LECTURE 8

CY11001
Spring 2018

- Maxwell Relations

Department of Chemistry
Indian Institute of Technology
Kharagpur

Combination of First and Second Laws of Thermodynamics:

$dU = dw + dq$

True for any path

$dU = dw_{rev} + dq_{rev}$

$dS \geq dq/T$

$dS = dq_{rev}/T$

$$\boxed{dU = -pdV + TdS}$$

The Fundamental Equation of Thermodynamics

Applicable to both reversible and irreversible processes!

$$\begin{aligned} dA &= d(U - TS) \\ &= dU - TdS - SdT \\ &= -pdV + TdS - TdS - SdT \\ &= -pdV - SdT \end{aligned}$$

$$\begin{aligned} dH &= TdS + Vdp \\ dG &= Vdp - SdT \end{aligned}$$

The Fundamental Equation of *Chemical* Thermodynamics

Combination of First and Second Laws of Thermodynamics:
(The Gibbs Equations)

$$\boxed{\begin{aligned} dU &= -pdV + TdS \\ dA &= -pdV - SdT \\ dH &= TdS + Vdp \\ dG &= Vdp - SdT \end{aligned}}$$

A closed system (constant composition/change in composition reversibly), only pV work

The Maxwell Relations

if, $df = gdx + hdy$

then $\left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y$

The Euler Reciprocity Relation.

$$\boxed{dG = Vdp - SdT}$$

$$\boxed{-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p}$$

$$\boxed{dA = -pdV - SdT}$$

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V}$$

Isothermal variation of entropy with pressure and volume

$$\boxed{dU = -pdV + TdS}$$

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V}$$

$$\boxed{dH = Vdp + TdS}$$

$$\boxed{\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p}$$

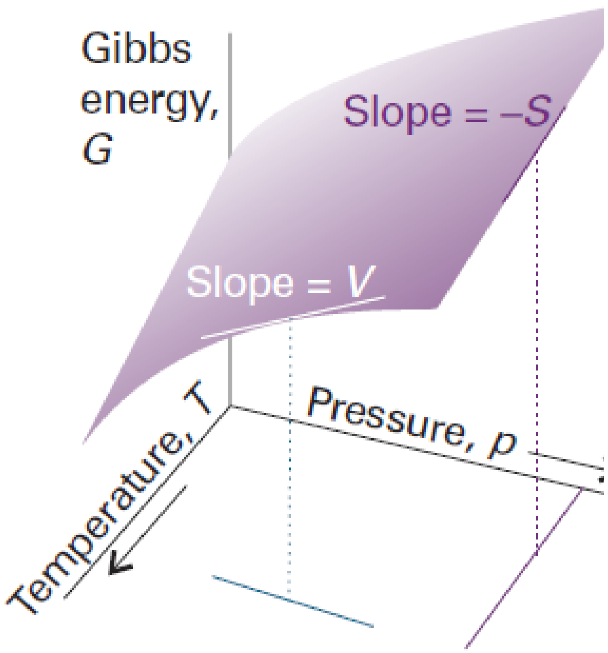
Variation of Gibbs free energy with T and p

$$\boxed{dG = Vdp - SdT}$$

The Fundamental Equation of *Chemical* Thermodynamics

$$\boxed{\left(\frac{\partial G}{\partial T}\right)_p = -S}$$

$$\boxed{\left(\frac{\partial G}{\partial p}\right)_T = V}$$



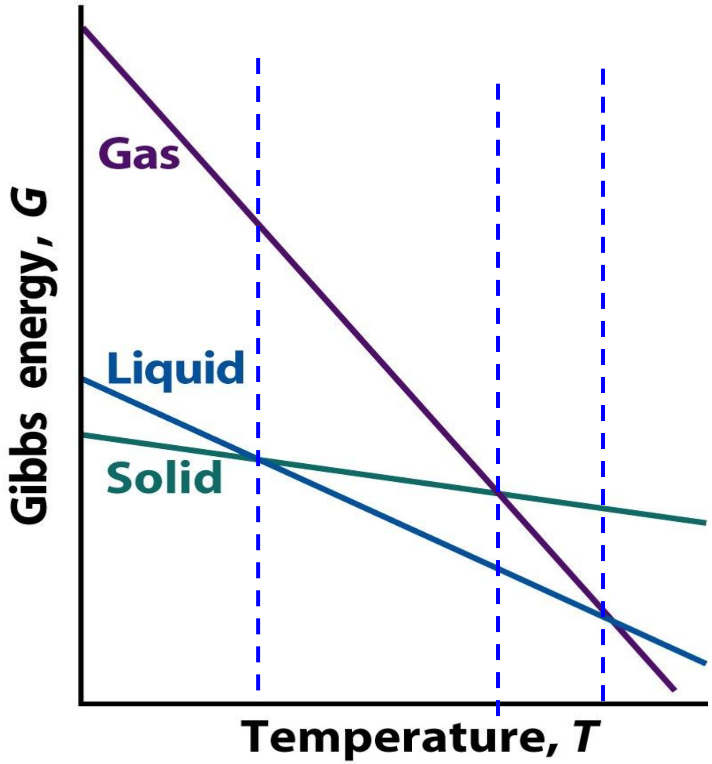


Figure 3-19
Atkins Physical Chemistry, Eighth Edition

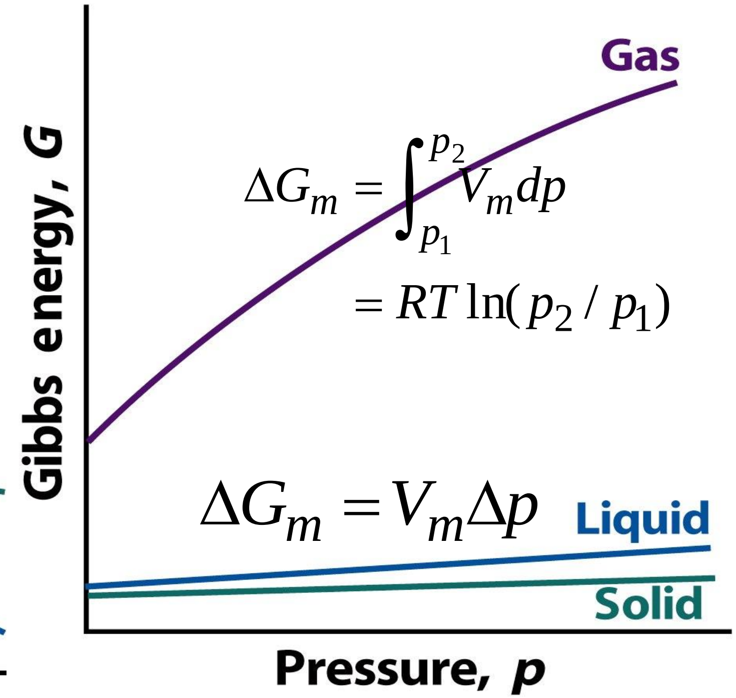


Figure 3-20
Atkins Physical Chemistry, Eighth Edition

Temperature dependence of Gibbs Energy Or Gibbs-Helmholtz Equation:

$$\boxed{G = H - TS}$$

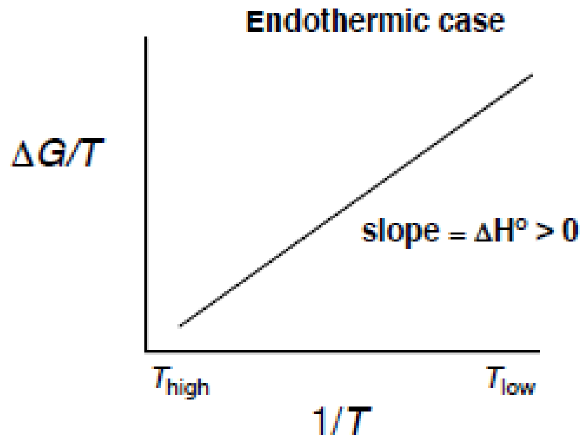
$$\left(\frac{\partial G}{\partial T}\right)_p = -S = (G-H)/T$$

$$\left(\frac{\partial (G/T)}{\partial T}\right)_p = ? \qquad \left(\frac{\partial (G/T)}{\partial (1/T)}\right)_p = ?$$

Show that (home work)

$$\boxed{\begin{aligned} \left(\frac{\partial (G/T)}{\partial T}\right)_p &= -\frac{H}{T^2} \\ \left(\frac{\partial (\Delta G/T)}{\partial T}\right)_p &= -\frac{\Delta H}{T^2} \end{aligned}} \qquad \boxed{\begin{aligned} \left(\frac{\partial (G/T)}{\partial (1/T)}\right)_p &= H \\ \left(\frac{\partial (\Delta G/T)}{\partial (1/T)}\right)_p &= \Delta H \end{aligned}}$$

Gibbs-Helmholtz Equations



If we know ΔH of a process, we can know how $\Delta G/T$ varies with T.

Show that, $\mathbf{\Delta G/T = -\Delta S_{univ}}$

Prove the following relations: Home work

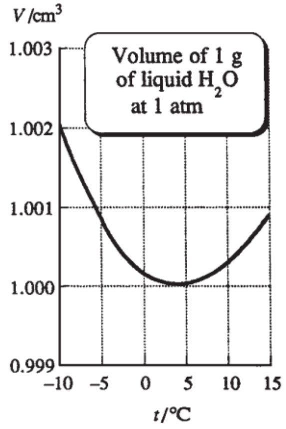
$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\alpha T}{\kappa} - p\right) = 0 \text{ (for ideal gas)} = an^2/V^2 \text{ (for vdW gas)}$$

$$\left(\frac{\partial H}{\partial p}\right)_T = V(1-\alpha T) = 0 \text{ (for ideal gas)} = ? \text{ (for vdW gas)}$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\alpha V \qquad \left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\kappa} \qquad \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \qquad \left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$$

$$\mu_{JT} = \frac{V}{C_p}(\alpha T - 1) = ? \text{ (for ideal gas)} = ? \text{ (for vdW gas)}$$

$$C_p - C_V = \frac{TV\alpha^2}{\kappa} = nR \text{ (for ideal gas)}$$



What is the relation between C_p and C_V of water at 3.98 ^{0}C?

Variation of entropy with temperature at constant *p* or constant *V*

$$dU = -pdV + TdS$$

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

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

$$\boxed{\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}}$$

$$dH = VdP + TdS$$

$$\left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

$$\boxed{\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}}$$

Variation of entropy with temperature and pressure

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p = -\alpha V$$

From Maxwell relation

$$dS = \frac{C_p}{T}dT - \alpha V dp$$

$$\boxed{\Delta S = \int \frac{C_P}{T}dT - \int \alpha V dP}$$

Dependence of state functions (*U*, H, and *S*) on *T*, *p*, and *V*

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad \left(\frac{\partial U}{\partial T}\right)_V = C_V \qquad \left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\alpha T}{\kappa} - p\right)$$

$$\boxed{\Delta U = \int C_V dT + \int \left(\frac{\alpha T}{\kappa} - p\right) dV}$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp \qquad C_p = \left(\frac{\partial H}{\partial T}\right)_p \qquad \left(\frac{\partial H}{\partial p}\right)_T = V(1 - \alpha T)$$

$$\boxed{\Delta H = \int C_p dT + \int (V - TV\alpha) dp}$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp \qquad \left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \qquad \left(\frac{\partial S}{\partial p}\right)_T = -\alpha V$$

$$\boxed{\Delta S = \int \frac{C_P}{T} dT - \int \alpha V dP}$$