

Lecture 14

Chemistry 163B

Free Energy

ESR (\approx ch 6)



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spontaneity (system + surroundings)

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

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

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goals of lecture

- 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

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spontaneity

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

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

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

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

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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

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'

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

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

Why "good for spontaneity" ?

$\Delta H_{\text{sys}} < 0$ exothermic: disorders surroundings	$\Delta S_{\text{sys}} > 0$ disorders system
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Chemistry 163B Winter 2020 Lecture 14
Free Energy, Introduction, Spontaneity

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

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

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

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

ΔH - $T\Delta S$ < 0 ?

ΔH	ΔS	Spontaneous ??
- (<i>exothermic: disorders surr</i>)	+ (<i>disorders sys</i>)	yes !!
+ (<i>endothermic: orders surr</i>)	- (<i>orders sys</i>)	no !! (<i>reverse spontaneous</i>)
- (<i>exothermic: disorders surr</i>)	- (<i>orders sys</i>)	maybe !!
+ (<i>endothermic: orders surr</i>)	+ (<i>disorders sys</i>)	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

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

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

[HW5 problem #35, sign of ΔG for T 'around' T_{ϕ}]

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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

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

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

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

TdS - PdV

$$dH = dU + PdV + VdP$$

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

TdS - PdV

$$dA = dU - TdS - SdT$$

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

TdS + VdP

$$dG = dH - TdS - SdT$$

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

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

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

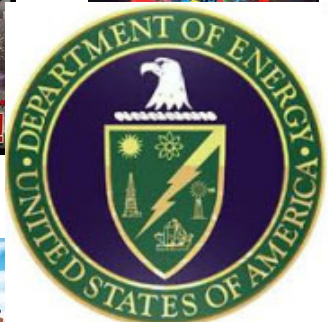
$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$

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

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



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why "free" energy (E&R eqn 6.10_{4th} 6.9_{3rd})

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

spontaneity at const T,P

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

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

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

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

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

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

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why "free" energy (E&R eqn 6.10)

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

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

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

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

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

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

$G \equiv H - TS$

$A \equiv U - TS$

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

spontaneity for constant T, P ($\vec{d}_{\text{wother}} = 0$)

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

spontaneity for constant T, V ($\vec{d}_{\text{wother}} = 0$)

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

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

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

G: T dependence at constant P

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

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 6)

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

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

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

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

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

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

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

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

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

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

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° 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 kJ mol^{-1} BUT \bar{S}° in $\text{J K}^{-1}\text{mol}^{-1}$

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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 for dG and dA
- ✓ temperature and pressure dependence of G, A
- ✓ what's 'free' about free energy

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End of Lecture 14



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

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

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