Lecture 14
Chemistry 163B
Free Energy
E&R (≈ ch 6)

$$\Delta S \geq \int \frac{đq}{T}$$

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

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

- **define Gibbs (G) and Helmholtz (A) free energies**

- **show $\Delta G_{T,P} < 0$ and $\Delta A_{T,V} < 0$ for spontaneity**

- **differentials for dG and dA**

- **temperature and pressure dependence of G, A**

- **what's 'free' about free energy**

spontaneity

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

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

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

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

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

$$\left(q_{sys}\right)_P = \Delta H_P \quad (đw_{other} = 0)$$

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

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

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

$$define: \quad G \equiv H - TS \quad (general, \text{ even if T, P not constant})$$

$$\text{but}$$

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

$$spontaneity \ for \ constant \ T, P \ (đ_{wother} = 0)$$

motivation for, A

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

spontaneity at const T,V

$$\left(q_{sys}\right)_V = \Delta U_V \quad (đw_{other} = 0)$$

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

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

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

$define: \quad A \equiv U - TS \quad (general, \text{ even if T, V not constant})$

but

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

spontaneity for constant T,V ($đ_{wother} = 0$)

Definitions: A ≡ U-TS

G ≡ H-TS

Spontaneity (in terms of properties of system):

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

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

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

spontaneous: ΔH < 0 and ΔS>0 ➔ ΔG<0

Why "good for spontaneity" ?

ΔH$_{sys}$ < 0 **exothermic:** **disorders surroundings**	**ΔS$_{sys}$ > 0** **disorders system**

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

spontaneous: ΔU < 0; ΔS>0 ⇨ΔA<0

ΔU$_{sys}$ < 0 **exothermic:** **disorders surroundings**	**ΔS$_{sys}$ > 0** **disorders system**

$ΔG_{T,P} = ΔH - TΔS$

$$\Delta H \quad - \quad T\Delta S \quad < \quad 0 \quad ?$$

ΔH	ΔS	Spontaneous ??
− (*exothermic:* disorders surr)	**+** (disorders sys)	**yes !!**
+ (*endothermic:* orders surr)	**−** (orders sys)	**no !!** *(reverse spontaneous*)
− (*exothermic:* disorders surr)	**−** (orders sys)	**maybe !!**
+ (*endothermic:* orders surr)	**+** (disorders sys)	**maybe !!**

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

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 ΔG for T 'around' T$_{\phi}$]

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differential relationships and Maxwell-Euler

U ≡ internal energy
H ≡ U + PV
A ≡ U −TS
G ≡ H −TS

$$dU = đq + đw = đq - PdV$$

$$dS = \frac{đq_{rev}}{T} \quad dq = TdS$$

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

TdS − PdV

$$dH = dU + PdV + VdP$$

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

TdS − PdV

$$dA = dU - TdS - SdT$$

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

TdS + VdP

$$dG = dH - TdS - SdT$$
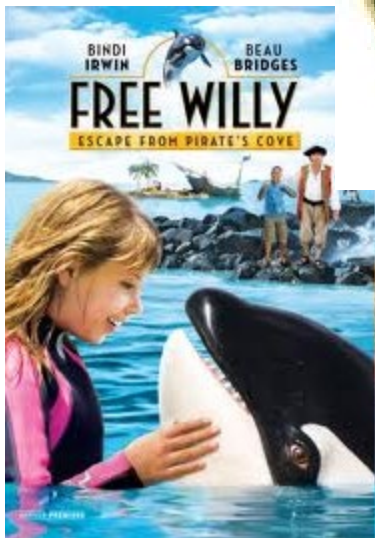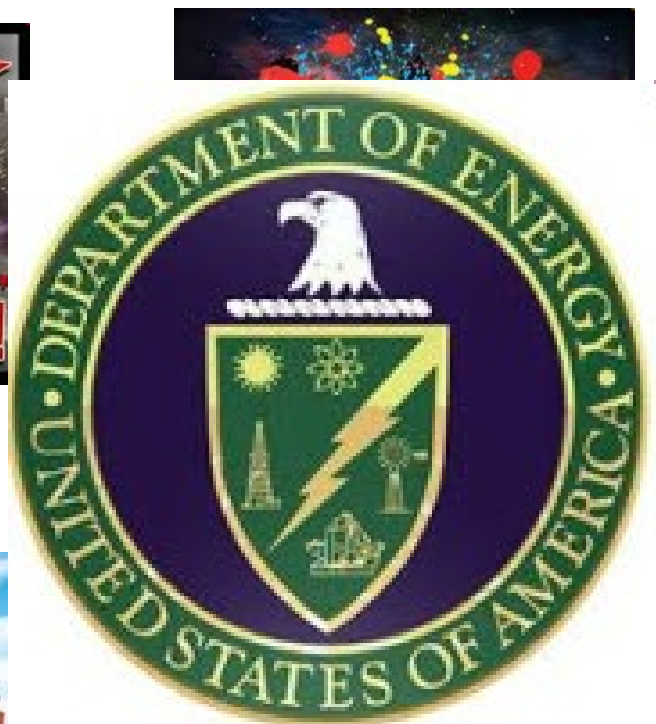
$$dG = -SdT + VdP \qquad G(T,P)$$

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

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

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

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

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

spontaneity at const T,P

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

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

$$\Delta S_{sys} + \frac{-\left(\Delta H_P - w_{other}\right)}{T} \geq 0$$

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

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

$$\Delta G_{T,P} \quad - w_{other} \leq 0 \quad \text{(eqn 6.10 E\&R}_{4th})$$

$$\Delta G_{T,P} - w_{other} \leq 0 \ \ (\text{eqn 6.10 E\&R}_{4th} \ \ 6.9_{3rd})$$

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

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

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

$$-\Delta G_{T,P} \geq -\left(w_{other}\right)_{system} = \left(w_{other}\right)_{surroundings}$$

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

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

ΔG: energy FREE to do work, other than expansion work

$$G \equiv H\text{-}TS \qquad\qquad A \equiv U\text{-}TS$$

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

spontaneity for constant T, P ($\displaystyle{\not{d}}w_{\text{other}} = 0$)

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

spontaneity for constant T, V ($\displaystyle{\not{d}}w_{\text{other}} = 0$)

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

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

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G: T dependence at constant P

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

G: P dependence at constant T

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

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

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and *ΔG$_{reaction}$* for chemical reaction (HW 6)

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

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

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

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

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

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here ΔG ≡ ΔG_{reaction}

1. **ΔG < 0 spontaneous** *('natural', irreversible)*
   ΔG = 0 equilibrium *(reversible)*
   ΔG > 0 spontaneous in reverse direction

2. **ΔG$_T$ = ΔH−TΔS**

3. **ΔG^o all reactants and products in standard states**

4. $\Delta \bar{G}_f^0 \equiv \bar{G}_f^0$ **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)*

$$\Delta \bar{G}_f^0 \left(O_2(g) \right) \equiv 0 \quad \Delta \bar{G}_f^0 \left(C(gr) \right) = 0$$

5.
$$\Delta G_{reaction}^0 = \sum_i v_i \Delta \bar{H}_f^0 - T \sum_i v_i \bar{S}_i^0$$

$$\Delta G_{reaction}^0 = \Delta H_{reaction}^0 - T \Delta S_{reaction}^0$$

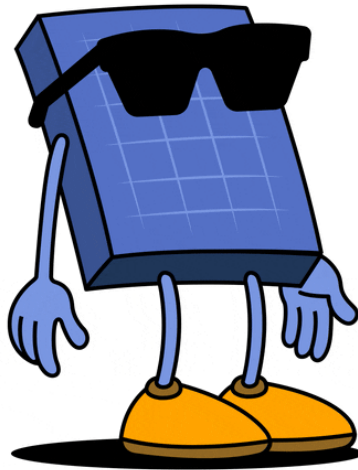$NOTE : in$ Appendix A: $\Delta \bar{G}_f^0$ and $\Delta \bar{H}_f^0$ in **kJ** mol^{-1} BUT $\bar{S}^0$ in **J** K^{-1}mol^{-1}

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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 for dG and dA**

✓ **temperature and pressure dependence of G, A**

✓ **what's 'free' about free energy**

End of Lecture 14

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

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

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

thus: $\left(q_{surr}\right)_{rev} = -q_{sys}$ $\qquad \Delta S_{surr} = \dfrac{\left(q_{surr}\right)_{rev}}{T} = -\dfrac{q_{sys}}{T}$

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