

Chemistry 163B Winter 2014  
Free Energy, Introduction, Spontaneity

Chemistry 163B  
Free Energy  
E&R ( $\approx$  ch 6)

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spontaneity

$$\Delta S \geq \int \frac{\bar{d}q}{T}$$

$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surr} \geq 0$$

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

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goals of lecture

- 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

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

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

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

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

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

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

spontaneity at const T,P

$$(q_{sys})_P = \Delta H_P \quad (\bar{\alpha}v_{surr} = 0)$$

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

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

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

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

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

spontaneity for constant T, P ( $\bar{\alpha}v_{surr} = 0$ )

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motivation for, A

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

spontaneity at const T,V

$$(q_{sys})_V = \Delta U_V \quad (\bar{\alpha}v_{surr} = 0)$$

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

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

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

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

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

spontaneity for constant T, V ( $\bar{\alpha}v_{surr} = 0$ )

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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):  
 $\Delta A_{T,V} \leq 0$  (no  $w_{\text{other}}$ )  
 $\Delta G_{T,P} \leq 0$  (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>	$\Delta S_{\text{sys}} > 0$ <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 ??
- <small>(exothermic: disorders surr)</small>	+ <small>(disorders sys)</small>	<b>yes !!</b>
+ <small>(endothermic: orders surr)</small>	- <small>(orders sys)</small>	<b>no !!</b> <small>(reverse spontaneous)</small>
- <small>(exothermic: disorders surr)</small>	- <small>(orders sys)</small>	<b>maybe !!</b>
+ <small>(endothermic: orders surr)</small>	+ <small>(disorders sys)</small>	<b>maybe !!</b>

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

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

**for reversible, equilibrium process**

**example: equilibrium phase transition**

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

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

[HW6 problem #35, sign of  $\Delta G$  for  $T$  'around'  $T_{\phi}$ ]

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**differential relationships and Maxwell-Euler**

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$U \equiv \text{internal energy}$ $H \equiv U + PV$ $A \equiv U - TS$ $G \equiv H - TS$	$dU = \delta q + \delta w = \delta q - PdV$ $dS = \frac{\delta q_{\text{rev}}}{T} \quad \delta q = TdS$
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$dU = TdS - PdV$ <small><math>TdS - PdV</math></small> $dH = dU + PdV + VdP$ $dH = TdS + VdP$ <small><math>TdS - PdV</math></small> $dA = dU - TdS - SdT$ $dA = -SdT - PdV$ <small><math>TdS + VdP</math></small> $dG = dH - TdS - SdT$ $dG = -SdT + VdP$	$U(S, V)$ $H(S, P)$ $A(T, V)$ $G(T, P)$	$\left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V$ $\left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial S} \right)_P$ $\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V$ $\left( \frac{\partial S}{\partial P} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_P$
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## Free Energy, Introduction, Spontaneity

**G, A what's "FREE" about free energy ?**

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

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

spontaneity at const T,P

$$(q_{sys})_P = \Delta H_P \quad (\bar{w}_{other} = 0)$$

$$(q_{sys})_P + \bar{w}_{other} = \Delta H_P \quad (\bar{w}_{other} \neq 0)$$

$$\Delta S_{sys} + \frac{-(\Delta H_P - \bar{w}_{other})}{T} \geq 0$$

$$T\Delta S_{sys} - \Delta H_P + \bar{w}_{other} \geq 0$$

$$\Delta H_P - T\Delta S_{sys} - \bar{w}_{other} \leq 0$$

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

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

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

$$\Delta G_{T,P} \leq \bar{w}_{other}$$

Thus if  $\Delta G_{\text{reaction}} < 0$  (spontaneous), the maximum  $w_{\text{other}}$  done ON surroundings is  $-\Delta G_{\text{reaction}}$

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

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**

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**G≡H-TS**

$\Delta G_{T,P} = (\Delta H_{T,P})_{sys} - T\Delta S_{sys} \leq 0$   
*spontaneity for constant T,P ( $\bar{w}_{other}=0$ )*

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

**A≡U-TS**

$\Delta A_{T,V} = (\Delta U_{T,V})_{sys} - T\Delta S_{sys} \leq 0$   
*spontaneity for constant T,V ( $\bar{w}_{other}=0$ )*

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

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

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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  $\Delta G_{\text{reaction}}$  for chemical reaction (HW 7)**

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

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

$$\left(\frac{\partial \Delta G_{\text{reaction}}}{\partial T}\right)_P = -\Delta S_{\text{reaction}} \quad \left(\frac{\partial \Delta G_{\text{reaction}}}{\partial P}\right)_T = \Delta V_{\text{reaction}}$$

$$\Delta S_{\text{reaction}} = \sum_i \nu_i \bar{S}_i \quad \Delta V_{\text{reaction}} = \sum_i \nu_i \bar{V}_i$$

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

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

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

- $\Delta G < 0$  spontaneous ('natural', irreversible)  
 $\Delta G = 0$  equilibrium (reversible)  
 $\Delta G > 0$  spontaneous in reverse direction
- $\Delta G_r = \Delta H - T\Delta S$
- $\Delta G^\circ$  all reactants and products in standard states
- $\Delta \bar{G}_f^\circ \equiv \bar{G}_f^\circ$  Appendix A at 298.15K (reaction where reactants are elements in their most stable form and in their standard states,  $P=1$  atm, [conc]=1M, etc)  
 $\Delta \bar{G}_f^\circ(\text{O}_2(\text{g})) = 0$   $\Delta \bar{G}_f^\circ(\text{C}(\text{gr})) = 0$

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

- $\Delta G_{\text{reaction}}^\circ = \Delta H_{\text{reaction}}^\circ - T \Delta S_{\text{reaction}}^\circ$

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  $\text{JK}^{-1} \text{mol}^{-1}$

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*End of Lecture*

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spontaneity (argument II)

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0$$

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

statement: the surroundings are so 'massive' that any transfer of heat from system appears reversible to surroundings

$$\text{thus: } (q_{\text{surr}})_{\text{rev}} = -q_{\text{sys}} \quad \Delta S_{\text{surr}} = \frac{(q_{\text{surr}})_{\text{rev}}}{T} = -\frac{q_{\text{sys}}}{T}$$

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

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