LECTURE

5

CHE 415 Chemical Engineering Thermodynamics II

Department of Chemical Engineering
College of Science and Engineering
Landmark University, Omu-Aran,
Kwara State.

Partial Molar Properties and Phase Equilibrium

Learning Objectives for today's lecture

- At the end of this week's lecture, you should be able to:
  – Partial molar property
  – Conceptualize the various criteria for phase equilibria and develop the Gibbs-Duhem equation.

Partial Molar Properties

- This is the hypothetical contribution that a component (specie) make to the property of the solution or system of which it is a component at a given temperature, pressure and composition.
- It is a response function, representing the change of total property nM due to addition at constant T and P of a differential amount of specie I to a finite amount of solution.
- Thus, $$\overline{M_i} = \left[\frac{\partial(nM)}{\partial n_i}\right]_{T,P,n_j} \qquad 5\text{-}1$$
  - where M represents any molar thermodynamic property of a solution in which it is a component. $\overline{M_i}$ may be $\overline{H_i}$, $\overline{S_i}$ etc.
- Previously, it has been shown that
- $$\mu_i = \left[\frac{\partial(nU)}{\partial n_i}\right]_{nS,nV,n_j} = \left[\frac{\partial(nH)}{\partial n_i}\right]_{nS,P,n_j} = \left[\frac{\partial(nA)}{\partial n_i}\right]_{nV,T,n_j} = \left[\frac{\partial(nG)}{\partial n_i}\right]_{T,P,n_j}$$
  - where n_j indicates constancy of all mole numbers other than n_i,
- We can thus write, $\mu_i = f(T,P,n_1,n_2,\ldots n_i)$ 5-2
- Differentiating totally
- $$d\mu_i = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,n} dT + \left(\frac{\partial \mu_i}{\partial P}\right)_{T,n} dP + \sum\left(\frac{\partial \mu_i}{\partial n_i}\right) dn \qquad 5\text{-}3$$

Partial Molar Properties

- Application of the reciprocating criterion to the differential expression on the RHS of eqn gives
- $\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n} = -\left[\frac{\partial (nS)}{\partial n_i}\right]_{T,P,n_j} = -\bar{S_i}$ (partial molar entropy) 5-4
- And, $\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n} = \left[\frac{\partial (nV)}{\partial n_i}\right]_{T,P,n_j} = \bar{V_i}$ (partial molar volume) 5-5
- Generally, nM = $\sum(ni.\overline{M_i})$ 5-6
- Dividing by n yields, M = $\sum(x_i.\overline{M_i})$ 5-7
  - Where x_i = mole fraction of component I in solution when M is related on mass basis, it is called partial specific property
- Therefore the three kind of properties used in solution thermodynamics are distinguished by the following symbolism:
- Solution Properties, M, for example: V, S, U, H and G
- Partial properties, $\overline{M_i}$ for example: $\bar{V_i},\ \bar{S_i},\ \bar{U_i},\ \bar{H_i},\ and\ \bar{G_i}$
- Pure specie properties, M_i for example: V_i, S_i, U_i, H_i and G_i
- Thus every equation relating molar thermodynamic properties for a constant composition solution has a counterpart analogous equation relating the corresponding partial molar properties for any component in the solution;

Developing the Gibbs-Duhem Equation

- Thus, $d\overline{U_i} = Td\overline{S_i} - Pd\overline{V_i}$ 5-8
- $d\overline{H_i} = Td\overline{S_i} + \overline{V_i}dP$ 5-9
- $d\overline{A_i} = -\overline{S_i}dT - Pd\overline{V_i}$ 5-10
- Differentiating the general eqn.5-6 yields,
- $$d(nM) = \sum_i (n_i d\overline{M_i}) + \sum_i (\overline{M_i} dn_i) \quad 5\text{-}11$$
  - Where d(nM) represents changes in T,P, or n_i's
- i.e. nM = f(T, P, n1, n2,…..ni…) 5-12
- Thus, $d(nM) = \left(\frac{\partial(nM)}{\partial T}\right)_{P,n} dT + \left(\frac{\partial(nM)}{\partial P}\right)_{T,n} dP + \sum_i (\overline{M_i} dn_i)$ 5-13
- Or, $d(nM) = n\left(\frac{\partial M}{\partial T}\right)_{P,x} dT + n\left(\frac{\partial M}{\partial P}\right)_{T,x} dP + \sum_i (\overline{M_i} dn_i)$ 5-14
- Eqns.5-13 and 5-14 can only be true simultaneously if
- $$n\left(\frac{\partial M}{\partial T}\right)_{P,x} dT + n\left(\frac{\partial M}{\partial P}\right)_{T,x} dP - \sum_i (n_i d\overline{M_i}) = 0$$
- And dividing by n gives,
- $$\left(\frac{\partial M}{\partial T}\right)_{P,x} dT + \left(\frac{\partial M}{\partial P}\right)_{T,x} dP + \sum_i (x_i d\overline{M_i}) = 0 \quad 5\text{-}15$$
- Eqn.5-15 is the Gibbs-Duhem equation, valid for any molar thermodynamic property M in a homogenous phase.

Developing the Gibbs-Duhem Equation

- At constant T and P, eqn.5-15 reduces to
- $$\sum_i (x_i d\overline{M_i}) = 0 \qquad 5\text{-}16$$
- This is the most widely used form of the Gibbs-Duhem equation used in phase equilibrium.
- A useful form of the Partial molar property expression (eqn.5-1) for numerical calculation is that which relates $\overline{M_i}$ to M and x. such an equation is
- $$\overline{M_i} = M - \sum_{k \neq i} \left[x_k \left(\frac{\partial M}{\partial x_k} \right) \right]_{T,P,x_{\ell \neq i.k}} \qquad 5\text{-}17$$
  - The index i denotes the component of interest, whereas k identifies any other component. The subscript xi indicates that the partial derivative is taken with all mole fractions held constant except i and k ($\ell \neq$ i,k).
- For example, for a binary mixture, eqn.5-17 can be derived for individual component as follows:
- $$M = x_1.\overline{M_1} + x_2.\overline{M_2} \qquad 5\text{-a}$$
- and $$dM = x_1 d\overline{M_1} + \overline{M_1} dx_1 + x_2 d\overline{M_2} + \overline{M_2} dx_2 \qquad 5\text{-b}$$
- From eqn.5-16, $$x_1 d\overline{M_1} + x_2 d\overline{M_2} = 0 \qquad 5\text{-c}$$
- Since $x_1 + x_2 = 1$
- $dx_1 = -dx_2$

Developing the Gibbs-Duhem Equation

- Eliminating dx_2 in 5-b and combining result with 5-c gives
- and $dM = \overline{M_1}dx_1 - \overline{M_2}dx_1$
- or $\frac{dM}{dx_1} = \overline{M_1} - \overline{M_2}$ 5-d
- Eliminating $\overline{M_2}$ from 5-a and 5-d, and solving for $\overline{M_1}$, yields
- $\overline{M_1} = M + x_2\frac{dM}{dx_1}$ 5-e
- Similarly, elimination of $\overline{M_1}$ and solution for $\overline{M_2}$ gives
- $\overline{M_2} = M - x_1\frac{dM}{dx_1}$ 5-f

- EXAMPLE
- The need arises in a laboratory for 2000cm^3 of an antifreeze solution consisting of 30-mol-% methanol in water. What volumes of pure methanol and of pure water at 25^{0}C must be mixed to form the 2000cm^3 of antifreeze, also at 25^{0}C? Partial molar volumes for methanol and water in a 30-mol-% methanol solution and their pure-species molar volumes, both at 25^{0}C, are:
- Methanol(1): $\overline{V_1} = 38.632\ cm^3\ mol^{-1}$ $V_1 = 40.727$ cm^3 mol^{-1}
- Water(2): $\overline{V_2} = 38.632\ cm^3\ mol^{-1}$ $V_2 = 40.727$ cm^3 mol^{-1}

SOLUTION TO EXAMPLE 1

- Eqn.5-7 is written for the molar volume of the binary antifreeze solution,
- $V = x_1\overline{V_1} + x_2\overline{V_2}$
- Substituting the known values for the mole fractions and partial volumes
- $V = (0.3)(38.632) + (0.7)(17.765) = 24.025\ cm^3\ mol^{-1}$
- Because the required total volume of solution $V^t = 2000 cm^3$, the total number of moles required is:
- $n = \frac{V^t}{V} = \frac{2000}{24.025} = 83.246\, mol.$
- of this, 30% is methanol, and 70% water:
- $n_1 = (0.3)(83.246) = 24.974$ mol
- and $n_2 = (0.7)(83.246) = 58.272$ mol
- The volume of each pure species is $V_i^t = n_i V_i$
- $V_1^t = (24.974)(40.727) = 1017\ cm^3$
- and $V_2^t = (58.272)(18.068) = 1053\ cm^3$

EXAMPLE 2

The enthalpy of a binary liquid system of species 1 and 2 at fixed T and P is represented by the equation:

$$H = 400x_1 + 600x_2 + x_1x_2(40x_1 + 20x_2)$$

Where H is in Jmol[-1]. Determine expressions for $\overline{H_1}$ and $\overline{H_2}$ as functions of x_1.

- Solution:
- Replaced x_2 by $1 - x_1$ in the given equation for H and simplify:
- $$H = 600 - 180x_1 - 20x_1^3$$
- Whence, $\frac{dH}{dx_1} = -180 - 60x_1^2$
- By eqn.5-e, $\overline{H_1} = H + x_2\frac{dH}{dx_1}$
- Then, $\overline{H_1} = 600 - 180x_1 - 20x_1^3 - 180x_2 - 60x_1^2x_2$
- Replaced x_2 by $1 - x_1$ and simplify:
- $$\overline{H_1} = 420 - 60x_1^2 + 40x_1^3$$
- By eqn.5-f $\overline{H_2} = H - x_1\frac{dH}{dx_1}$
- $$= 600 - 180x_1 - 20x_1^3 + 180x_1 + 60x_1^3$$
- or $$\overline{H_2} = 600 + 40x_1^3$$

THANK YOU
FOR
YOUR
ATTENTION!
ANY QUESTIONS?