

Chemistry 163B Winter 2020 Lecture 14

Free Energy, Introduction, Spontaneity

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

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

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

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

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

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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

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

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

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

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

define: $G \equiv H - TS$ (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 ($\bar{d}w_{other} = 0$)

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motivation for, A

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

spontaneity at const T,V

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

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

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

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

define: $A \equiv U - TS$ (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 ($\bar{d}w_{other} = 0$)

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summary

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

Spontaneity (in terms of properties of system):
 $\Delta A_{T,V} \leq 0$ (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: $\Delta H < 0$ 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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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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$\Delta G_{T,P} = \Delta H - T\Delta S$

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

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

$\Delta G_{T,P} = \Delta H_{\phi} - T_{\phi}\Delta S_{\phi}$ 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
 $H \equiv U + PV$
 $A \equiv U - TS$
 $G \equiv H - TS$

$dU = \delta q + \delta w = \delta q - PdV$
 $dS = \frac{\delta q_{\text{rev}}}{T} \quad \delta q = TdS$

$dU = TdS - PdV$	$U(S, V)$	$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V$
$dH = dU + PdV + VdP$	$H(S, P)$	$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P$
$dA = dU - TdS - SdT$	$A(T, V)$	$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$
$dG = dH - TdS - SdT$	$G(T, P)$	$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P$








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G, A 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

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

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

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

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

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

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

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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=H-TS

$\Delta G_{T,P} = (\Delta H_{T,P})_{\text{sys}} - T\Delta S_{\text{sys}} \leq 0$
spontaneity for constant T,P (if $w_{\text{other}}=0$)

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

A=U-TS

$\Delta A_{T,V} = (\Delta U_{T,V})_{\text{sys}} - T\Delta S_{\text{sys}} \leq 0$
spontaneity for constant T,V (if $w_{\text{other}}=0$)

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

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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)

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

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

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

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

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

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Free Energy, Introduction, Spontaneity

$\Delta G_{\text{reaction}}$ 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. $\Delta G_r = \Delta H - T\Delta S$
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
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- ✓ differentials for dG and dA
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- ✓ what's 'free' about free energy

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End of Lecture 14



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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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