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

FREE

1

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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)**

2

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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**

3

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spontaneity

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

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

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

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

4

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

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

$$\boxed{\text{spontaneity at const T,P}}$$

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

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

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

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

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

but

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

spontaneity for constant T, P ($dw_{other}=0$)

5

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motivation for, A

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

$$\boxed{\text{spontaneity at const T,V}}$$

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

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

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

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

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

but

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

spontaneity for constant T,V ($dw_{other}=0$)

6

Slide 7

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})

7

Slide 8

what's 'good for spontaneity'

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

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

Why "good for spontaneity" ?

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

8

Slide 9

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

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

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

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

9

Slide 10

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

ΔH	$-$	$T\Delta S$	$<$ 0 ?

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 !!**

10

Slide 11

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

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

11

Slide 12

differential relationships and Maxwell-Euler

$U \equiv$ internal energy
$H \equiv U + PV$
$A \equiv U - TS$
$G \equiv H - TS$

$dU = dq + dw = dq - PdV$

$dS = \dfrac{dq_{rev}}{T} \quad dq = TdS$

$dU = TdS - PdV$	$U(S,V)$
$TdS - PdV$	
$dH = dU + PdV + VdP$	
$dH = TdS + VdP$	$H(S,P)$
$TdS - PdV$	
$dA = dU - TdS - SdT$	
$dA = -SdT - PdV$	$A(T,V)$
$TdS + VdP$	
$dG = dH - TdS - SdT$	
$dG = -SdT + VdP$	$G(T,P)$

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

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

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

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

12

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7   8   9   10   11   12

2

Slide 13

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

13

13

Slide 14

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

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

spontaneity at const T,P

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

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

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

14

14

Slide 15

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

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

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

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

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

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

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

15

15

Slide 16

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 ($đ_{wother}=0$)

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

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

16

16

Slide 17

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

G: T dependence at constant P

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

G: P dependence at constant T

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

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

17

17

Slide 18

and $\Delta G_{reaction}$ for chemical reaction (HW 6)

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

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

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

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

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

18

18

3

ΔG$_{reaction}$ and equilibrium (first pass)

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

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

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}

19

19

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goals of lecture

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

✓ **show ΔG$_{T,P}$ < 0 and ΔA$_{T,V}$ < 0 for spontaneity**

✓ **differentials for dG and dA**

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

✓ **what's 'free' about free energy**

20

20

End of Lecture 14

21

21

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

22

22