

5.12 Using the fact that  $S$  is a state function to determine the Dependence of  $S$  on  $V$  and  $T$ .

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV = \frac{1}{T} \left[ C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \right] + \frac{P}{T} dV$$

↳ difference in entropy as an exact differential

when we equate the coefficients of  $dT$  and  $dV$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \text{ and } \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left[ P + \left(\frac{\partial U}{\partial V}\right)_T \right]$$

by substitution and canceling double mixed derivative of  $U$ :

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

provides a way to calculate the internal pressure of the system if the equation of state for the substance is known

a practical equation is obtain for the dependence of entropy on  $V$  under constant  $P$

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

$B$  = coefficient for thermal expansion at constant pressure

$K$  = isothermal compressibility coefficient.

$$\text{by expressing } dS \text{ in terms of } dT \text{ and } dV: dS = \frac{C_V}{T} dT + \frac{B}{K} dV$$

by integrating both sides of the equation along a reversible path:

$$\Delta S = \int \frac{C_V}{T} dT + \int \frac{B}{K} dV$$

5.13 The Dependence of  $S$  on  $T$  and  $P$

while chemical transformations are carried out at constant pressure,

we need to know how  $S$  varies with  $T$  and  $P$ .

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

pressure dependence of  $S$  at constant  $T$  allows for experimental determination

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

~~earliest concept of idea~~

$$\Delta S = \int_{T_i}^{T_f} \frac{C_p}{T} dT - \int_{P_i}^{P_f} V B dP$$

single-phase system of a pure liquid, solid, or gas that undergoes a transformation from initial values  $T_i, P_i$  to  $T_f, P_f$  provided that no phase changes or chemical reactions occur in the system.

## 6.1 Gibbs Free Energy and the Helmholtz Energy

Helmholtz energy : the combination of state functions  $U - TS$ ,  
(A) the general conditions of spontaneity  
in isothermal processes become :

$$dA - dW_{\text{expansion}} - dU_{\text{noneexpansion}} \leq 0$$

Gibbs Energy ( $G$ ) : the combination of state functions  $H - TS$   
the condition for spontaneity and equilibrium  
in an isothermal process at constant pressure becomes

$$dG - dW_{\text{noneexpansion}} \leq 0$$

for macroscopic changes at constant  $P$  and  $T$ , where  $\Delta G_R \leq 0$

$$\Delta G_R = \Delta H_R - T \Delta S_R$$

R = remember that the process of interest is a chemical reaction

In Helmholtz energy macroscopic changes :

$$\Delta A_R = \Delta U_R - T \Delta S_R$$

## 6.2 The Differential Forms of U, H, A, and G

U and H used to calculate changes in energy

A and G used to calculate the direction in which processes

occur and the maximum work the reactions can produce.

$$H = U + PV ; \quad dU = TdS - PdV$$

$$dH = TdS - PdV + PdV + VdP = TdS + VdP$$

$$A = U - TS ; \quad dA = TdS - PdV - TdS - SdT = - SdT - PdV$$

$$G = H - TS = U + PV - TS ; \quad dG = TdS + VdP - TdS - SdT = - SdT + VdP$$

Maxwell Relations (are extremely useful in transforming seemingly

obscure partial derivatives in other partial derivatives that can

be directly measured)

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

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

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

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

## 6.3 The Dependence of the Gibbs and Helmholtz Energies on P, V, and T

A and G are important because it determines the direction of spontaneous change in a reaction mixture. We need to know

how A changes with T and V, and how G changes with T and P.

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

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

for a macroscopic change in P at constant T :

$$\int_{P^0}^P dG = G(T, P) - G^0(T, P^0) = \int_{P^0}^P VdP'$$

where  $P' = 1 \text{ bar}$

Calculating the change of  $G_m$  with  $P$  at constant  $T$ , any path connecting the same initial and final states gives the same results. Choosing the irreversible path and assuming ideal gas

$$G(T, P) = G^\circ(T) + \int_{P^o}^P V dP' = G^\circ(T) + \int_{P^o}^P \frac{nRT}{P'} dP' = G^\circ(T) + nRT \ln \frac{P}{P^o}$$

Gibbs-Helmholtz equation:  $\frac{\partial G}{\partial T} = -H$   $\frac{\partial U}{\partial T} = -A$

$$\left( \frac{\partial G}{\partial T} \right)_P = \frac{1}{T} \left( \frac{\partial G}{\partial T} \right)_P + G \frac{\partial \left[ 1/T \right]}{\partial T}$$
$$= \frac{1}{T} \left( \frac{\partial G}{\partial T} \right)_P - \frac{G}{T^2} = -\frac{S}{T} - \frac{G}{T^2} = -\frac{G+TS}{T^2} = -\frac{H}{T^2}$$