UNIT6-DAY2-LaB1230

Monday, February 11, 2013
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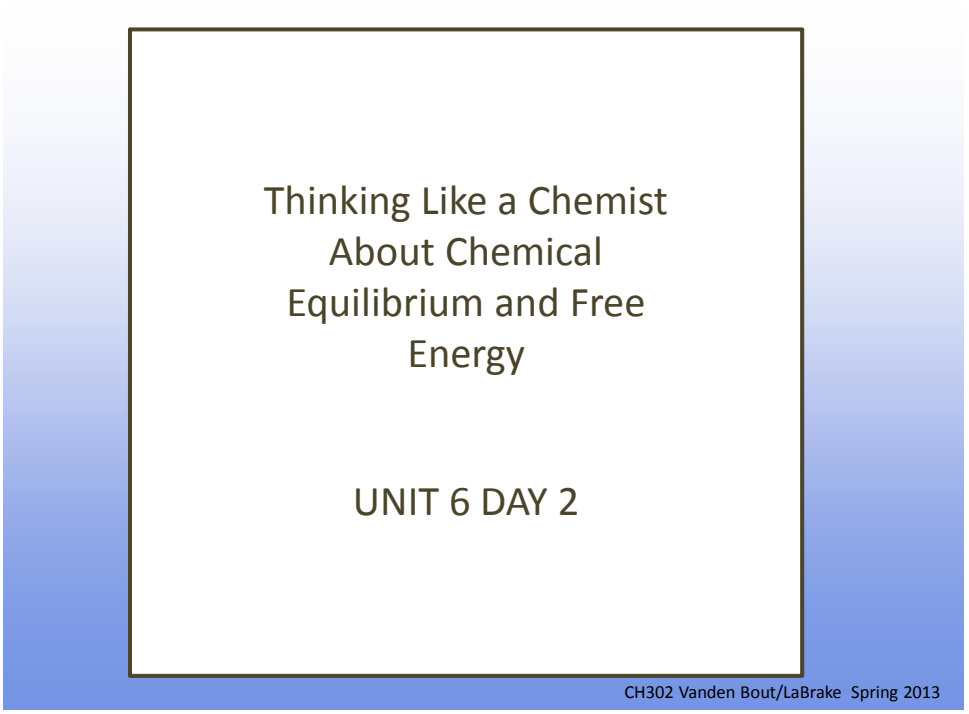
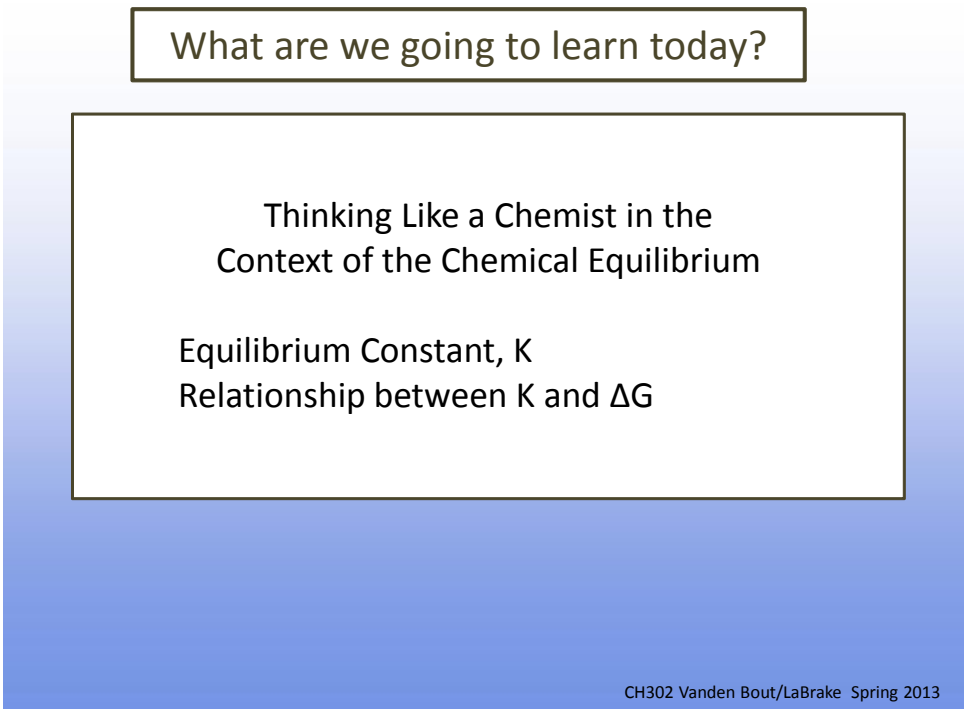




IMPORTANT INFORMATION

LM15 LeChatelier's Principle due Th 9AM
LM16 Intro Acids & Bases due Th 9AM

EXAM AVERAGES GREAT!

Piazza Bonus Pts
- answering questions
- asking questions
- reading answers

Quiz Clicker Question 1

Write equilibrium constant expressions for the following:

1) $CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g)$

2) $Ca(OH)_2(s) \leftrightarrow Ca^{2+}(aq) + 2\ OH^-(aq)$

	(1)	(2)
A)	$K = \frac{[CaO][CO_2]}{[CaCO_3]}$	$K = \frac{[Ca^{2+}][OH^-]^2}{[Ca(OH)_2]}$
B)	$K = P_{CO_2}$	$K = P_{Ca^{2+}}(P_{OH^-})^{-2}$
C)		
~~D)~~	$K = P_{CO_2}$	$K = [Ca^{2+}][OH^-]^2$

Poll Clicker Question 2

Calculate K_c given K_p for

$$N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$$

$K_p = (RT)^{-2} K_c$

$\nu = -2$

A) $K_c = K_p$

Poll: Clicker Question 2

Calculate K_c given K_p for

$$N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$$

A) $K_c = K_p$

B) $K_c = RTK_p$

C) $K_c = K_p^{-2}$

D) $K_c = K_p(RT)^{+2}$

$K_p = \frac{K_c}{(RT)^2}$

$K_p = (RT)^{\Delta n} K_c$

$\Delta n = n_{gas\ final} - n_{gas\ initial}$

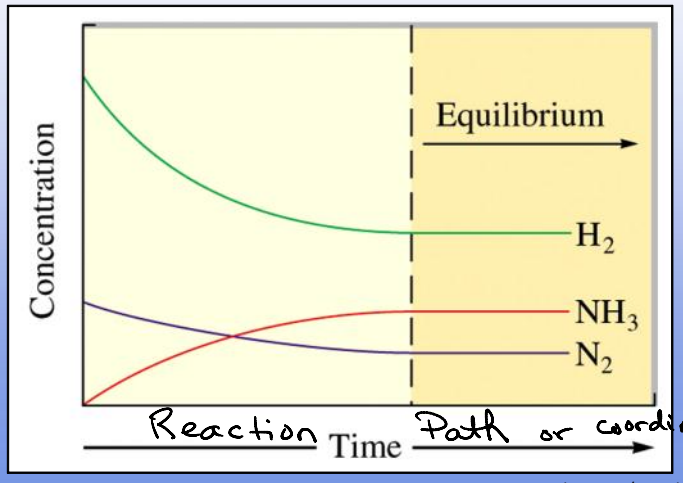
$\Delta n = 2 - 4 = -2$

Poll: Clicker Question 3

Which is lower in Free Energy

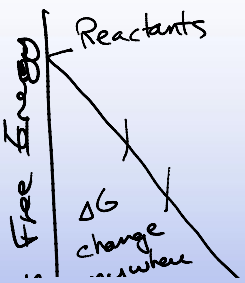
A) mixture at beginning

B) mixture at end



Rxn goes toward lower free energy spontaneously

Free energy and Equilibrium



$\Delta G^\circ_{Rxn} = G^\circ_p - G^\circ_r$

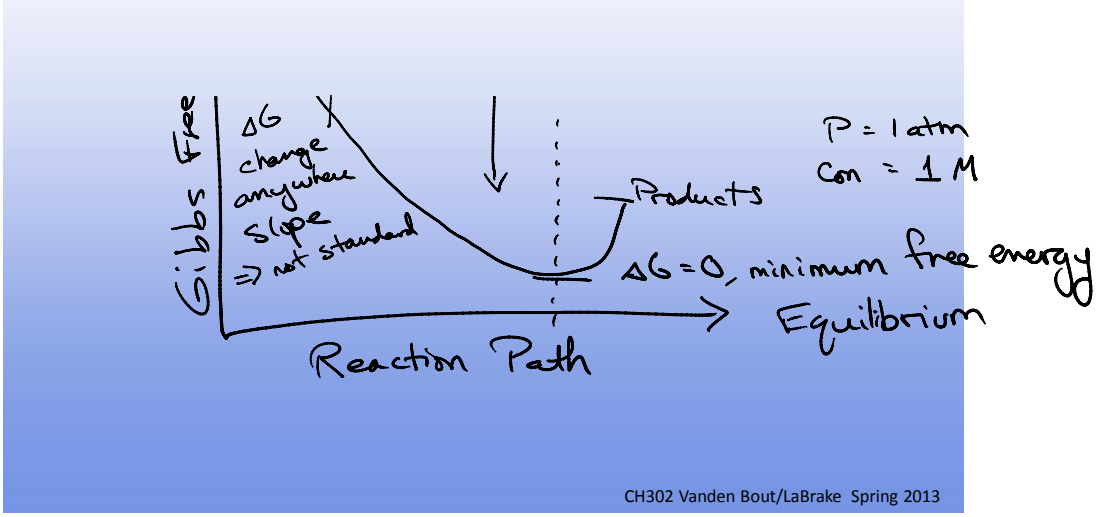
Standard conditions:

100% reactant → 100% product

$T = 298K$

$P = 1\ atm$

$Con = 1\ M$



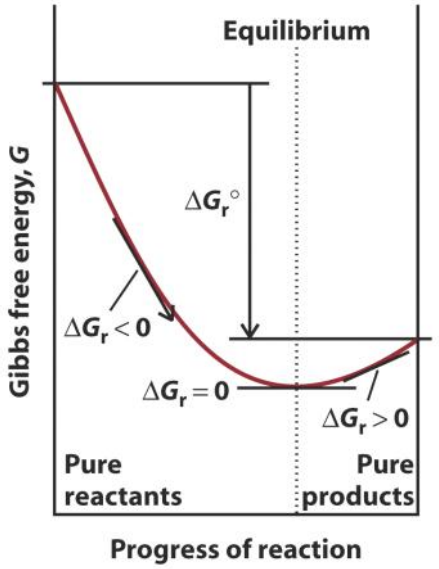
Interpreting K and $\Delta_r G°$

Pure **Products** (in standard state) are Lower in Free Energy

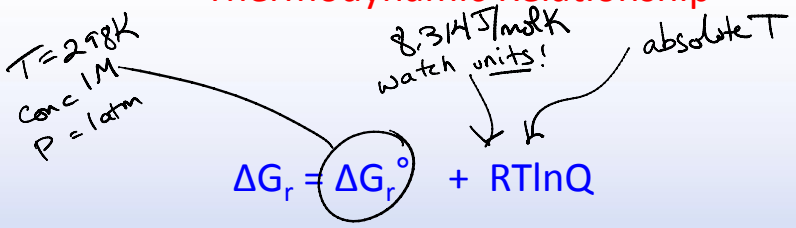
$$\Delta G = \Delta G_r^\circ + RT \ln Q$$

↑ standard

ΔG_r difference in molar free energy of products and reactants at *any* definite fixed composition of reactants and products



Thermodynamic Relationship



Q = <u>activities of products</u> =
activities of reactants

Q is the reaction quotient. Very important to tell us where on the "reaction path we are located" …before or after equilibrium.

Thermodynamic Relationship

$$\Delta G_{Rxn} = \Delta G^{\circ}_{Rxn} + RT \ln Q$$

at equilibrium

$\Delta G_{Rxn} = 0$

$Q = K$

$$0 = \Delta G^{\circ}_{Rxn} + RT \ln K$$

$$\boxed{\Delta G^{\circ}_{Rxn} = -RT \ln K}$$

super important! memorize

K depends on $\Delta_r G°$

$\Delta G^\circ_{rxn} = -RT\ln K$ memorize

$\Delta G = \Delta H - T\Delta S$

You need to be able to use a table to find $\Delta_r G°$
from $\Delta_f G°$ or
from $\Delta_f H°$ to find $\Delta_r H°$ and $S°$ to find $\Delta_r S°$

Poll: Clicker Question 4

$\Delta_r H° = 10\ kJ\ mol^{-1}$ and $\Delta_r S° = 20\ J\ K^{-1}\ mol^{-1}$

Assuming $\Delta_r H°$ and $\Delta_r S°$ don't change with temperature
does this reaction favor the products or the reactants at 400K?

$\Delta G = \Delta H - T\Delta S$

$= 10100J - (400)(20)$

$= 10000 - 8000 = +2000J$

A. Products

B. Reactants

C. There is no way to know without a balance equation

$\Delta G > 0$
Reactant favored
non spontaneous

water

$$2H_2O(g) \longleftrightarrow 2H_2(g) + O_2(g)$$

What is K for this reaction at 298K

$K = \frac{products}{reactants}$

Poll: Clicker Question 5

A. extremely small

What is K for this reaction at 298K

Poll: Clicker Question 5

A. extremely small $K<1$ LOTS more reactants $\Delta G>0$

B. extremely large $K>1$ LOTS more products $\Delta G<0$

C. approximately one $K=1$ ⇒ same amt products & reactants $\Delta G=0$

$$2H_2O(g) \longleftrightarrow 2H_2(g) + O_2(g)$$

What is K for this reaction at 298K
given that $\Delta_r G° = +113.4$ kJ mol^{-1} $R = 8.314 J/mol\,K$

Poll: Clicker Question 6

A) 9.6×10^{-1}

B) 6.4×10^{19}

C) 1.3×10^{-20}

D) 1.5×10^{-25}

$\Delta G^{o}_{Rxn} = -RT\ln K$ $T = 298K$

$113.4\times10^{3} = -8.314 \cdot 298 \ln K$

$e^{\left(\frac{113.4\times10^{3}}{-8.314\cdot298}\right)}$

$K = 1.3\times10^{-20}$

Poll: Clicker Question 7

At 313 K, $\Delta_r G° = +41$ kJ mol^{-1} for this reaction

$$2H_2S(g) \longleftrightarrow 2H_2(g) + S_2(g)$$

You find the following partial pressures at 313K
H_2 is 1 atm, S_2 is 1 atm, H_2S = 2 atm

not at equilibrium

How will this reaction proceed? What should you do 1st?

A. move toward the products $\Delta G^{o} = -RT\ln K$ $K = 1.442\times10^{-7}$

B. move towards the reactants

How will this reaction proceed?

A. move toward the products

B. move towards the reactants

C. the reaction is at equilibrium

$\Delta G^\circ = -RT\ln K$ $K = 1.44 \times 10^{-7}$

$Q = 0.25$

$Q > K$

has too much product

moves toward Reactants

At 313 K, $\Delta_r G^\circ$ = +41 kJ mol^{-1} for this reaction

$$2H_2S(g) \longleftrightarrow 2H_2(g) + S_2(g)$$

You find the following partial pressures at 313K

H_2 is 1 atm, S_2 is 1 atm, H_2S = 2 atm

$K = 2.2 \times 10^{-3}$ for this reaction (at some T)

$$2HI(g) \longleftrightarrow H_2(g) + I_2(g)$$

You start with a partial pressure of 1atm of HI

what are the partial pressures at a constant P of 1atm and constant T

	$2HI$	$\longrightarrow$	H_2	I_2
I	1		$\emptyset$	$\emptyset$
C	$-2x$		$+x$	$+x$
E	$1-2x$		x	x

$K = \frac{P_{H_2} P_{I_2}}{P_{HI}^2} = \frac{x \cdot x}{(1-2x)^2}$

$\sqrt{2.2 \times 10^{-3}} = \sqrt{\frac{x^2}{(1-2x)^2}}$

$x = 0.043$

E	$1-2x$	x	x
	$1-2(0.043) = 0.914$	0.043	0.043

$x = 0.043$

Poll: Clicker Question 8

$2HI \rightarrow H_2 + I_2$

0.914 0.043 0.043 ← equilibrium

Consider the previous example at equilibrium.

Add 0.5 atm of HI(g).

$K = 2.2 \times 10^{-3}$

What is going to happen to the reaction mixture? added more

A) No Shift
B) Shift Left
C) Shift Right

$$Q = \frac{P_{H_2} P_I}{(P_{HI})^2} = \frac{(0.043)(0.043)}{(0.914 + 0.5)^2}$$

$Q < K$

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Poll: Clicker Question 9

$2HI \rightarrow H_2 + I_2$ equilibrium

0.914 0.043 0.043

Consider the previous example at equilibrium.

Add 0.5 atm of HI(g) and 0.5 atm of H_2 (g).

$K = 2.2 \times 10^{-3}$

$$Q = \frac{P_{H_2} P_I}{P_{HI}^2} = \frac{(0.543)(0.043)}{(1.414)^2}$$

What is going to happen to the reaction mixture?

A)No Shift
B)Shift Left
C)Shift Right

$Q = 1.8 \times 10^{-2}$

$Q > K$

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Equilibria response to change

- Le Chatelier's Principle: When a stress is applied to a system in dynamic equilibrium, the equilibrium tends to adjust to minimize the effect of the stress.

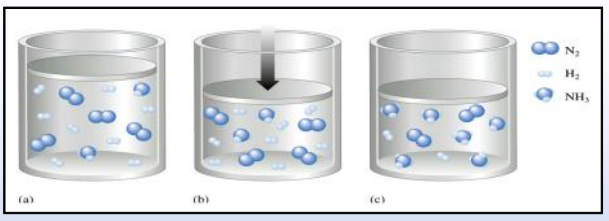
- Types of stress:
  - Adding or removing reagents
  - Changing volume of gas phase
  - Adding or removing heat

Left Reactant Right Product

- Consider the equilibrium $SO_3(g) + NO(g) \leftrightarrow SO_2(g) + NO_2(g)$. Predict the effect on the equilibrium of
  a) the addition of NO — add reactant, shift Right
  b) the removal of SO_2 — shift Right, remove product
  c) the addition of NO_2. — shift left

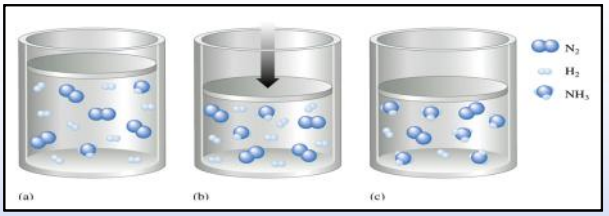
Poll: Clicker Question 10

Effect of Volume Change on Gas phase reaction



reduce moles

- Compression: Composition will change in a way that minimizes the resulting increase in pressure



reduce # moles of gas

- Compression: Composition will change in a way that minimizes the resulting increase in pressure
- Expansion: Composition will change in a way to increase the pressure
- Introduction of Inert Gas: although affect total pressure, does not effect partial pressure of gases, thus no effect on Q, thus no shift at constant volume

Compress, inc pressure, to relieve pressure, dec gas moles

Predict the effect of compression on the equilibrium composition of the reaction $CH_4(g) + H_2O(g) \leftrightarrow CO(g) + 3H_2(g)$

A) SHIFT LEFT
B) SHIFT RIGHT
c) No change

Temperature and Equilibrium

Data from an exothermic reaction

Temperature (K)	K (L^2/mol^2)	
500	Product favored	90
600		3
700	Reactant favored	0.3
800		0.04

T inc

K is dependent on T

T↑, K↓

ENDO

T↑ K↑

heat is like a reactant

What is the relationship here? What could be the explanation?

$H_2 + N_2 \leftrightarrow NH_3 + Heat$

heat is a product in exothermic rxn

Poll: Clicker Question 11

Equilibria response to change

Consider the equilibrium
$SO_3(g) + NO(g) \leftrightarrow SO_2(g) + NO_2(g) + heat.$
Predict the effect on the equilibrium of

5. the addition of NO — right
4. the removal of SO_2 — right
3. the addition of NO_2 — left
2. Decrease the volume of reaction vessel — no change, equal moles
1. Increase the temperature

A) SHIFT RIGHT
B) SHIFT LEFT

the addition of NO

the removal of SO_2

(3) the addition of NO_2 — shift left

(2) Decrease the volume of reaction vessel — no change, equal gas moles

(1) Increase the temperature — shift left

A) SHIFT RIGHT B) SHIFT LEFT C) No change

What did we learn today?

K is related to ΔG

Equilibrium is achieved at minimum free energy – depends on the energies of reactants and products and entropy of mixing

Equilibrium can be disturbed, reaction will adjust to return to equilibrium condition.

Learning Outcomes

Describe the relationship between free energy and equilibrium.

Convert ΔG to K and vice versa

Determine if a system is at equilibrium and if not which direction the reaction will shift to achieve equilibrium

Predict the direction of a reaction after an applied stress. Stresses include concentration changes, increase or decrease in temperature and global volume change.