,

$$
\mu_i \equiv \left[\partial(nG) / \partial n_i \right]_{P,T,nj} \tag{11.1}
$$

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

$$
\mu_i^{\alpha} = \mu_i^{\beta} \qquad (i=1,2,\ldots,N)
$$

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**

$$
M_i \equiv \left[\partial(nM) / \partial n_i \right]_{P,T,nj}
$$
 (11.7)

Partial molar property of species i in solution $\overline{U_i}$, $\overline{H_i}$, $\overline{S_i}$, $\overline{G_i}$,etc.

It is a response function, 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:

$$
\mathbf{A}\text{-}\n\qquad\n\mathbf{M} = \sum_{i} \mathbf{x}_i \mathbf{M}_i\n\qquad\n\mathbf{M} = \sum_{i} \mathbf{n}_i \mathbf{M}_i\n\qquad (11.11)
$$
\n
$$
\mathbf{n}\mathbf{M} = \sum_{i} \mathbf{n}_i \mathbf{M}_i\n\qquad (11.12)
$$

"Summability Relations"

B- Gibbs/Duhem equation

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

At constant T and P

$$
\sum x_i \, d^{\top} M_i = 0 \tag{11.14}
$$

• In summary,

M, Solution Properties.

 \bar{M} _i, Partial Properties.

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

 $\mathbf{M}_1 = \mathbf{M} + \mathbf{x}_2 \quad \mathbf{d}\mathbf{M}/\mathbf{dx}_1$ (11.15) $\mathbf{M}_2 = \mathbf{M} + \mathbf{x}_1 \quad \mathbf{d}\mathbf{M}/\mathbf{dx}_1$ (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.**

- **Values of intercept,**

 $\mathbf{I}_1 = \mathbf{M}_1$, $\mathbf{I}_2 = \mathbf{M}_2$ **The tangent intercepts gives directly the partial properties.**

- **The intercepts shift as point tangency moves along the curve and the limiting value are indicated by fig 11.1 (b).**
- At pure species $2 [(x_1=0), (x_2=1)]$ **Subs. in 11.16,** $M_2 = M_2$ **The molar property = partial property.**

The opposite intercept gives $\overline{M_1} = \overline{M_1}^{\infty}$ **(Partial property of species 1 when it** is present at infinite dilution)

- **Similar at pure species 1** $[(x_1=1), (x_2=0)]$ **Subs. in 11.16,** $M_1 = M_1$ **The molar property = partial property.**

The opposite intercept gives $\overline{M_2} = M_2^{\infty}$ (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:

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 $V^t = 2,000$ cm³, the total number of moles required is:

$$
n = \frac{V^t}{V} = \frac{2,000}{24.025} = 83.246 \text{ mol}
$$

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

 $n_1 = (0.3)(83.246) = 24.974$ $n_2 = (0.7)(83.246) = 58.272$ mol

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

$$
V_1' = (24.974)(40.727) = 1,017
$$
 $V_2' = (58.272)(18.068) = 1,053$ cm

Note that the simple sum of the initial volumes $= 2.070$ cm³. A volume more than 3% larger than that of solution formed (2000 $cm³$).

- Plot V curve from the known values. $(V_1=40.727, V_2=18.068, V_{(Q)X_1=0.3}=24.025)$
- Draw tangent line to the V curve $@x_1=0.3$ Obtain values \overline{V}_1 , \overline{V}_2
- Now construct \overline{V}_1 , \overline{V}_2 by the same method. (Or substitute in a given equation as in ex. 11.4)
- From intercept at $x_1 = 0 \rightarrow \overline{V_1}^{\infty}$ From intercept at $x_1 = 1 \rightarrow \overline{V_2}$ ∞
- Note that \overline{V}_1 curve becomes horizontal (slope = 0) ($\overline{d}V_1 / dx_1 = 0$) at $x_1 = 1$ And V_2 curve becomes horizontal (slope = 0) (d⁻V₂ / dx₁ = 0) at x₁ = 0 This is required by Gibbs/Duhem equation $\sum x_i d^m M_i = 0$ (11.14)

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

- The results show: $d^{\top}V_1/dx_1$ and $d^{\top}V_2/dx_1$ must be of opposite signs.
- **Read Ex.11.4**

Plot values of \bar{y}_1, \bar{y}_2 and V for the binary solution methanol(1)/water(2) at 25^oc as function of x₁.

11.4 Ideal Gas Mixtures

$$
\Rightarrow \bar{m}_{i}^{12} \quad (\tau \circ \rho) = m_{i}^{12} \quad (\tau_{1}, \rho) \quad (1, 21)
$$

For Problems indel, of Perivative, such as
$$
(H \cap U)
$$

\n
$$
\frac{11^{12} \div h; \quad (11.12)}{H^{12} = 59; h; \quad (11.23)}
$$
\n
$$
\frac{11^{12} - 59; h; \quad (11.23)}{H^{12} - 59; h; \quad (11.23)}
$$
\n
$$
\frac{11^{12} - 59; h; \quad (11.23)}{H^{12} - 59; \quad (11.23)}
$$
\nFor Property 4.8.8. The answer of mixing is $\frac{13}{5}$, $(7, \rho) = R \ln 9$;

\n
$$
\frac{13}{5!} = \frac{13}{5!} = R \ln 9; \quad (11.24)
$$
\nBy the summability eq'n $m = \sum y; m; \quad \text{or} \quad \frac{13}{5} \leq \sum y; \quad \$

Problem 11.2

11.2
\n
$$
\frac{m_2}{32000}
$$
 $\frac{F_{12}}{1360}$
\n
$$
\frac{F_{20}}{13600}
$$
 $\frac{F_{12}}{13600}$
\n
$$
\frac{F_{20}}{13600}
$$

\n
$$
\frac{F_{20}}{13600}
$$

\n
$$
\frac{F_{20}}{13600}
$$

\n
$$
\frac{F_{20}}{13600}
$$

\n
$$
\frac{F_{20}}{1360}
$$
<

New Calculate Enckary by two step *Path*:
\nOb Birny induced by the miskure
$$
TRP
$$

\nOnix proves @ mix. TRP .
\n
$$
5S = SS_{n_1} + DS_{n_1} + DS_{n_1}
$$
\n
$$
SS_{n_2} = n_{n_1} [C_{n_2} ln(\frac{1}{T_{n_2}}) - R ln(\frac{P}{n_{n_2}})]
$$
\n
$$
SS_{nr} = n_{nr} [C_{n_1} ln(\frac{1}{T_{n_1}}) - R ln(\frac{P}{n_{n_1}})]
$$
\n
$$
W_{n_2} = n_{nr} [C_{n_2} ln(\frac{1}{T_{n_2}}) - R ln(\frac{P}{n_{n_1}})]
$$
\n
$$
W_{n_1} = n^k (-RS_{n_1} ln \frac{n_1}{n_1})
$$
\n
$$
W_{n_2} = n^k (-RS_{n_1} ln \frac{n_1}{n_1})
$$
\n
$$
W_{n_1} = n_{nr} [C_{n_1} ln \frac{n_1}{n_1} - \frac{n_1}{n_1} -
$$

* Application of equili. Criteria is Facilated by the use of ce Fugacion" * The origine of fugacity concept comes from egn 11.27 $G^{\prime} = \int_{i}^{1} (T) + RT \ln P$ Valid only for Pure species i in the ideal-Jas state. * For Real Fluid, write an analoge eq'n: $G_i = \int_{i}^{1} (T) + RT \ln f_i$ (11.30) * Fugacity (F) : is athermodynamic function uzed in Place of Partial Pressure in rxns involving real joses & mixtures. * subtract 11.27 from 11.30 $G_i - G_i^{\dagger} = RT \ln \frac{F_i}{\rho}$
 $G_i^R = \mu$ acity coeff.
 $G = RT \ln \phi_i$ (11.31)
 $\boxed{\frac{P_i}{\rho} = \phi_i}$ (11.34)

(dimensionless)

11.5 Fugacity and Fugacity Coefficient: Pure Species

$$
x \rightarrow \text{Fugacity}
$$
\n
$$
y = \frac{1}{2} \int \frac{1}{2} \
$$

Ī

11-XI Calc.
$$
\phi
$$
 and f be a by the R. $\frac{R}{2}$ of s to be a complex
\n1. $\frac{R}{2}$ to the $\frac{R}{2}$ to the $\frac{R}{2}$ to the $\frac{R}{2}$.

\n2. $\frac{R}{2}$ is a complex

\n3. $\frac{R}{2}$ is a complex

\n4. $\frac{1}{2}$ is a 3.80

\n5. $\frac{1}{2}$ is a 3.80

\n6. $\frac{1}{2}$ is a 3.80

\n7. $\frac{1}{2}$ is a 3.80

\n8. $\frac{R}{2}$ is a 3.80

\n9. $\frac{R}{2}$ is a 3.80

\n1. $\frac{R}{2}$

Continue iteration till $Z = 0.925$

$$
\Theta_{*} \quad 1 \quad from \quad (6.62b) \quad \mathcal{I} = \{n \left(\frac{6 \times 60}{6 \times 60}\right)\} = \frac{3.0214}{4}
$$
\n
$$
\Theta_{*} \quad \{n\phi_{i} = \phi_{i-1} - 1 \cdot n \cdot \epsilon_{i-1} = \theta_{i}\} - \phi_{i} \quad \{1, \frac{3.0346}{400}\} = \frac{3.0214}{4}
$$
\n
$$
= \phi_{i} = \exp\left[\frac{0.925}{4000}\right] = \frac{3.0975}{40000}
$$
\n
$$
= \exp\left[\frac{0.925}{4000}\right] = \frac{3.975}{40000}
$$
\n
$$
= \frac{3.0975}{400000}
$$

Generalized Correlation

second Part @ 15 box => Le by Jen. corr. use Virial from APPB for Acceptere $T_{\mathbf{C}}$ 308.3 k $P_{\mathbf{C}} = 61.39$ ber $W = 0.187$ $P_1 = P_2 = 0.244$ $T_r = \frac{r}{T_c} = 1.6$ Sq $B^{\circ} = 6.083 - \frac{0.422}{7^{1.6}}$ (3.61) $= 0.023 - \frac{0.422}{(1.054)^{1.6}} = -0.3049$ $\beta = 0.139 - \frac{0.172}{T_1^{4}2}$ (3.62) $= 0.001$ $\phi = \exp \left[\frac{Pr}{I} (B^6 + w \hat{B}) \right] \qquad (11.65)$ = $exp\left[-\frac{e^{i2a}}{1+cos^{2}}\left(-e^{i30a}+(-e^{i18a})(e^{i00})\right)\right]$ 0.932 $F_i = \phi_i P_j = (\sigma_{-932}) \cos \phi_{-13.98}$

vapor - liquid Equilibrium for Pure species: $G_i = \int_{I} (T^3 + RT) n f_i^{V}$ (11.38 a) $G_i^L = F_i(T) + RT \ln F_i^L$ (11.386) By Liffrance $G_{j}^{v} - G_{j}^{L} = RT ln \frac{F_{j}}{F_{j}}$ $G_i - G_i^L = 0$ (6.66) $F_i^k = F_i^k = F_i^{s_{\text{ack}}}$ (11.38) $\phi_i^s = \frac{F_i^{s_{\text{ack}}}}{s_{\text{left}}}$ (1) $\phi_i^v = \phi_j^t = \phi_i^{s_{a_{t-1}}}$ (11.4) There of said 1_{i_1} , or said rapor. for afure species coexisting lipsid & vapor phases are in equilibrium when they have the same T 8P and (funzacion) Fugueiog of Pure liquido 1 Fugacion coeff. of said valor \$, at - Integral of (11.34) $\ln \phi_i = \int_{0}^{P} (B_i - 1) \frac{d\rho}{\rho}$ $=(1.40)$ find $F_j^{Sat} = \phi_j^{sat}$ p sats B As ρ^{sav} , state satisfied by Comprensed lig. From enjoyity change

valid find the set of soc = $\frac{v_i^L (P - P_i^{s_{\text{adv}}})}{R + P_i^{s_{\text{adv}}}}$ $B_i - G_i$
 $\Rightarrow F_i$ ^{sac} = ϕ_i ^{sac} p^{sac} Po Inting factor
 $\Rightarrow F_i = \phi_i$ ^{sac} p^{sac} exp $\frac{V_i}{R}$ (p-p) (n.44) $(x11.6)$

 $EX. 11.5$ H_{20} @ $T:300^{\circ}C$ P up to log ooo KPa (100 ber) Calc. volves of f; and ϕ , from data in steam tables 8 plot vsP. Sol'n: $\frac{3!3!1!}{(Vapor then |quid)}$ $*$ write en^2 11.34 buile, For a scale at Provence P $G_i = F_i(T) + 8T \log P_i$ 8 for a low Prevoure ref. scote 6.5 = $(1) + 87 ln \frac{1}{6}$ * The difference In $\frac{f_i}{f_i^*} = \frac{1}{RT} (G_i - G_i^*)$ $*$: by definition $G_i = H_i - T S_i$ $\ln \frac{f}{f^*} = \frac{1}{RT} \left[\frac{H-H_1}{T} - (S_1 - S_1^*) \right]$ * From Speam bables @ 300°C, lowert Pressure, 1 KPa : for Practical reasons can be origined IDEAL GAS where $\vec{f} = \vec{P}^* = 1$ \vec{P} (As we said for ideal \vec{P} \vec{P} = \vec{P}) and $H_i^* = 3,076.8 \frac{3}{3}$ $S_i = 10.345 \frac{J}{3k}$ * For the state of superheated steam @ 300C for various Pressures from IKPa to the Soln Pressure of [8,592.7] the α p/y ϵ η' α . (adel 1) P.721 T=300C in F.1 3) hall P=3,400 منز تصويرات الدولوجية ت بن مه معده P=3,400 بعد المسائدوستم وجيهو عندى (.14) . For example, @ $\begin{bmatrix} P = 4000 & kPa \end{bmatrix}$ & 300°C (F.2) P.711 $H_i = 2,962$ $5/2$ 5.5642 $3/2K$ 3008 saidpress. Superheard 14wid

Comments on fig. 11.3:

- \bullet 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).
- \bullet 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 200 mixtures. (Change if by id) (1118)
(1118)
* Reflace Residual Profusies by EXCess ProPerties (E) (Sec. 11.9)