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

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spontaneity

$$\Delta S \geq \int \frac{đq}{T}$$

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

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

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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

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

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

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

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

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

but

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

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

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motivation for, A

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

spontaneity at const T,V

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

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

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

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

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

but

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

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

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summary

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

Spontaneity (in terms of properties of system):
$\Delta A_{T,V} \leq 0$ (no w_{other})
$\Delta G_{T,P} \leq 0$ (no w_{other})

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what's 'good for spontaneity'

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

spontaneous: ΔH < 0 and ΔS>0 ⇨ ΔG<0

$\Delta H_{sys} < 0$ exothermic: disorders surroundings	$\Delta S_{sys} > 0$ disorders system

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what's 'good for spontaneity'; similarly for ΔA at const T,V

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

spontaneous: ΔU < 0; ΔS>0 ⇨ΔA<0

$\Delta U_{sys} < 0$ exothermic: disorders surroundings	$\Delta S_{sys} > 0$ disorders system

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$\Delta G_{T,P}$= ΔH- TΔS

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 !!**

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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

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

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

[HW6 problem #35, sign of ΔG for T 'around' T_ϕ]

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differential relationships and Maxwell-Euler

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

$$dU = đq + đw = đq - PdV$$

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

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

$$dH = dU + PdV + VdP \quad (dU = TdS - PdV)$$

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

$$dA = dU - TdS - SdT \quad (dU = TdS - PdV)$$

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

$$dG = dH - TdS - SdT \quad (dH = TdS + VdP)$$

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

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

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

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

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

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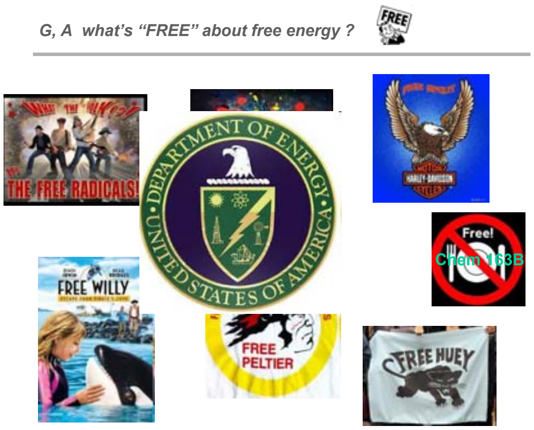
G, A what's "FREE" about free energy ?



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

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

spontaneity at const T,P

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

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

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

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

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

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

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

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

$$\Delta G_{T,P} \quad \leq \quad đw_{other}$$

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

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

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

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motivation for G, A

G≡H-TS	A≡U-TS
$\Delta G_{T,P} = (\Delta H_{T,P})_{sys} - T\Delta S_{sys} \leq 0$ spontaneity for constant T,P ($đ_{wother}$=0)	$\Delta A_{T,V} = (\Delta U_{T,V})_{sys} - T\Delta S_{sys} \leq 0$ spontaneity for constant T,V ($đ_{wother}$=0)
$\Delta G_{T,P} \quad \leq \quad w_{other}$	$\Delta A_{T,V} \quad \leq \quad w_{other}$

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

G: T dependence at constant P

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

G: P dependence at constant T

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

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

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

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

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

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

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

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

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

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

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. **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. $$\Delta G^0_{reaction} = \sum_i \nu_i \Delta \bar{H}_f^0 - T\sum_i \nu_i \bar{S}_i^0$$
   $$\Delta G^0_{reaction} = \Delta H^0_{reaction} - T\Delta S^0_{reaction}$$

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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End of Lecture

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spontaneity (argument II)

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

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

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

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