CH365 Chemical Engineering Thermodynamics

Lesson 34
Chemical Potential and Partial Properties

Block 6 – Solution Thermodynamics

Review of Lesson 32 – Phase Equilibria

$$A(\text{liquid}) \rightleftharpoons A(\text{vapor})$$

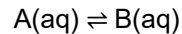$$K = \frac{\text{"activity" of products}}{\text{"activity" of reactants}}$$

$$\Delta G = -RT\ln(K)$$

"Van't Hoff Isotherm"
Derivations:
Link 1   Link 2

In general chemistry, "activity" was molar concentration:

$$A(aq) \rightleftharpoons B(aq)$$

$$K = \frac{[A(aq)]}{[B(aq)]}$$

Square brackets denote molar concentration in moles per L.

This is called an "ideal solution."

$\Delta G < 0$ "product side" favored

$\Delta G > 0$ "reactant side" favored

$\Delta G = 0$ "equilibrium"

$$G_{\text{vapor}} = G_{\text{liquid}}$$

$$dG = V\cancel{dP} - S\cancel{dT}$$

0, const P   0, const T

(Eq. 6.11)

"Clapeyron" and "Clausius-Clapeyron" equations

$$\frac{dP^{\text{sat}}}{dT} = \frac{\Delta S^{lv}}{\Delta V^{lv}} = \frac{\Delta H^{lv}}{T\Delta V^{lv}}$$ Clapeyron Equation

(Eq. 6.85)

Clausius-Clapeyron Equation

$$\Delta H^{lv} = -R\frac{d\ln(P^{\text{sat}})}{d(1/T)}$$

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 properties*

    -Properties of individual species as they exist in solution

    -Composition-dependent and distinct from molar properties of pure components. We will investigate their mathematical properties in this lesson

- Define *fugacity*

    -Improved version of chemical potential

- Define *excess properties*

    -Concept of ideal solution model as a reference, like we have 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)

$$dQ_{rev} = Td(nS)$$

$$dW_{rev} = -Pd(nV)$$

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

(Eq. 1.3)

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

$$d(nU) = Td(nS) - Pd(nV)$$

(Eq. 6.1)

$$dU = TdS - PdV$$

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

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

Additional properties arise by definition:

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

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

Gibbs Energy: $\quad G \equiv H - TS \quad$ (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)

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

$$nG = f(P,T)$$

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

Leads to Eq. 6.17

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

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

4th Maxwell Relation
Slide 12 L27 or p. 218

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

$$nG = f(P, T, n_1, n_2, ..., n_j) \quad \text{more general expression}$$

$$d(nG) = \left(\frac{\partial(nG)}{\partial P}\right)_{T,n} dP + \left(\frac{\partial(nG)}{\partial T}\right)_{P,n} dT + \left(\frac{\partial(nG)}{\partial n_1}\right)_{P,T,n_{j\neq1}} dn_1 + \left(\frac{\partial(nG)}{\partial n_2}\right)_{P,T,n_{j\neq2}} dn_2 + ...$$

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

Fundamental Property Relation

Modified to Include Chemical Potentials

$$d(nG) = (nV)dP - (nS)dT \quad \text{(Eq. 6.7, page 216)}$$

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

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

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

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

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

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

$$\text{(Eq. 10.4)} \qquad\qquad \text{(Eq. 10.5)} \qquad\qquad \text{(Eq. 10.1)}$$

Phase Equilibria

(Closed System)

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

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

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

"Equilibrium Condition"

$$\therefore \mu_i^\alpha = \mu_i^\beta$$

(Eq. 10.6, page 361)

Very Important!

Partial Molar Properties

Molar properties of individual species as they exist in solution

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

(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	$\overline{M}_i$	$\overline{V}_i, \overline{U}_i, \overline{H}_i, \overline{S}_i, \overline{G}_i$
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:

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

(Eq. 10.1, p. 359)

(Eq. 10.8, p. 362)

Example 10.1

The partial molar volume is defined as

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

What physical interpretation can be given to this equation?

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

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

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

effective molar volume of water in solution

Partial Molar Properties

Partial Molar Properties – Gibbs/Duhem

Special Case – Binary Systems

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:

(Eq. 10.15)

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

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

(Eq. 10.16)

Problem 10.53

The molar volume (cm^3 mol^{-1}) of a binary liquid mixture at T and P is given by:

$$V = 120x_1 + 70x_2 + (15x_1 + 8x_2)x_1x_2$$

(a) Find expressions for the partial molar volumes of species 1 and 2 in terms of x_1.

(b) Show that the given equation for V is recovered when these expressions are combined using Eq. 10.11.

(c) Show that these expressions satisfy Eq. 10.14.

(d) Show that $\left(d\overline{V}_1 / dx_1\right)_{x_1=1} = \left(d\overline{V}_2 / dx_1\right)_{x_1=0} = 0$.

(e) Make a plot of $V, \overline{V}_1$, and $\overline{V}_2$ versus x_1.

(f) Label points $V_1, V_2, \overline{V}_1^{x_1 \to 0}$ and $\overline{V}_2^{x_2 \to 0}$, and show their values.

Use file "PlotExampleCadet.nb" in Canvas for part (f).

Homework

Manipulation of $d\overline{M}_i$ in Equation 10.14

$$\sum_i x_i \, d\overline{M}_i = 0 \qquad \text{(Eq. 10.14)}$$

Gibbs-Duhem Equation
at constant T and P:

$$d\overline{M}_i = ?$$

$$\overline{V}_1 = 128 - 2x_1 - 20x_1^2 + 14x_1^3$$

$$d\overline{V}_1 = d\left(128 - 2x_1 - 20x_1^2 + 14x_1^3\right)$$

$$d\overline{V}_1 = d(128) - d(2x_1) - d\left(20x_1^2\right) + d\left(14x_1^3\right)$$

$$d\overline{V}_1 = d(128) - 2dx_1 - (20)(2)x_1dx_1 + (14)(3)x_1^2dx_1$$

$$d\overline{V}_1 = \left(-2 - (20)(2)x_1 + (14)(3)x_1^2\right)dx_1 = \overline{V}_1'dx_1$$

$$d\overline{V}_2 = \left(2x_1 + (14)(3)x_1^2\right)dx_1 = \overline{V}_2'dx_1$$

$$x_1d\overline{V}_1 + x_2d\overline{V}_2 = 0$$

$$x_1\overline{V}_1'd\!\!\not{x}_1 + x_2\overline{V}_2'd\!\!\not{x}_1 = 0$$

$$x_1\overline{V}_1' + x_2\overline{V}_2' = 0$$