

Gibbs energy

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

$G \downarrow$  with  $T \uparrow$ ;  $G \uparrow$  with  $T \downarrow$

For change in  $P$  @ constant  $T$  integrated @ constant  $T$

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

Gibbs-Helmholtz equation:

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

Replace  $G$  by  $\Delta G$  and integrate @ constant  $P$

$$\int_{T_1}^{T_2} d\left(\frac{\Delta G}{T}\right) = \int_{T_1}^{T_2} \Delta H d\left(\frac{1}{T}\right)$$

$$\frac{\Delta G(T_2)}{T_2} = \frac{\Delta G(T_1)}{T_1} + \Delta H(T_1) \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Kylee McDonald

### 6.2 Differential forms of U, H, A, G

$$dU = TdS - PdV$$

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

$$dA = TdS - PdV - TdS - SdT = -SdT - PdV$$

$$dG = TdS + VdP - TdS - SdT = -SdT + VdP$$

express  $U$  as  $U(S, V)$ , enthalpy as  $H(S, P)$ , Helmholtz as  $A(T, V)$ , Gibbs as  $G(T, P)$ .  
 → these are natural variables!

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

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

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

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

### MAXWELL RELATIONS:

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

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

derived based on property that  $U, H, A, G$  are state functions

### 6.3 Dependence of $G$ & $A$ on $P, V, T$

How  $A$  changes w/  $T$  and  $V$

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

$S$  and  $P$  always positive!

thus,  $A \downarrow$  as  
 $T$  or  $V \uparrow$

# CH 6 chemical equilibrium

kyler mcdonald

## 6.1 Gibbs and Helmholtz energy

- formulate spontaneity in terms of G + H energies
- G + H energies allow us to calc the max work that can be extracted from a chemical reaction

\* only satisfied for a reversible process

$$\text{CLAVIUS INEQUALITY: } TdS \geq d\dot{Q} \Rightarrow TdS \geq dU - dW$$

$$-dU + dW + TdS \geq 0$$

- constant T and p or V does not imply that they are constant throughout the process but rather they are the same for the initial and final states of the process

$$\text{For isothermal processes } TdS = d(TS),$$

$$-dU + TdS \geq -dW_{\text{exp}} - dW_{\text{nonexp}} \text{ or}$$

$$d(U - TS) \leq dW_{\text{exp}} + dW_{\text{nonexp}}$$

Helmholtz energy (A) general condition of spontaneity for isothermal process

$$dA - dW_{\text{exp}} - dW_{\text{nonexp}} \leq 0$$

condition that defines spontaneity + equilib:  $|dA| \leq 0$

$$d(U + PV - TS) = d(H - TS) \leq dW_{\text{noneexpansion}}$$

comb of H + TS  
→ Gibbs Energy

used to calc  
max nonexp.  
work

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

CONSTANT P AND T FOR WHICH NONEXP. WORK IS NOT POSSIBLE:  
 $dG \leq 0$

FOR MACROSCOPIC CHANGES @ CONSTANT P AND T IN WHICH NO NONEXP WORK IS POSSIBLE, THE CONDITION FOR SPONTANEITY IS  $\Delta G_R < 0$   
where  $\Delta G_R = \Delta H_R - T\Delta S_R$

FOR CHANGES CONSTANT V AND T IN WHICH NO NONEXP WORK DOESN'T ADD UP +  $\Delta A_R < 0$   
 $\Delta A_R = \Delta U_R - T\Delta S_R$

## Reading HW6 - Kylee McDonald

5.12  $S$  is a state function used to determine dependence  $\frac{\partial S}{\partial V}$

- entropy of a system  $\uparrow$  w/  $I \infty$  @ constant  $V$
- $\uparrow$  w/  $V \uparrow$  @ constant  $T \infty$

$dS$  in terms of partial derivatives wrt  $V$  and  $T$ :  $dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$

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

$$\text{temp dependence of entropy @ constant } V = dS = \frac{C_V}{T} dT$$

eqn for dependency of entropy on  $V$  under constant  $T$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = - \frac{(2V/\partial T)_P}{(2V/\partial P)_T} = \frac{\beta}{K}$$

$\beta$  = coeff for thermal expansion @ constant  $P$

$K$  = isothermal compressibility coeff

$dS$  expressed in terms of  $dT$  and  $dV$  integrated along a reversible path:  $\Delta S = \int_{T_i}^{T_f} \frac{C_V}{T} dT + \int_{V_i}^{V_f} \frac{P}{K} dV$

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

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

pressure dependency of entropy @ constant  $T$ :

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

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

Integrated along a reversible path =  $\Delta S = \int_{T_i}^{T_f} \frac{C_P}{T} dT - \int_{P_i}^{P_f} V\beta dP$