

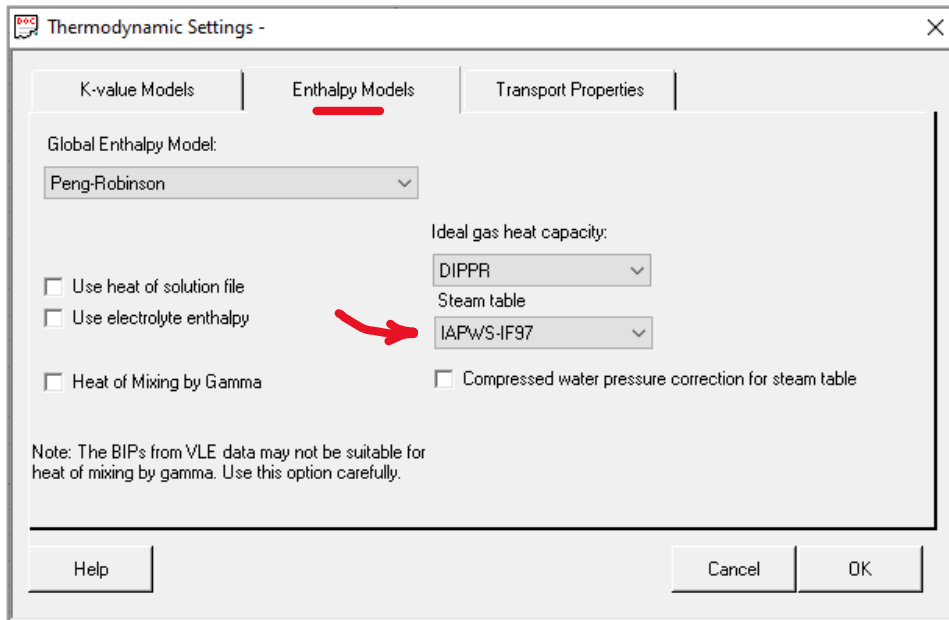
CH365 Chemical Engineering Thermodynamics

Lesson 27 Fundamental Property Relations (for Homogeneous Phases)

Professor Andrew Biaglow
28 October 2022

Motivation – Understanding CHEMCAD

CHEMCAD Thermodynamic Settings Window



when water is a pure component, CHEMCAD defaults to IAPWS-IF97

Gibbs energy generating function for water:

$$\frac{g(p, T)}{RT} = \gamma(\pi, \tau) = \sum_{i=1}^{34} n_i (7.1 - \pi)^{I_i} (\tau - 1.222)^{J_i} \quad (7)$$

where $\pi = p/p^*$ and $\tau = T^*/T$ with $p^* = 16.53$ MPa and $T^* = 1386$ K; R is given by Eq. (1).

$$R = 0.461526 \text{ kJ kg}^{-1} \text{ K}^{-1} \quad (1)$$

IAPWS R7-97(2012)

The International Association for the Properties of Water and Steam

Lucerne, Switzerland
August 2007

Revised Release on the IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam (The revision only relates to the extension of region 5 to 50 MPa)

©2007 International Association for the Properties of Water and Steam
Publication in whole or in part is allowed in all countries provided that attribution is given to the
International Association for the Properties of Water and Steam

Table 3. Relations of thermodynamic properties to the dimensionless Gibbs free energy γ and its derivatives^a when using Eq. (7)

Property	Relation
Specific volume $v = (\partial g / \partial p)_T$	$v(\pi, \tau) \frac{p}{RT} = \pi \gamma_\pi$
Specific internal energy $u = g - T(\partial g / \partial T)_p - p(\partial g / \partial p)_T$	$\frac{u(\pi, \tau)}{RT} = \tau \gamma_\tau - \pi \gamma_\pi$
Specific entropy $s = -(\partial g / \partial T)_p$	$\frac{s(\pi, \tau)}{R} = \tau \gamma_\tau - \gamma$
Specific enthalpy $h = g - T(\partial g / \partial T)_p$	$\frac{h(\pi, \tau)}{RT} = \tau \gamma_\tau$

James Clerk Maxwell (1831-1879)



James and Katherine Maxwell
Wikipedia, "James Clerk Maxwell."



- Albert Einstein described Maxwell's work as the "most profound and the most fruitful that physics has experienced since the time of Newton."
- Maxwell's equations have been called the "second great unification in physics" after Isaac Newton's theory of gravitation. They first appeared in fully developed form in his textbook *A Treatise on Electricity and Magnetism* in 1873
- Between 1859 and 1866, developed the theory of the distributions of velocities in particles of a gas, which led to the formulation of the Maxwell–Boltzmann distribution.
- "On Governors," *Proceedings of the Royal Society*, vol. 16 (1867–1868), a central paper in the early days of control theory.
- In 1871 he published the thermodynamic relations between 2nd derivatives of thermodynamic potentials that we are covering today.

Maxwell's dog Toby, in Stoddart's sculpture on George Street in Edinburgh, "Six famous Edinburgh Dog Statues," Edinburgh News, <http://www.edinburghnews.scotsman.com>, photo by Hannah Robinson,

Chapter 5 Look-back

- Entropy from postulates:

$$dS^t = \frac{dQ_{\text{rev}}}{T} \Leftrightarrow \Delta S^t = \int \frac{dQ_{\text{rev}}}{T} \Leftrightarrow S = \frac{Q}{T} \quad (\text{Eq. 5.1})$$

- Carnot's Equations
- Ideal gas PV cycle

- Derived entropy change for ideal gas:

$$\frac{\Delta S}{R} = \int_{T_0}^T \frac{C_P^{\text{ig}}}{R} \frac{dT}{T} - \ln \frac{P}{P_0} \quad (\text{Eq. 5.10})$$

- Derived lost work in open systems:

$$\dot{W}_{\text{lost}} = T_{\sigma} \dot{S}_G \quad (\text{Eq. 5.29})$$

- Developed concept “ideal” work

Combination of 1st and 2nd
laws, L24 slide13

$$W_{\text{ideal}} = \Delta H - T_{\sigma} \Delta S \quad (\text{Eq. 5.22})$$

Chapter 6 Look-ahead

- Phase rule – tells us how many intensive variables but not how to calculate them.
 - We will develop the fundamental relationships and Maxwell relations - basis of the mathematical structure of modern classical thermodynamics
 - We will derive equations that allow calculation of enthalpy and entropy “residuals.”
 - We will examine “generalized correlations.”
-

Today's Agenda

- Property Relations.
- Maxwell Relations.
- H & S as Functions of T & P .
- U as a Function of P .
- Ideal Gas
- U & S as Functions of T & V .
- Gibbs Generating Function.

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

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

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

(Eq. 5.1)

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

(Eq. 1.3)

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

(Eq. 6.1)

$$dU = TdS - PdV \quad (\text{Eq. 6.8})$$

$n=1$ or constant comp.

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

Additional properties arise by definition:

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

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

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

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

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

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

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

(Eq. 5.1)

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

(Eq. 1.3)

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

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

$$nH = nU + P(nV)$$

$$d(nH) = d(nU + P(nV)) \Rightarrow d(nH) = d(nU) + Pd(nV) + (nV)dP$$

$$d(nH) = Td(nS) - \cancel{Pd(nV)} + \cancel{Pd(nV)} + (nV)dP$$

$$d(nH) = Td(nS) + (nV)dP \quad (\text{Eq. 6.5})$$

- Includes H, T, S, P, and V

Distributive Property:

$$\frac{d}{dx}(u + v) = \frac{du}{dx} + \frac{dv}{dx}$$

$$d(u + v) = du + dv$$

Product Rule:

$$\frac{d}{dx}(u \cdot v) = \frac{du}{dx} \cdot v + u \cdot \frac{dv}{dx}$$

$$d(u \cdot v) = du \cdot v + u \cdot dv$$

$$dH = TdS + VdP \quad (\text{Eq. 6.9})$$

n=1 or constant comp.

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)

(Problem 6.1 - first homework problem)

(derive the “?” expressions)

Mathematics

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

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

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

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

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

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

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

(order doesn't matter; symmetry of 2nd derivatives; Clairaut's theorem from calculus; a.k.a. Schwarz's theorem and Young's theorem)

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

(Basis of Maxwell's equations)

Maxwell's Equations

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

S and V are
"special" to U

$$dU = T dS - P dV \quad (\text{fundamental property relation Eq. 6.8, slide 8})$$

$$T \equiv \left(\frac{\partial U}{\partial S} \right)_V$$

$$P \equiv - \left(\frac{\partial U}{\partial V} \right)_S$$

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

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

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

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

(First of the four Maxwell equations)

Maxwell's Equations

$$G = G(P, T) \quad \Rightarrow \quad dG = \left(\frac{\partial G}{\partial P} \right)_T dP + \left(\frac{\partial G}{\partial T} \right)_P dT$$

T and P are
"special" to G

$$dG = V dP - S dT \quad (\text{fundamental property relation Eq. 6.11, slide 8})$$

$$V \equiv \left(\frac{\partial G}{\partial P} \right)_T$$

$$S \equiv - \left(\frac{\partial G}{\partial T} \right)_P$$

$$\left(\frac{\partial V}{\partial T} \right)_P = \left(\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P} \right)_T \right)_P = \frac{\partial^2 G}{\partial T \partial P}$$

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial}{\partial P} \left(\frac{\partial G}{\partial T} \right)_P \right)_T = - \frac{\partial^2 G}{\partial P \partial T}$$

$$\frac{\partial^2 G}{\partial T \partial P} = \frac{\partial^2 G}{\partial P \partial T}$$

$$\therefore \left(\frac{\partial V}{\partial T} \right)_P = - \left(\frac{\partial S}{\partial P} \right)_T \quad (\text{Eq. 6.17})$$

(Fourth of the four Maxwell equations)

Summary of Maxwell's Relations

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

$\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_V \quad \checkmark$ <p>(Eq. 6.14)</p>	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad ?$ <p>(Eq. 6.15)</p>
$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \quad ?$ <p>(Eq. 6.16)</p>	$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \quad \checkmark$ <p>(Eq. 6.17)</p>

(Problem 6.4 - second homework problem)

(derive the “?” expressions)

Enthalpy and Entropy as Functions of T and P

The most useful property relations for enthalpy and entropy are functions of T and P

$$H = H(T, P)$$

To write the total differential for this function (H), we need partial derivatives:

$$\left(\frac{\partial H}{\partial P} \right)_T \quad \text{and} \quad \left(\frac{\partial H}{\partial T} \right)_P$$

$$dH = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP$$

$$S = S(T, P)$$

To write the total differential for this function (S), we need partial derivatives:

$$\left(\frac{\partial S}{\partial P} \right)_T \quad \text{and} \quad \left(\frac{\partial S}{\partial T} \right)_P$$

$$dS = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP$$

Enthalpy as a Function of T and P

$$H = H(T, P)$$

$$dH = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP$$

(Eq. 2.19)

$$\left(\frac{\partial H}{\partial T} \right)_P = C_P$$

$$dH = TdS + VdP \quad (\text{Eq. 6.9, slide 8})$$

$$\frac{dH}{dP} = T \frac{dS}{dP} + V \quad (\text{divide 6.9 by } dP)$$

$$\left(\frac{dH}{dP} \right)_T = T \left(\frac{dS}{dP} \right)_T + V \quad (\text{constant } T)$$

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P \quad \begin{array}{l} \text{(Maxwell Equation)} \\ \text{(Eqn. 6.17)} \\ \text{(from Slide 12)} \end{array}$$

$$\left(\frac{dH}{dP} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_P \quad (\text{Eq. 6.20})$$

$$dH = C_P dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP \quad (\text{Eq. 6.21})$$

(V is a function of T and P)

Entropy as a Function of T and P

$$S = S(T, P)$$

$$dS = \underbrace{\left(\frac{\partial S}{\partial T} \right)_P}_{\text{blue arrow}} dT + \underbrace{\left(\frac{\partial S}{\partial P} \right)_T}_{\text{blue arrow}} dP \quad \text{(Maxwell Equation)}$$

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P \quad \text{(Eq. 6.17) (slide 12)}$$

$$dH = TdS + VdP \quad \text{(Eq. 6.9) (slide 8)}$$

$$\frac{dH}{dT} = T \frac{dS}{dT} + V \frac{dP}{dT} \quad \text{(divide 6.9 by } dT \text{)}$$

$$\left(\frac{\partial H}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_P \quad \text{(constant P)}$$

$$\left(\frac{\partial H}{\partial T} \right)_P = C_P \quad \text{(Eq. 2.20)}$$

$$C_P = T \left(\frac{\partial S}{\partial T} \right)_P$$

$$\frac{C_P}{T} = \left(\frac{\partial S}{\partial T} \right)_P \quad \text{(Eq. 6.18)}$$

$$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T} \right)_P dP$$

(V is a function of T and P)

(Eq. 6.22)

(leads directly to formal derivation of eq. 5.10)

Internal Energy as a Function of P

$$U = H - PV$$

(T constant - implied)

$$dU = dH - PdV - VdP$$

$$U = U(P)$$

$$dU = \left(\frac{\partial U}{\partial P} \right)_T dP$$

$$\frac{dU}{dP} = \frac{dH}{dP} - \frac{PdV}{dP} - \frac{VdP}{dP} \quad (\text{divide } dP)$$

$$\left(\frac{dU}{dP} \right)_T = \left(\frac{dH}{dP} \right)_T - P \left(\frac{dV}{dP} \right)_T - V \quad (\text{constant } T)$$

$$\left(\frac{dH}{dP} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_P \quad (\text{Eq. 6.20, Slide 14})$$

$$\left(\frac{dU}{dP} \right)_T = \cancel{V} - T \left(\frac{\partial V}{\partial T} \right)_P - P \left(\frac{dV}{dP} \right)_T - \cancel{V}$$

$$\left(\frac{\partial U}{\partial P} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_P - P \left(\frac{\partial V}{\partial P} \right)_T \quad (\text{page 215, not numbered})$$

$$dU = \left[-T \left(\frac{\partial V}{\partial T} \right)_P - P \left(\frac{\partial V}{\partial P} \right)_T \right] dP \quad (\text{Equation not given in text})$$

Ideal Gas State

$$dH = C_P dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP \quad (\text{Eq. 6.21, slide 14})$$

$$P \cdot V^{\text{ig}} = R \cdot T \quad \Rightarrow \quad V^{\text{ig}} = \frac{R \cdot T}{P} \quad \Rightarrow \quad \left(\frac{\partial V^{\text{ig}}}{\partial T} \right)_P = \frac{R}{P}$$

$$dH = C_P dT + \left[V - T \frac{R}{P} \right] dP = C_P dT + [V - V] dP = C_P dT$$

$$dH^{\text{ig}} = C_P^{\text{ig}} dT \quad (\text{Eq. 6.23; Eq. 2.21 p.43, and 3.14a p. 79})$$

(See L 11, slide 3)

$$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T} \right)_P dP \quad (\text{Eq. 6.22, slide 14})$$

$$dS^{\text{ig}} = \frac{C_P^{\text{ig}}}{T} dT - \frac{R}{P} dP \quad (\text{Eq. 6.24; leads to Eq. 5.10, p. 188})$$

(See L 23, slide 9)

(restatements of equations for ideal gases derived in Sections 3.3 and 5.5)

Internal Energy and Entropy as Functions of T and V

Sometimes T and V are more convenient than T and P.
The most useful property relations are for U and S.

$$U = U(T, V)$$

Need: $\left(\frac{dU}{dT}\right)_V$ and $\left(\frac{\partial U}{\partial V}\right)_T$ $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$

$$S = S(T, V)$$

Need: $\left(\frac{\partial S}{\partial T}\right)_V$ and $\left(\frac{\partial S}{\partial V}\right)_T$ $dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$

Internal Energy as a Function of T and V

$$U = U(T, V)$$

$$dU = TdS - PdV \quad (\text{Eq. 6.8})$$

$$\frac{dU}{dT} = T \frac{dS}{dT} - P \frac{dV}{dT} \quad (\text{divide by } dT)$$

$$\left(\frac{dU}{dT} \right)_V = T \left(\frac{dS}{dT} \right)_V \quad (\text{constant } V)$$

$$C_V \equiv \left(\frac{dU}{dT} \right)_V \quad (\text{Eq. 2.15})$$

$$\left(\frac{dS}{dT} \right)_V = \frac{C_V}{T} \quad (\text{Eq. 6.30})$$

$$dU = TdS - PdV \quad (\text{Eq. 6.8})$$

$$\frac{dU}{dV} = T \frac{dS}{dV} - P \frac{dV}{dV} \quad (\text{divide by } dV)$$

$$\left(\frac{dU}{dV} \right)_T = T \left(\frac{dS}{dV} \right)_T - P \quad (\text{constant } T)$$

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \quad (\text{Maxwell Equation})$$

(Eq. 6.16)

$$\left(\frac{dU}{dV} \right)_T = T \left(\frac{dP}{dT} \right)_V - P \quad (\text{Eq. 6.31})$$

Internal Energy as a Function of T and V

$$U = U(T, V)$$

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

$$C_V \equiv \left(\frac{dU}{dT} \right)_V \quad (\text{Eq. 2.15})$$

$$\left(\frac{dU}{dV} \right)_T = T \left(\frac{dP}{dT} \right)_V - P \quad (\text{Eq. 6.31})$$

$$dU = C_V dT + \left[T \cdot \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV \quad (\text{Eq. 6.32})$$

$$S = S(T, V)$$

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV$$

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \quad (\text{Maxwell Equation})$$

(Eq. 6.16)

$$\left(\frac{dS}{dT} \right)_V = \frac{C_V}{T} \quad (\text{Eq. 6.30})$$

$$dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T} \right)_V dV \quad (\text{Eq. 6.33})$$

Gibbs Energy Generating Function

Equations 6.7-6.10 imply that each of the thermodynamic properties is related to a special pair of variables. These are the canonical variables.

$$dG = VdP - SdT \quad (\text{Eq. 6.11})$$

$G = G(T, P)$ (special)
 $A = A(T, V)$
 $U = U(S, V)$
 $H = H(S, P)$
 $G \equiv H - TS$

$$d\left(\frac{G}{RT}\right) \equiv \frac{1}{RT}dG - \frac{G}{RT^2}dT$$

$$d\left(\frac{G}{RT}\right) = \frac{VdP - SdT}{RT} - \frac{H - TS}{RT^2}dT$$

$$d\left(\frac{G}{RT}\right) = \frac{V}{RT}dP - \frac{S}{RT}dT - \frac{H}{RT^2}dT + \frac{TS}{RT^2}dT$$

$$d\left(\frac{G}{RT}\right) = \frac{V}{RT}dP - \frac{H}{RT^2}dT \quad (\text{Eq. 6.37})$$

Gibbs Energy Generating Function

$$d\left(\frac{G}{RT}\right) = \frac{V}{RT} dP - \frac{H}{RT^2} dT \quad (\text{Eq. 6.37})$$

$$f = f(x, y) \quad \Rightarrow \quad dF \equiv \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy \quad (\text{Slide 8})$$

$$\therefore \frac{V}{RT} = \left(\frac{\partial(G/RT)}{\partial P}\right)_T \quad \text{and} \quad -\frac{H}{RT^2} = \left(\frac{\partial(G/RT)}{\partial T}\right)_P$$

(Eq. 6.38)

Carefully note that both terms V/RT and $-H/RT^2$ are functions of G/RT – Significant Result!

$$\frac{H}{RT} = -T \cdot \left(\frac{\partial(G/RT)}{\partial T}\right)_P \quad (\text{Eq. 6.39})$$

$$G \equiv H - TS$$

$$H \equiv U + PV$$

$$A \equiv U - TS$$

$$\frac{S}{R} = \frac{H}{RT} - \frac{G}{RT}$$

$$\frac{U}{RT} = \frac{H}{RT} - \frac{PV}{RT}$$

$$\frac{A}{RT} = \frac{U}{RT} - \frac{S}{R}$$

Equation 6.11 leads to equations for all thermodynamic properties

Homework

Problem 6.1

- (a) Starting with the definition of the Helmholtz energy in Equation 6.3, derive the fundamental property relation in Equation 6.10.

- (b) Starting with the definition of the Gibbs energy in Equation 6.4, derive the fundamental property relation in Equation 6.11.

Problem 6.4

- (a) Starting with the fundamental property relation Equation 6.10, derive the Maxwell relation given in Equation 6.16.

- (b) Starting with the fundamental property relation Equation 6.9, derive the Maxwell relation given in Equation 6.15.