

## Reading Assignment 5

S.12) Using the fact that  $S$  is a State Function to determine the dependence of  $S$  on  $V$  and  $T$

- The main idea of this section is to relate  $S$  to experimental functions

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

$\left( \frac{\partial S}{\partial T} \right)_V$   $\uparrow$   $S$  dependence on Temperature  
 $\left( \frac{\partial S}{\partial V} \right)_T$   $\uparrow$  on Volume

No internal  $E$   
 since not  
 exper. function

$$dS = \frac{C_V}{T} dT + \frac{\beta}{\alpha} dV$$

measurable variables

S.13) The Dependence of  $S$  on  $T$  &  $P$

- Similar to prev. section but pressure instead of volume

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

$\left( \frac{\partial S}{\partial T} \right)_P$   $\uparrow$  dep. on  $T$        $\left( \frac{\partial S}{\partial P} \right)_T$   $\uparrow$  dep. on  $P$

$$dS = \frac{C_P}{T} dT - V\beta dP$$

- 6.1) The Gibbs Energy and the Helmholtz Energy  
 - The main idea is to introduce two new state functions for the discussion on spontaneity.

For isothermal process:  $d(U - TS) \leq \delta W_{exp} + \delta W_{con}$   
 we define  $U - TS$  as Helmholtz energy  $A$   
 $dA \leq \delta W_{exp} + \delta W_{con}$

Similarly,  $H - TS$  is defined as Gibbs free energy  $G$

$$\Delta G_p = \Delta H_p - T \Delta S_p$$

- 6.2) The Differential Forms of  $U$ ,  $H$ ,  $A$ , and  $G$   
 - The main idea is to introduce differential forms for the state functions in order to further manipulate them.

Maxwell relations (4):

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

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

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

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P = V\beta$$

- 6.3) The Dependence of the Gibbs & Helmholtz Energies on  $P$ ,  $V$ , and  $T$

Helmholtz  $\left(\frac{\partial A}{\partial T}\right)_V = -S$   $\left(\frac{\partial A}{\partial V}\right)_T = -P$

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