

# Chemistry 163B

## Free Energy

### E&R ( $\approx$ ch 6)

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*spontaneity*

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$$\Delta S \geq \int \frac{dq}{T}$$
$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surr} \geq 0$$

goal: Define function which allows evaluation  
of spontaneity in terms of state functions of  
**SYSTEM** (only)

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*goals of lecture*

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- define Gibbs (G) and Helmholtz (A) free energies
- show  $\Delta G_{T,P} < 0$  and  $\Delta A_{T,V} < 0$  for spontaneity
- differentials dG and dA
- temperature and pressure dependence of G, A
- what's 'free' about free energy

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*spontaneity*

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$$\Delta S_{\text{sys}} \geq \frac{q_{\text{sys}}}{T}$$

$$\Delta S_{\text{sys}} - \frac{q_{\text{sys}}}{T} \geq 0$$

$$q_{\text{surr}} = -q_{\text{sys}}$$

$$\Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \geq 0$$

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*motivation for G (spontaneity at const T,P in terms of system)*

$$\Delta S_{\text{sys}} + \frac{-q_{\text{sys}}}{T} \geq 0$$

**spontaneity at const T,P**

$$(q_{\text{sys}})_P = \Delta H_P \quad (\bar{d}w_{\text{other}} = 0)$$

$$\Delta S_{\text{sys}} + \frac{-\Delta H_P}{T} \geq 0$$

$$T\Delta S_{\text{sys}} - \Delta H_P \geq 0$$

$$\Delta H_P - T\Delta S_{\text{sys}} \leq 0$$

*define:  $G \equiv H - TS$  (general, even if T, P not constant)*

*but*

$$\Delta G_{T,P} = (\Delta H_{T,P})_{\text{sys}} - T\Delta S_{\text{sys}} \leq 0$$

*spontaneity for constant T,P ( $\bar{d}w_{\text{other}} = 0$ )*

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*motivation for, A*

$$\Delta S_{\text{sys}} + \frac{-q_{\text{sys}}}{T} \geq 0$$

**spontaneity at const T,V**

$$(q_{\text{sys}})_V = \Delta U_V \quad (\bar{d}w_{\text{other}} = 0)$$

$$\Delta S_{\text{sys}} + \frac{-\Delta U_V}{T} \geq 0$$

$$T\Delta S_{\text{sys}} - \Delta U_V \geq 0$$

$$\Delta U_V - T\Delta S_{\text{sys}} \leq 0$$

*define:  $A \equiv U - TS$  (general, even if T, V not constant)*

*but*

$$\Delta A_{T,V} = (\Delta U_{T,V})_{\text{sys}} - T\Delta S_{\text{sys}} \leq 0$$

*spontaneity for constant T,V ( $\bar{d}w_{\text{other}} = 0$ )*

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*summary*

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**Definitions:  $A \equiv U-TS$   
 $G \equiv H-TS$**

**Spontaneity** (in terms of properties of system):

$$\Delta A_{T,V} \leq 0 \quad (\text{no } w_{\text{other}})$$

$$\Delta G_{T,P} \leq 0 \quad (\text{no } w_{\text{other}})$$

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*what's 'good for spontaneity'*

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$$\Delta G_{T,P} = \Delta H - T\Delta S \leq 0$$

**spontaneous:  $\Delta H < 0$  and  $\Delta S > 0 \Rightarrow \Delta G < 0$**

$\Delta H_{\text{sys}} < 0$ <b>exothermic:</b> <b>disorders surroundings</b>
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$\Delta S_{\text{sys}} > 0$ <b>disorders system</b>
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*what's 'good for spontaneity'; similarly for  $\Delta A$  at const  $T, V$*

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$$\Delta A_{T,V} = \Delta U - T\Delta S \leq 0$$

spontaneous:  $\Delta U < 0$ ;  $\Delta S > 0 \Rightarrow \Delta A < 0$

$\Delta U_{\text{sys}} < 0$ <b>exothermic:</b> <b>disorders surroundings</b>	$\Delta S_{\text{sys}} > 0$ <b>disorders system</b>
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$$\Delta G_{T,P} = \Delta H - T\Delta S$$


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$\Delta H$	$\Delta S$	Spontaneous ??
– ( <i>exothermic: disorders surr</i> )	+ ( <i>disorders sys</i> )	<b>yes !!</b>
+ ( <i>endothermic: orders surr</i> )	– ( <i>orders sys</i> )	<b>no !!</b> ( <i>reverse spontaneous</i> )
– ( <i>exothermic: disorders surr</i> )	– ( <i>orders sys</i> )	<b>maybe !!</b>
+ ( <i>endothermic: orders surr</i> )	+ ( <i>disorders sys</i> )	<b>maybe !!</b>

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$$\Delta G_{T,P}=0$$

$$\Delta G_{T,P} = \Delta H - T \Delta S = 0$$

for reversible, equilibrium process

example: equilibrium phase transition

$$\Delta G_{T,P} = \Delta H_{\phi} - T_{\phi} \Delta S_{\phi} \quad \text{with } \Delta S_{\phi} = \frac{\Delta H_{\phi}}{T_{\phi}}$$

$$= \Delta H_{\phi} - T_{\phi} \left( \frac{\Delta S_{\phi}}{T_{\phi}} \right) = 0$$

[HW5 problem #35, sign of  $\Delta G$  for  $T$  'around'  $T_{\phi}$ ]

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differential relationships and Maxwell-Euler

U  $\equiv$  internal energy  
H  $\equiv$  U + PV  
A  $\equiv$  U - TS  
G  $\equiv$  H - TS

$$dU = \bar{d}q + \bar{d}w = \bar{d}q - PdV$$

$$dS = \frac{\bar{d}q_{rev}}{T} \quad dq = TdS$$

$$dU = TdS - PdV \quad U(S,V)$$

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

$$dH = dU + PdV + VdP$$

$$dH = TdS + VdP \quad H(S,P)$$

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

$$dA = dU - TdS - SdT$$

$$dA = -SdT - PdV \quad A(T,V)$$

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

$$dG = dH - TdS - SdT$$

$$dG = -SdT + VdP \quad G(T,P)$$

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

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G, A why "FREE" energy ?



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why "free" energy (E&R eqn 6.9)

$$\Delta S_{\text{sys}} + \frac{-q_{\text{sys}}}{T} \geq 0$$

spontaneity at const T,P

$$(q_{\text{sys}})_P = \Delta H_P \quad (\bar{d}w_{\text{other}} = 0)$$

$$(q_{\text{sys}})_P + \bar{d}w_{\text{other}} = \Delta H_P \quad (\bar{d}w_{\text{other}} \neq 0)$$

$$\Delta S_{\text{sys}} + \frac{-(\Delta H_P - \bar{d}w_{\text{other}})}{T} \geq 0$$

$$T\Delta S_{\text{sys}} - \Delta H_P + \bar{d}w_{\text{other}} \geq 0$$

$$\Delta H_P - T\Delta S_{\text{sys}} - \bar{d}w_{\text{other}} \leq 0$$

$$\Delta G_{T,P} - \bar{d}w_{\text{other}} \leq 0 \quad (\text{eqn 6.9 E\&R})$$

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why "free" energy (E&R eqn 6.9)

$$\Delta G_{T,P} - \bar{d}w_{\text{other}} \leq 0 \quad (\text{eqn 6.9 E\&R})$$

$$\Delta G_{T,P} \leq \bar{d}w_{\text{other}}$$

Thus if  $\Delta G_{\text{reaction}} < 0$  (spontaneous), the maximum

$w_{\text{other}}$  done ON surroundings is  $-\Delta G_{\text{reaction}}$

$$-\Delta G_{T,P} \geq -(\bar{d}w_{\text{other}})_{\text{system}} = (\bar{d}w_{\text{other}})_{\text{surroundings}}$$

For example  $w_{\text{other}}$  might be the free energy of a reaction

converted to electrical work in an electrochemical cell or a neuron.

$\Delta G$ : energy **FREE** to do work, other than expansion work

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motivation for G, A

$$G \equiv H - TS$$

$$A \equiv U - TS$$

$$\Delta G_{T,P} = (\Delta H_{T,P})_{\text{sys}} - T\Delta S_{\text{sys}} \leq 0$$

spontaneity for constant T, P ( $\bar{d}w_{\text{other}} = 0$ )

$$\Delta A_{T,V} = (\Delta U_{T,V})_{\text{sys}} - T\Delta S_{\text{sys}} \leq 0$$

spontaneity for constant T, V ( $\bar{d}w_{\text{other}} = 0$ )

$$\Delta G_{T,P} \leq \bar{d}w_{\text{other}}$$

$$\Delta A_{T,V} \leq \bar{d}w_{\text{other}}$$

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*temperature and pressure dependence of G, A (no  $w_{other}$ )*

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**G: T dependence at constant P**

$$\left(\frac{\partial G}{\partial T}\right)_P dG = -SdT + VdP \implies \left(\frac{\partial G}{\partial T}\right)_P = -S \quad \left(\frac{\partial \bar{G}}{\partial T}\right)_P = -\bar{S}$$

**G: P dependence at constant T**

$$\left(\frac{\partial G}{\partial P}\right)_T dG = -SdT + VdP \implies \left(\frac{\partial G}{\partial P}\right)_T = V \quad \left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V}$$

$$dA = -SdT - PdV \implies \left(\frac{\partial A}{\partial T}\right)_V = -S \quad \left(\frac{\partial A}{\partial V}\right)_T = -P$$

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*and  $\Delta G_{reaction}$  for chemical reaction (HW 6)*

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$$\Delta G_{reaction} = \sum_i \nu_i \bar{G}_i \quad [\text{molar free energy of formation, in a moment and Appendix A}]$$

$$\left(\frac{\partial \bar{G}}{\partial T}\right)_P = -\bar{S}$$

$$\left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V}$$

$$\left(\frac{\partial \Delta G_{reaction}}{\partial T}\right)_P = -\Delta S_{reaction}$$

$$\left(\frac{\partial \Delta G_{reaction}}{\partial P}\right)_T = \Delta V_{reaction}$$

$$\Delta S_{reaction} = \sum_i \nu_i \bar{S}_i$$

$$\Delta V_{reaction} = \sum_i \nu_i \bar{V}_i$$

$$\left(\frac{\partial \Delta G_{reaction}}{\partial T}\right)_P = \sum_i \nu_i \left(\frac{\partial \bar{G}_i}{\partial T}\right)_P = \sum_i \nu_i (-\bar{S}_i) = -\Delta \bar{S}_{reaction} \quad \text{'proof'}$$

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$\Delta G_{\text{reaction}}$  and equilibrium (first pass)

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here  $\Delta G \equiv \Delta G_{\text{reaction}}$

1.  $\Delta G < 0$  spontaneous ('natural', irreversible)  
 $\Delta G = 0$  equilibrium (reversible)  
 $\Delta G > 0$  spontaneous in reverse direction
2.  $\Delta G_T = \Delta H - T\Delta S$
3.  $\Delta G^\circ$  all reactants and products in standard states
4.  $\Delta \bar{G}_f^\circ \equiv \bar{G}_f^\circ$  Appendix A at 298.15K (reaction where reactants are elements in their most stable form and in their standard states,  $P=1 \text{ atm}$ ,  $[\text{conc}]=1M$ , etc)  
 $\Delta \bar{G}_f^\circ(O_2(g)) \equiv 0$     $\Delta \bar{G}_f^\circ(C(gr)) = 0$

5.

$$\Delta G_{\text{reaction}}^\circ = \sum_i \nu_i \Delta \bar{H}_f^\circ - T \sum_i \nu_i \bar{S}_i^\circ$$
$$\Delta G_{\text{reaction}}^\circ = \Delta H_{\text{reaction}}^\circ - T \Delta S_{\text{reaction}}^\circ$$

NOTE : in Appendix A:  $\Delta \bar{G}_f^\circ$  and  $\Delta \bar{H}_f^\circ$  in  $\text{kJ mol}^{-1}$  BUT  $\bar{S}^\circ$  in  $\text{J K}^{-1} \text{mol}^{-1}$

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*End of Lecture*

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