CH365 Chemical Engineering Thermodynamics

Lesson 34
Chemical Potential and Partial Properties

Block 6 – Solution Thermodynamics

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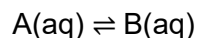
Review of Lesson 32 – Phase Equilibria

$$A(liquid) \rightleftharpoons A(vapor)$$

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

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

"Van't Hoff Isotherm"
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"

$$G_{vapor} = G_{liquid}$$

0, const P   0, const T

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

(Eq. 6.11)

"Clapeyron" and "Clausius-Clapeyron" equations

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

Clapeyron Equation

(Eq. 6.85)

Clausius-Clapeyron Equation

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

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)   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)

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

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

(Eq. 5.1) (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: $$H \equiv U + PV$$ (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)

From Lesson 27, Slide 7

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 211)

Mathematics

$$f = f(x, y) \implies dF \equiv \left(\frac{\partial f}{\partial x} \right)_y dx + \left(\frac{\partial f}{\partial y} \right)_x dy$$

$$dF = M \, dx + N \, dy \qquad \text{(Eq. 6.12)}$$

$$M \equiv \left(\frac{\partial f}{\partial x} \right)_y \qquad\qquad N \equiv \left(\frac{\partial f}{\partial y} \right)_x$$

$$\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right)_y \right)_x = \frac{\partial^2 f}{\partial x \partial y} \qquad\qquad \left(\frac{\partial N}{\partial x} \right)_y = \left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right)_x \right)_y = \frac{\partial^2 f}{\partial y \partial x}$$

From calculus, the order of differentiation does not matter

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$$

$$\therefore \left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y \qquad \text{(Eq. 6.13)}$$

Maxwell's Equations

(Maxwell's equations are based on pure mathematics)

(Fund. Prop Eq.6.8)

$$dU = TdS - PdV$$

$$U = U(S,V) \quad \Longrightarrow \quad dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\therefore T \equiv \left(\frac{\partial U}{\partial S}\right)_V \quad \text{and} \quad \therefore P \equiv -\left(\frac{\partial U}{\partial V}\right)_S$$

$$\left(\frac{\partial T}{\partial V}\right)_S = \frac{\partial^2 U}{\partial S \partial V} \qquad \left(\frac{\partial P}{\partial S}\right)_V = \frac{\partial^2 U}{\partial V \partial S}$$

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S}$$

$$\therefore \left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_V \qquad \text{(Eq. 6.14)}$$

Summary of Maxwell's Relations

These equations are the basis for a large number of equations relating thermodynamic properties.

$\left(\dfrac{\partial T}{\partial V}\right)_S = \left(\dfrac{\partial P}{\partial V}\right)_S$ (Eq. 6.14)	$\left(\dfrac{\partial T}{\partial P}\right)_S = \left(\dfrac{\partial V}{\partial S}\right)_P$ (Eq. 6.15)
$\left(\dfrac{\partial P}{\partial T}\right)_V = \left(\dfrac{\partial S}{\partial V}\right)_T$ (Eq. 6.16)	$\left(\dfrac{\partial V}{\partial T}\right)_P = -\left(\dfrac{\partial S}{\partial P}\right)_T$ (Eq. 6.17)

From Lesson 27, Slide 11

Instructor derived 6.14 and 6.17
Cadets derived 6.15 and 6.16
in problem 6.4 of PS10

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 211)

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

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

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. 213

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

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

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

$$\mu_i \equiv \left[\frac{\partial(nG)}{\partial n_i}\right]_{P,T,n_{j\neq i}} \quad \text{(Eq. 10.1, page 350)}$$

Fundamental Property Relation
(Now Modified to Include Chemical Potentials)

$$d(nG) = (nV)dP - (nS)dT \quad \text{(Eq. 6.7, page 211)}$$

$$d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i dn_i \quad \text{(Eq. 10.2, page 350)}$$

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

$$d(G) = V\,dP - S\,dT + \sum_i \mu_i\,dx_i \quad \text{(Eq. 10.3, page 350)}$$

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

"Canonical" variables for G are now T, P, and x_i

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

(Eq. 10.4) $\qquad\qquad$ (Eq. 10.5) $\qquad\qquad$ (Eq. 10.1)

Phase Equilibria

(Closed System)

$$d(nG) = (nV)\,dP - (nS)\,dT + \sum_i \mu_i\,dn_i \quad \text{(Eq. 10.2, page 350)}$$

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 211, 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"
$$\boxed{\therefore \mu_i^\alpha = \mu_i^\beta}$$
(Eq. 10.6, page 352)

Very Important!

Partial Molar Properties

Molar properties of individual species as they exist in solution

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

(Eq. 10.7, page 352)

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:

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

(Eq. 10.1, p. 350)

(Eq. 10.8, p. 353)

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 353)

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

Start with "function" called nM:

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

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

inserting equation 10.7 and assuming constant n yields:

$$d(nM) = n\left(\frac{\partial M}{\partial P}\right)_{T,x} dP + n\left(\frac{\partial M}{\partial T}\right)_{P,x} dT + \sum_i \bar{M}_i dn_i \qquad \text{(Eq. 10.9, page 355)}$$

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

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

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

collect terms:

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

(terms in brackets must each be zero)

Partial Molar Properties – Gibbs/Duhem

(1st term in brackets)

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

(Eq. 10.10, page 355)

(2nd term in brackets)

$$M - \sum_i \bar{M}_i x_i = 0 \quad \Rightarrow \quad M = \sum_i x_i \bar{M}_i \quad \text{(Eq. 10.11)} \quad \text{(homework)}$$

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

subtract (A) – (B)

take derivative using product rule

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

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

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

Constant T and P:

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

(Eq. 10.14 p.356)

(homework)

$$0 = \left(\frac{\partial M}{\partial P}\right)_{T,x} dP + \left(\frac{\partial M}{\partial T}\right)_{P,x} dT - \sum_i x_i \, d\bar{M}_i \quad \text{(Eq. 10.13, page 356)}$$

Gibbs-Duhem Equation (famous)

Special Case – Binary Systems

Eq. 10.11 (slide 15) for 2 components $\quad M = x_1 \bar{M}_1 + x_2 \bar{M}_2$

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

Eq 10.14, 2 components:

$x_1 d\bar{M}_1 + x_2 d\bar{M}_2 = 0 \quad$ previous slide

Rearrange $\quad dM = (\bar{M}_1 dx_1 + \bar{M}_2 dx_2) + (x_1 d\bar{M}_1 + x_2 d\bar{M}_2)$

sum of mole fractions

$x_1 + x_2 = 1$

$x_2 = 1 - x_1$

$dx_2 = -dx_1$

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

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

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

$x_1 = 1 - x_2$

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

$x_2 = 1 - x_1$

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

(homework)

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

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

(homework)

Homework

Problem 10.53

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

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

(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 SharePoint for part (f).