

CH365 Chemical Engineering Thermodynamics

Lesson 34

Chemical Potential and Partial Properties

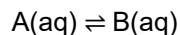
Block 6 – Solution Thermodynamics

Review of Lesson 32 – Phase Equilibria



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

In general chemistry, “activity” was molar concentration:



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

Square brackets denote molar concentration in moles per L.

This is called an “ideal solution.”

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

“Van’t Hoff Isotherm”

Derivations:

[Link 1](#) [Link 2](#)

$\Delta G < 0$ “product side” favored

$\Delta G > 0$ “reactant side” favored

$\Delta G = 0$ “equilibrium”

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

$$dG = \cancel{VdP} - \cancel{SdT} \quad \begin{matrix} 0, \text{ const } P \\ 0, \text{ const } T \end{matrix}$$

(Eq. 6.11)

“Clapeyron” and “Clausius-Clapeyron” equations

Clausius-Clapeyron Equation

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

Clapeyron Equation
(Eq. 6.85)

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

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.

$$dG = VdP - SdT$$

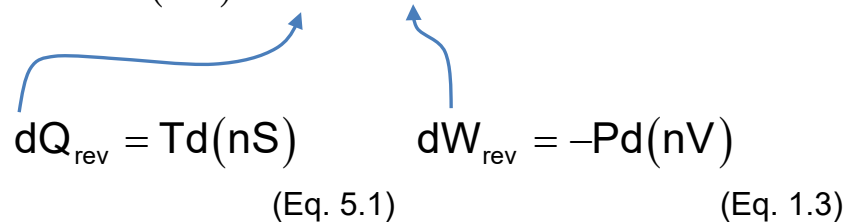
(L27 slide 8, eq. 6.11 p. 212
and PS10 problem 6.1b)

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)

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


$$dQ_{\text{rev}} = Td(nS) \quad (Eq. 5.1)$$

$$dW_{\text{rev}} = -Pd(nV) \quad (Eq. 1.3)$$

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

$$dU = TdS - PdV$$

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

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

- 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.

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

From 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 211)

Mathematics

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

$$df = M dx + N dy \quad (\text{Eq. 6.12})$$

$$M \equiv \left(\frac{\partial f}{\partial x} \right)_y$$

$$N \equiv \left(\frac{\partial f}{\partial y} \right)_x$$

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

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

From calculus, the order of differentiation does not matter

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

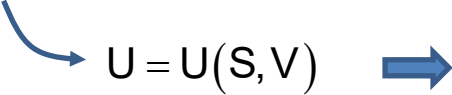
$$\therefore \left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y \quad (\text{Eq. 6.13})$$

Maxwell's Equations

(Maxwell's equations are based on pure mathematics)

(Fund. Prop Eq.6.8)

$$dU = TdS - PdV$$



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

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

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

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

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

Summary of Maxwell's Relations

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

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

From Lesson 27, Slide 12

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)

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

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

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

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. 213

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

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

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

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

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, $n_i = x_i$

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

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

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

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

(Eq. 10.4)
(Eq. 10.5)
(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: $\sum_i \mu_i^\alpha dn_i^\alpha + \sum_i \mu_i^\beta dn_i^\beta = 0$

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

“Equilibrium Condition”

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

(Eq. 10.6, page 352)

Very Important!

Partial Molar Properties

Molar properties of individual species as they exist in solution

$$\bar{M}_i \equiv \left[\frac{\partial(nM)}{\partial n_i} \right]_{P,T,n_{j \neq i}} \quad (\text{Eq. 10.7, page 352})$$

Response function – response of “nM” to addition of “dn_i”

Total solution properties	M	V, U, H, S, G
Partial molar properties	\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:

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

(Eq. 10.1, p. 350) (Eq. 10.8, p. 353)

Example 10.1

The partial molar volume is defined as

$$\bar{V}_i \equiv \left[\frac{\partial(nV)}{\partial n_i} \right]_{P,T,n_j} \quad (\text{A, page 353})$$

What physical interpretation can be given to this equation?

Consider the total volume of an equimolar solution of alcohol and water:

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

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?

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

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



effective molar volume of water in solution

Homework

Problem 10.53

The molar volume ($\text{cm}^3 \text{mol}^{-1}$) 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 $\left(d\bar{V}_1 / dx_1\right)_{x_1=1} = \left(d\bar{V}_2 / dx_1\right)_{x_1=0} = 0$.
- (e) Make a plot of V , \bar{V}_1 , and \bar{V}_2 versus x_1 .
- (f) Label points V_1 , V_2 , $\bar{V}_1^{x_1 \rightarrow 0}$ and $\bar{V}_2^{x_2 \rightarrow 0}$, and show their values.

Use file “PlotExampleCadet.nb” in SharePoint for part (f).