CH365 Chemical Engineering Thermodynamics

Lesson 34
Chemical Potential and Partial Properties

Block 6 – Solution Thermodynamics

Example 10.1

The partial molar volume is defined as

$$\bar{V}_i \equiv \left[\frac{\partial(nV)}{\partial n_i}\right]_{P,T,n_j} \qquad \text{(A, page 362)}$$

What physical interpretation can be given to this equation?

It is the volume of "i" as it exists in solution.

Consider the <u>total volume</u> of an equimolar solution of alcohol and water:

$$nV\left(=V^{TOT}\right) \qquad \text{at T and P}$$

Add pure water also at T and P containing Δn_w.
Allow it to mix thoroughly and re-equilibrate.
What is the change in total volume?

$$\Delta(nV) \overset{?}{=} V_w \Delta n_w \qquad \text{experiments show this is not true}$$

$$\Delta(nV) = \bar{V}_w \Delta n_w \qquad \text{we need to change the molar property}$$

effective molar volume of water in solution

Overview

Theoretical foundations for the study of gas mixtures and liquid solutions

- Relevant to mixing, separations, and chemical reactions
- Along with T and P, compositions are essential variables

Fundamental property relationship was developed earlier.

$$dG = VdP - SdT$$

(L27 slide 8, eq. 6.11 p. 212 and PS10 problem 6.1b)

needs to be more comprehensive

- Extend to open systems with variable composition
- Define *chemical potential*

  -Phase equilibria and chemical equilibria

- Define *partial molar properties* (derived this lesson)

  -Not the same as molar properties of pure components.

  -Properties of individual species as they exist in solution

  -Composition-dependent.

  -Used to build equations for solution properties

- Define *fugacity*

  -Improvement over models based on chemical potential

- Define *excess properties*

  -Concept of ideal solution model as a reference, like ideal gases

  -The excess Gibbs energy is the basis for activity and activity coefficients

Review from Lesson 27 (derivation of fundamental relations and Maxwell's equations):

(Eq. 2.6, 1st Law, closed system, reversible)

$$d(nU) = dQ + dW$$

$$dQ_{rev} = TdS^t$$

(Eq. 5.1)

$$dQ_{rev} = Td(nS) \qquad dW_{rev} = -Pd(nV)$$

$$dW_{rev} = -PdV^t$$

(Eq. 1.3)

$$d(nU) = Td(nS) - Pd(nV)$$ (Eq. 6.1)

- Not restricted to reversible processes
- **System must be closed, and**
- **Change must be between equilibrium states.**

$$dU = TdS - PdV$$

n=1 or const. comp. (Eq.6.7)

- Includes primary properties: U, S, T, P, and V

Additional properties arise by definition:

Enthalpy: $H \equiv U + PV$ (Eq. 2.10 and 6.2)

Helmholtz Energy: $A \equiv U - TS$ (Eq. 6.3)

Gibbs Energy: $G \equiv H - TS$ (Eq. 6.4)

Fundamental Property Relations

General equations for a homogenous fluid of constant composition.

$dU = TdS - PdV$ (Eq.6.8)	$dH = TdS + VdP$ (Eq. 6.9)
$dA = -PdV - SdT$ (Eq. 6.10)	$dG = VdP - SdT$ (Eq. 6.11)

Lesson 27, Slide 8

Instructor derived 6.8 and 6.9
Cadets derived 6.10 and 6.11 in problem 6.1 of PS10

$$d(nG) = (nV)dP - (nS)dT$$

(Eq. 6.7, page 216)

Definition of Chemical Potential

We were conspicuously silent about "n" because
for a pure component in a closed system n is a constant.

(Eq.6.7, page 216)

$$d(nG) = (nV)dP - (nS)dT$$

$$nG = f(P,T) \Rightarrow \therefore d(nG) = \left(\frac{\partial(nG)}{\partial P}\right)_{T,n} dP + \left(\frac{\partial(nG)}{\partial T}\right)_{P,n} dT$$

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

Leads to Eq. 6.17

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

4th Maxwell Relation
Slide 12 L27 or p. 218

Inclusion of mole numbers in analysis leads to definition of chemical potential:

$$nG = f(P, T, n_1, n_2, \ldots, n_j)$$ more general expression

$$d(nG) = \left(\frac{\partial(nG)}{\partial P}\right)_{T,n} dP + \left(\frac{\partial(nG)}{\partial T}\right)_{P,n} dT + \left(\frac{\partial(nG)}{\partial n_1}\right)_{P,T,n_{j\neq 1}} dn_1 + \left(\frac{\partial(nG)}{\partial n_2}\right)_{P,T,n_{j\neq 2}} dn_2 + \ldots$$

$$\mu_i \equiv \left(\frac{\partial(nG)}{\partial n_i}\right)_{P,T,n_{j\neq i}}$$ (Eq. 10.1, page 359)

Fundamental Property Relation

Modified to Include Chemical Potentials

$$d(nG) = (nV)dP - (nS)dT$$ (Eq. 6.7, page 216)

$$d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i dn_i$$ (Eq. 10.2, page 359)

Special Case: n = 1 mole of solution, $n_i = x_i$

$$d(G) = V\ dP - S\ dT + \sum_i \mu_i\ dx_i$$ (Eq. 10.3, page 359)

$$nG = g(T, P, x_1, x_2, \ldots x_i, \ldots)$$

"Canonical" variables for G have changed. They are now T, P, and x_i.

$$\left(\frac{\partial G}{\partial P}\right)_{T,x} = V$$ (Eq. 10.4)

$$-\left(\frac{\partial G}{\partial T}\right)_{P,x} = S$$ (Eq. 10.5)

$$\left(\frac{\partial G}{\partial x_i}\right)_{T,P} = \mu_i$$ (Eq. 10.1)

Phase Equilibria

(Closed System)

$$d(nG) = (nV)\,dP - (nS)\,dT + \sum_i \mu_i\,dn_i$$ (Eq. 10.2, page 359)

Phase α: $$d(nG)^\alpha = (nV)^\alpha\,dP - (nS)^\alpha\,dT + \sum_i \mu_i^\alpha\,dn_i^\alpha$$

Phase β: $$d(nG)^\beta = (nV)^\beta\,dP - (nS)^\beta\,dT + \sum_i \mu_i^\beta\,dn_i^\beta$$

Sum: $$d(nG) = (nV)\,dP - (nS)\,dT + \sum_i \mu_i^\alpha\,dn_i^\alpha + \sum_i \mu_i^\beta\,dn_i^\beta$$

$$d(nG) = (nV)dP - (nS)dT$$

(Eq. 6.1, page 216, still valid for closed system)

Subtract: $$\sum_i \mu_i^\alpha\,dn_i^\alpha + \sum_i \mu_i^\beta\,dn_i^\beta = 0$$

$$dn_i^\alpha = -dn_i^\beta \Rightarrow \sum_i \left(\mu_i^\alpha - \mu_i^\beta\right)dn_i^\alpha = 0 \Rightarrow \therefore \mu_i^\alpha - \mu_i^\beta = 0$$

"Equilibrium Condition" $$\boxed{\therefore \mu_i^\alpha = \mu_i^\beta}$$ (Eq. 10.6, page 361) Very Important!

Partial Molar Properties

Molar properties of individual species as they exist in solution

$$\bar{M}_i \equiv \left[\frac{\partial(nM)}{\partial n_i}\right]_{P,T,n_{j\neq i}}$$ (Eq. 10.7, page 361)

Response function – response of "nM" to addition of "dn_i"

Total solution properties	M	V, U, H, S, G
Partial molar properties	$\bar{M}_i$	$\bar{V}_i, \bar{U}_i, \bar{H}_i, \bar{S}_i, \bar{G}_i$
Pure-species properties	M_i	V_i, U_i, H_i, S_i, G_i

Definition 10.7 gives partial molar properties from total molar property

We can reverse this and get total molar properties from partial molar properties (Problem 10.53b)

Partial molar Gibbs energy is the chemical potential:

$$\mu_i \equiv \left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_{j\neq i}} \Longleftrightarrow \bar{G}_i \equiv \mu_i$$

(Eq. 10.1, p. 359) (Eq. 10.8, p. 362)

Partial Molar Properties

Start with function "nM"

$$nM = nM(T, P, n_1, n_2, \ldots n_i, \ldots) = func(T, P, n_1, n_2, \ldots n_i, \ldots)$$

$$d(nM) = \left(\frac{\partial(nM)}{\partial P}\right)_{T,n} dP + \left(\frac{\partial(nM)}{\partial T}\right)_{P,n} dT + \sum_i \left(\frac{\partial(nM)}{\partial n_i}\right)_{T,P,n_{j\neq i}} dn_i$$

inserting equation 10.7 and assuming constant n yields:

$$d(nM) = n\left(\frac{\partial M}{\partial P}\right)_{T,x} dP + n\left(\frac{\partial M}{\partial T}\right)_{P,x} dT + \sum_i \bar{M}_i dn_i \qquad \text{(Eq. 10.9, page 364)}$$

$$\bar{M}_i \equiv \left[\frac{\partial(nM)}{\partial n_i}\right]_{P,T,n_{j\neq i}} \qquad \text{(Eq. 10.7)}$$

$$d(nM) \xrightarrow{\text{product rule}} d(nM) = ndM + Mdn$$

$$n_i = x_i n \xrightarrow{\text{product rule}} dn_i = d(x_i n) = x_i dn + ndx_i$$

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

$$\sum_i \bar{M}_i (x_i dn + ndx_i) = dn\sum_i \bar{M}_i x_i + n\sum_i \bar{M}_i dx_i$$

collect terms by n and dn:

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

Terms in brackets must each be zero.

Partial Molar Properties – Gibbs/Duhem

(1st term in brackets)

$$dM - \left(\frac{\partial M}{\partial P}\right)_{T,x} dP - \left(\frac{\partial M}{\partial T}\right)_{P,x} dT - \sum_i \bar{M}_i dx_i = 0 \Rightarrow dM = \left(\frac{\partial M}{\partial T}\right)_{P,x} dT + \left(\frac{\partial M}{\partial P}\right)_{T,x} dP + \sum_i \bar{M}_i dx_i \quad \text{(A)}$$

(Eq. 10.10, page 364)

(2nd term in brackets)

$$M - \sum_i \bar{M}_i x_i = 0 \Rightarrow M = \sum_i x_i \bar{M}_i$$

(Eq. 10.11) (homework)

or $nM = \sum_i n_i \bar{M}_i$ (Eq. 10.12)

take derivative using product rule

subtract (A) – (B)

$$dM = \sum_i x_i d\bar{M}_i + \sum_i \bar{M}_i dx_i \quad \text{(B)}$$

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

$$-\quad dM = \sum_i x_i d\bar{M}_i + \sum_i \bar{M}_i dx_i \quad \text{(B)}$$

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

(Eq. 10.13, page 365)

Gibbs-Duhem Equation (famous)

Constant T and P:

$$\sum_i x_i d\bar{M}_i = 0$$

(Eq. 10.14 p.365)

(homework)

Special Case – Binary Systems

Eq. 10.11 (slide 12) for 2 components $$M = x_1\bar{M}_1 + x_2\bar{M}_2$$

Differentiate using the product rule $$dM = x_1\,d\bar{M}_1 + \bar{M}_1\,dx_1 + x_2\,d\bar{M}_2 + \bar{M}_2\,dx_2$$

Eq 10.14, 2 components:

$$x_1\,d\bar{M}_1 + x_2\,d\bar{M}_2 = 0$$ (slide 12)

Rearrange $$dM = \left(\bar{M}_1\,dx_1 + \bar{M}_2\,dx_2\right) + \cancel{\left(x_1\,d\bar{M}_1 + x_2\,d\bar{M}_2\right)}$$

sum of mole fractions

$$x_1 + x_2 = 1$$

$$x_2 = 1 - x_1$$

$$dx_2 = -dx_1$$

$$dM = \bar{M}_1\,dx_1 - \bar{M}_2\,dx_1$$

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

$$\frac{dM}{dx_1} = \bar{M}_1 - \bar{M}_2$$

$$x_1 = 1 - x_2$$

$$M = x_1\bar{M}_1 + x_2\bar{M}_2 \quad = (1 - x_2)\bar{M}_1 + x_2\bar{M}_2 \quad = \bar{M}_1 + x_2\left(\bar{M}_2 - \bar{M}_1\right) \quad = \bar{M}_1 - x_2\left(\frac{dM}{dx_1}\right)$$

$$\bar{M}_1 = M + x_2\left(\frac{dM}{dx_1}\right)$$ (Eq. 10.15)

(homework)

$$x_2 = 1 - x_1$$

$$M = x_1\bar{M}_1 + x_2\bar{M}_2 = x_1\bar{M}_1 + (1 - x_1)\bar{M}_2 = \bar{M}_2 + x_1\left(\bar{M}_1 - \bar{M}_2\right) = \bar{M}_2 + x_1\left(\frac{dM}{dx_1}\right)$$

$$\bar{M}_2 = M - x_1\left(\frac{dM}{dx_1}\right)$$ (Eq. 10.16)

(homework)

Summary of Equations Needed for Homework

(Eq. 10.11)

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

(Eq. 10.14)

$$\sum_i x_i \, d\bar{M}_i = 0$$

Gibbs-Duhem Equation at constant T and P:

$$\bar{M}_1 = M + x_2 \left(\frac{dM}{dx_1} \right)$$

(Eq. 10.15)

$$\bar{M}_2 = M - x_1 \left(\frac{dM}{dx_1} \right)$$

(Eq. 10.16)

Questions?