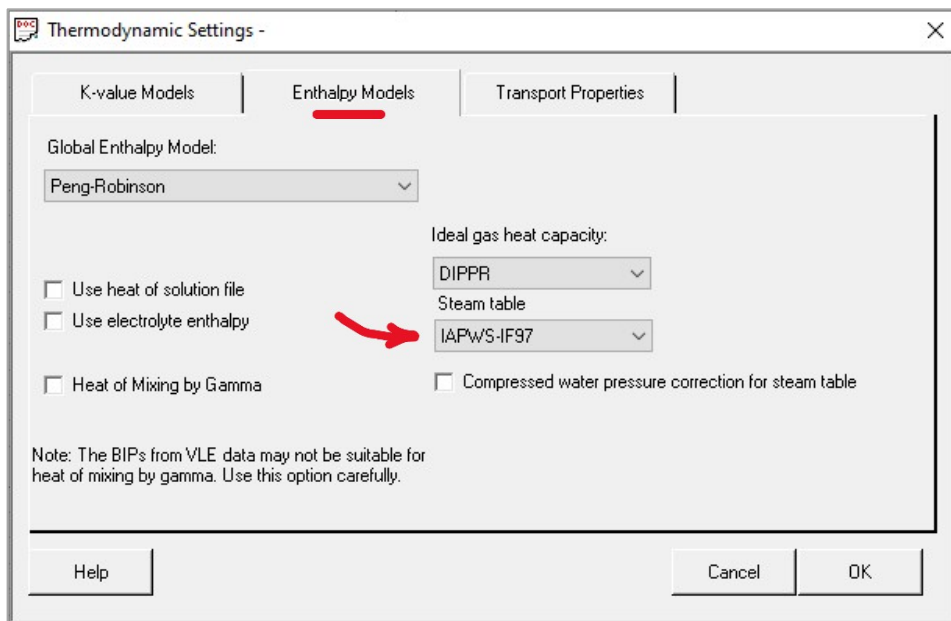


# CH365 Chemical Engineering Thermodynamics

## Lesson 27 Fundamental Property Relations (for Homogeneous Phases)

# 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)

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**Table 3.** Relations of thermodynamic properties to the dimensionless Gibbs free energy  $\gamma$  and its derivatives<sup>a</sup> when using Eq. (7)

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

# 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 2<sup>nd</sup> derivatives of thermodynamic potentials that we are covering today.

Maxwell's dog Toby, in Stoddart's sculpture on George Street in Edinburgh, "Five Statues of Edinburgh Dogs," <https://www.edinburghexpert.com/blog/five-statues-of-edinburgh-dogs>

# 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 the concept of “ideal” work

Combination of 1<sup>st</sup> and 2<sup>nd</sup>  
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. (followed closely – red headings)
- 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.

# Fundamental Property Relations

(Eq. 2.6, 1<sup>st</sup> Law, closed system, reversible)

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

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

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

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

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

$n=1$  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.**

# Fundamental Property Relations

(Eq. 2.6, 1<sup>st</sup> 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)



# Maxwell's Equations – 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 2<sup>nd</sup> 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)

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

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

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

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

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

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

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

(V is a function of T and P)

# Entropy as a Function of T and P

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

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

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

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

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

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

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

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

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

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

(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 and Entropy as Functions 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

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

$$\frac{G}{RT} = f(T, P) \quad \Rightarrow \quad df \equiv \left(\frac{\partial(G/RT)}{\partial P}\right)_T dP + \left(\frac{\partial(G/RT)}{\partial T}\right)_P dT \quad (\text{Slide 8})$$

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

(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

# Questions?