Solution Thermodynamics

- Fundamental property relation
- Chemical potential and Phase Equilibria
- Partial properties
- Ideal Gas Mixtures
- Fugacity and Fugacity Coefficients,
- Activity and Activity Coefficients
- Property changes of Mixing

Solution Thermodynamics

Why we have to study Solution Thermodynamics?.....

- In the chemical and pharmaceutical industries multicomponent gases or liquids commonly undergo composition changes as the result of mixing and separation processes, the transfer of species from one phase to another, or chemical reaction.
- Because the property of such systems depend strongly on composition as well as on temperature and pressure.

The prediction of the equilibrium existing between phases and to calculate phase and chemical reaction equilibria.

Solution Thermodynamics

What is the most important property ?.....

- ……G…….

➢For pure component;

$G = f(T, P)$

➢ For a homogeneous mixture e.g. containing *i* components mixture;

$G = f(T, P, n_1, n_2, \ldots, n_i)$

Fundamental property relations

- Total Gibbs energy change of any **CLOSED system:** $d(nG) = (nV)dP - (nS)dT$

  *applied to a single phase fluid in a closed system wherein no chemical reactions occurs & the composition is constant.

- At constant-T and constant-P:

$$\left[\frac{\partial(nG)}{\partial P}\right]_{T,n} = nV \quad \text{and} \quad \left[\frac{\partial(nG)}{\partial T}\right]_{P,n} = -nS$$

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

The subscript n indicates that the numbers of moles of all chemical species are held constant.

Fundamental property relations

- For the case of single-phase and open system, nG becomes a function of P, T & numbers of moles of chemical species:

$$nG = f(P, T, n_1, n_2, \ldots, n_i, \ldots)$$

where total differential of nG is then:

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

*where n_i is the no of moles of species i.

* n_j indicates that all mole no except the ith are held constant.

Chemical Potential

- By definition, chemical potential of species *i* in the mixture is:

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

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

This equation is a fundamental property relation for SINGLE-PHASE FLUID SYSTEM of variable mass & composition

When n = 1,

$$dG = VdP - SdT + \sum_i \mu_i dx_i$$

Fundamental property relations

- For special case of one mol of solution, n=1 & $n_i = x_i$,

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

becomes

$$dG = VdP - SdT + \sum_i \mu_i dx_i$$

$$G = f(T, P, x_1, x_2, \ldots x_i, \ldots)$$

G as a function of T, P and x_i

At constant T & x:

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

At constant P & x:

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,x}$$

At constant P & x:

$$H = G - T\left(\frac{\partial G}{\partial T}\right)_{P,x}$$

from $G = H - TS$

Chemical potential and phase equilibria

- For a **CLOSED** system consisting of **TWO** phases in equilibrium, **each individual phase** is **OPEN** to other (mass transfer between phases may occur).

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

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

phase

Presumption: At equilibrium, T & P are the same in all phases.

Chemical potential and phase equilibria

- The change in total Gibbs energy of the two-phase system is the **sum** of these equations:

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

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

+

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

Reduced to this form:

$$nM = (nM)^{\alpha} + (nM)^{\beta}$$

Total system property

$$nM = (nM)^{\alpha} + (nM)^{\beta}$$

Chemical potential and phase equilibria

- Total Gibbs energy change of any **CLOSED system:**

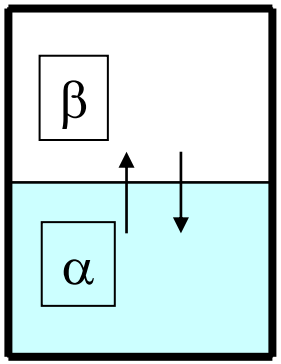
$$\boldsymbol{d(nG) = (nV)dP - (nS)dT}$$

- At equilibrium,

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

The changes of dn_i^{α} & dn_i^{β} result from mass transfer btween the phases.

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



Therefore,

$$\sum_i \mu_i^{\alpha} dn_i^{\alpha} + \sum_i \mu_i^{\beta} \left(-dn_i^{\alpha}\right) = 0$$

$$\sum_i \left(\mu_i^{\alpha} - \mu_i^{\beta}\right) dn_i^{\alpha} = 0$$

Chemical potential and phase equilibria

- Since $\sum_i \left(\mu_i^{\alpha} - \mu_i^{\beta}\right) dn_i^{\alpha} = 0$

Therefore, $\mu_i^{\alpha} - \mu_i^{\beta} = 0$ or $\mu_i^{\alpha} = \mu_i^{\beta}$

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

Multiple phases at the same T & P are in equilibrium when the chemical potential of each species is the SAME in all phases.

Partial Properties

Partial molar property, $\overline{M}_i$ of species i in solution,

$$\overline{M}_i \equiv \left[\frac{\partial(nM)}{\partial n_i}\right]_{P,T,n_j}$$

The partial molar property: any extensive property of a solution changes with respect to the number of moles of any component i in the solution at constant T, P and composition of the others.

Partial Properties

- Partial properties can be expressed on a unit mass basis and on a mole basis
- If n (mole) is replaced by m (mass), it is called partial specific property rather than partial molar property
- Three kinds of properties used in solution thermodynamics:
  - Solution properties $M(V, U, H, S)$
  - Partial properties $\overline{M}_i(\overline{V}_i, \overline{U}_i, \overline{H}_i, \overline{S}_i)$
  - Pure-species properties $M_i(V_i, U_i, H_i, S_i)$

Partial Properties

Since $$\overline{M}_i \equiv \left[\frac{\partial(nM)}{\partial n_i}\right]_{P,T,n_j}$$

Therefore,

$$\overline{G}_i = \left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_j} \quad \text{or} \quad \boxed{\overline{G}_i \equiv \mu_i}$$

Because:

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

Partial Properties

The total thermodynamic properties of a homogeneous phase are functions of T, P, and the no of moles of individual species.

$$nM = \mathrm{M}(T, P, n_1, n_2, \ldots, n_i, \ldots)$$

The total differential of *nM* is:

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

$$\overline{M}_i \equiv \left[\frac{\partial (nM)}{\partial n_i}\right]_{P,T,n_j}$$

At constant n,

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

*x denotes differentiation at constant composition

Partial Properties

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

$$n_i = x_i n$$

$$dn_i = d(x_i n)$$

$$d(x_i n) = x_i dn + n dx_i$$

$$d(nM) = n dM + M dn$$

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

Partial Properties

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

Factorizing *n* and *dn* terms,

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

Mathematically,

$$dM - \left(\frac{\partial M}{\partial P}\right)_{T,x} dP - \left(\frac{\partial M}{\partial T}\right)_{P,x} dT - \sum_i \overline{M}_i dx_i = 0$$

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

$$M - \sum_i x_i \overline{M}_i = 0$$

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

$x_i n$

$$\boxed{nM = \sum_i n_i \overline{M}_i}$$

Calculation of mixture properties from partial properties

Partial Properties

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

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

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

$$dM = d\left(\sum_i x_i \overline{M}_i\right)$$

Comparing

$$dM = \sum_i x_i d\overline{M}_i + \sum_i \overline{M}_i dx_i$$

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

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

Gibbs/Duhem equation

Partial properties in binary solution

For binary solution, the summability relation, $\boxed{M = \sum_i x_i \overline{M}_i}$ becomes:

$$M = x_1 \overline{M}_1 + x_2 \overline{M}_2 \qquad \text{(A)}$$

$$dM = x_1 d\overline{M}_1 + \overline{M}_1 dx_1 + x_2 d\overline{M}_2 + \overline{M}_2 dx_2 \qquad \text{(B)}$$

At constant T & P, Gibbs/Duhem eq,

$$\left(\frac{\partial M}{\partial P}\right)_{T,x} dP + \left(\frac{\partial M}{\partial T}\right)_{P,x} dT - \sum_i x_i d\overline{M}_i = 0 \xrightarrow{\text{becomes}} \sum_i x_i d\overline{M}_i = 0$$

Thus, for binary solution, Gibbs/Duhem eq. can be written as,

$$\boxed{x_1 d\overline{M}_1 + x_2 d\overline{M}_2 = 0} \qquad \text{(C)}$$

Partial properties in binary solution

Substituting (C) in (B)

$$dM = x_1 d\overline{M}_1 + \overline{M}_1 dx_1 + x_2 d\overline{M}_2 + \overline{M}_2 dx_2 \qquad \text{(B)}$$

$$dM = \overline{M}_1 dx_1 + \overline{M}_2 dx_2$$

Because $x_1+x_2=1$, $x_1=1-x_2$ and $dx_1=-dx_2$,

$$dM = \overline{M}_1 dx_1 - \overline{M}_2 dx_1$$

$$dM = \left(\overline{M}_1 - \overline{M}_2\right) dx_1$$

$$\frac{dM}{dx_1} = \left(\overline{M}_1 - \overline{M}_2\right)$$

Partial properties in binary solution

The summability relation, $M = x_1\overline{M}_1 + x_2\overline{M}_2$ can also be written as:

$$M = (1 - x_2)\overline{M}_1 + x_2\overline{M}_2$$

$$= \overline{M}_1 - x_2\overline{M}_1 + x_2\overline{M}_2$$

$$M = \overline{M}_1 - x_2\left(\overline{M}_1 - \overline{M}_2\right)$$

$$\overline{M}_1 = M + x_2\left(\overline{M}_1 - \overline{M}_2\right)$$

$$\boxed{\overline{M}_1 = M + x_2\frac{dM}{dx_1}}$$

$$\frac{dM}{dx_1} = \left(\overline{M}_1 - \overline{M}_2\right)$$

$$M = x_1\overline{M}_1 + (1 - x_1)\overline{M}_2$$

$$= x_1\overline{M}_1 + \overline{M}_2 - x_1\overline{M}_2$$

$$M = x_1\left(\overline{M}_1 - \overline{M}_2\right) + \overline{M}_2$$

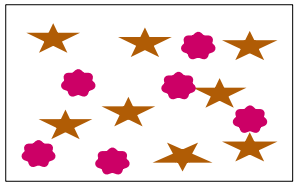
$$\overline{M}_2 = M - x_1\left(\overline{M}_1 - \overline{M}_2\right)$$

$$\boxed{\overline{M}_2 = M - x_1\frac{dM}{dx_1}}$$

The Ideal-Gas Mixture

If "n" moles of an ideal gas mixture occupy total volume "V^t" at the temperature "T", the pressure is

$$\boxed{P = \frac{nRT}{V^t}} \qquad \text{(A)}$$



If "n_i" moles of species "i" in the mixture occupy the same total volume "V^t" at the same temperature "T", the pressure is

$$\boxed{p_i = \frac{n_i RT}{V^t}} \qquad \text{(B)}$$

(B)/(A)

$$\frac{p_i}{P} = \frac{n_i}{n} = x_i \quad \Rightarrow \quad p_i = x_i P \qquad (i = 1,2, \ldots N)$$

- An ideal gas is a model gas comprised of imaginary molecules of zero volume that do not interact.
- Each chemical species in an ideal gas mixture therefore has its own private properties, uninfluenced by the presence of other species.

The Ideal-Gas Mixture

Gibbs Theorem:

A **partial molar property** (other than 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 **pressure equal to its partial pressure in the mixture**

Thus, for general partial property;

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

$$\boxed{\overline{M}_i^{ig} \neq \overline{V}_i^{ig}}$$

The enthalpy of an ideal gas is **independent** of pressure;

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

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

Also applies to other property that are independent of pressure