

Thinking Like a Chemist
About Chemical
Equilibrium and Free
Energy

UNIT 6 DAY 2

What are we going to learn today?

Thinking Like a Chemist in the
Context of the Chemical Equilibrium

Equilibrium Constant, K
Relationship between K and ΔG

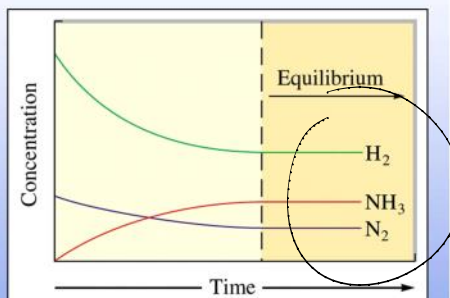
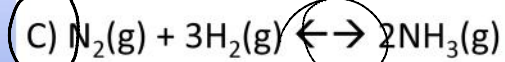
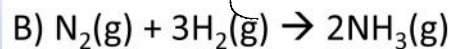
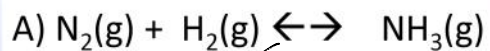
IMPORTANT INFORMATION

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

POLL: CLICKER

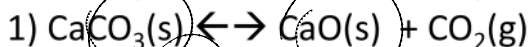
Try to interpret what is going on in this graph.

The chemical reaction is:



Individual Quiz Clicker Question; NO TALKING

Write equilibrium constant expressions for the following:



A) $K_c = [\text{CO}_2]$; $K_c = [\text{Ca}^{2+}] \times 2[\text{OH}^-]^2$

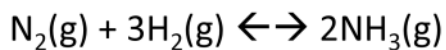
B) $K_c = [\text{CO}_2][\text{CaO}]/[\text{CaCO}_3]$; $K_c = [\text{Ca}^{2+}][\text{OH}^-]^2/[\text{Ca}(\text{OH})_2]$

C) $K_c = [\text{CO}_2][\text{CaO}]$; $K_c = [\text{Ca}^{2+}][\text{OH}^-]$

D) $K_c = [\text{CO}_2]$; $K_c = [\text{Ca}^{2+}][\text{OH}^-]^2$

Poll: Clicker Question

Calculate K_c given K_p for



A) $K_c = K_p$

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

C) $K_c = K_p^{-1}$

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

$\checkmark PV = nRT$

$P = \frac{n}{V} RT$

$\Delta n = n_p - n_r$

$P = C RT$

$\Delta n = -2$

$-\Delta n = +2$

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

$K_c = K_p \text{RT}^{-\Delta n}$

Given $K = 200$

$[H_2]_{eq} = 0.2 \text{ M}$, $[N_2]_{eq} = 0.4 \text{ M}$, $[NH_3]_0 = 0.1 \text{ M}$

Fill in the rest

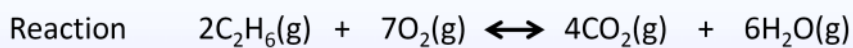
$$K = 200 = \frac{NH_3^2}{(H_2)^3 (N_2)} = (NH_3)_{eq} = .8$$



Initial	H_2	N_2	.1
Change	$-3x$	$-x$	$+2x$
Equilibrium	.2	.4	.8

$x = .35$

For the following reaction what is the equilibrium value for CO_2 ?



Initial	1.0	1.4	1.8	0
Change	$-2x$?	$+4x$?
Equilibrium	?	?	?	?

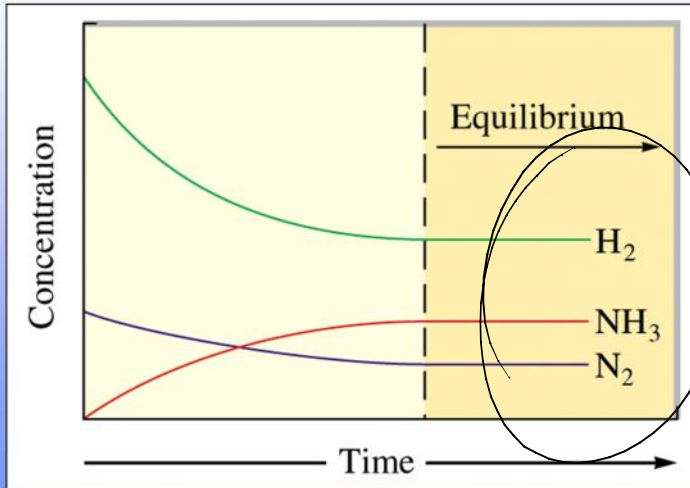
- A. $1.8-2x$ B. $1.8+2x$ C. $1.8+4x$ D. $1.0+6x$ E. $+x$

Poll: Clicker Question

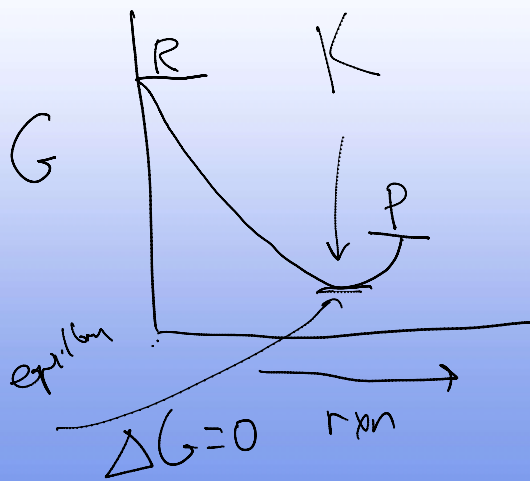
Which is lower in Free Energy

A) mixture at beginning

B) mixture at end



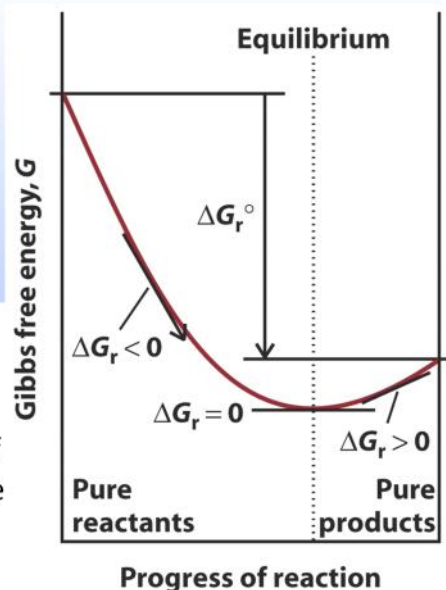
Free energy and Equilibrium



$\Delta G_{rxn}^{\circ} < 0$ - 298, 1 atm / mol
Spontaneous

Interpreting K and $\Delta_r G^\circ$

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



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

Thermodynamic Relationship

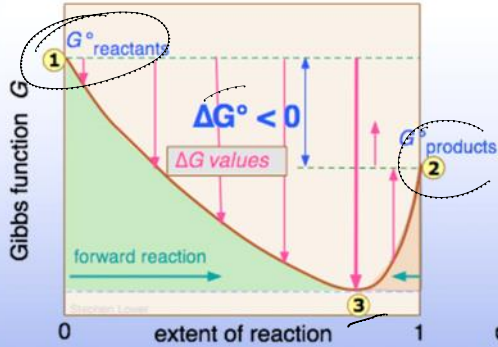
$$\Delta G_r = \Delta G_r^\circ + RT \ln Q$$

Q = $\frac{\text{activities of products}}{\text{activities of reactants}}$ =

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

gas "j"
activity

Thermodynamic Relationship

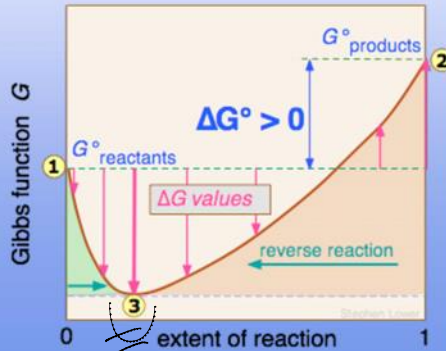


Spontaneous
product favored
 $\Delta G^\circ < 0$

$$\Delta G^\circ > 0$$

reactant favored

$$Q = K$$



$$\Delta G = 0$$

At Equil.

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

$$0 = \Delta G^\circ + RT \ln K$$

$$0 = \Delta G^\circ + RT \ln K$$

$$\Delta G^\circ = -RT \ln K$$

$$K \gg 1$$

$$K \ll 1$$

K depends on $\Delta_r G^\circ$

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

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

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

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

- A. Products
- B. Reactants
- C. There is no way to know without a balance equation

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

$$\Delta G = 10 - 400(.020) =$$

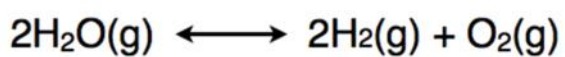
$$\Delta G = -RT \ln K$$

"+"

$$K < 1$$

Principles of Chemistry II

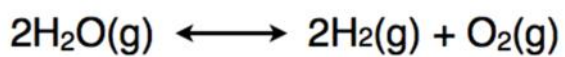
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What is K for this reaction at 298K

- A. extremely small
- B. extremely large
- C. approximately one

$$K = \frac{P_{\text{H}_2}^2 P_{\text{O}_2}}{P_{\text{H}_2\text{O}}^2}$$



What is K for this reaction at 298K
given that $\Delta_r G^\circ = +113.4 \text{ kJ mol}^{-1}$

$$\Delta G^\circ = -RT \ln K$$

$$K = \underline{\underline{1.3 \times 10^{-20}}}$$

011. Clicker Question

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

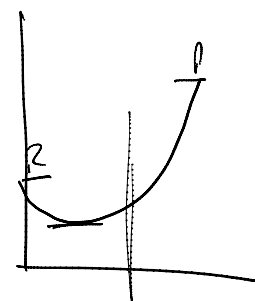


You find the following partial pressures at 313K
 H_2 is 1 atm, S_2 is 1 atm, $\text{H}_2\text{S} = 2 \text{ atm}$

How will this reaction proceed?

- A. move toward the products
- B. move towards the reactants
- C. the reaction is at equilibrium

$$\Delta G = -RT \ln K$$



$$Q = \frac{(1)^2(1)}{(2)^2} = \frac{1}{4}$$

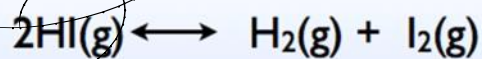
$$K = 1.3 \times 10^{-3}$$

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



You find the following partial pressures at 313K
 H_2 is 1 atm, S_2 is 1 atm, $\text{H}_2\text{S} = 2 \text{ atm}$

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



You start with a partial pressure of 1 atm of HI
what are the partial pressures at a constant P of 1 atm and constant T

R	$2\text{HI} \rightleftharpoons$	H_2	$+ \text{I}_2$
I	1 atm	0	0
C	$-2x$	$+x$	$+x$
E	$1-2x$.914	x .043	x .043

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

$$x = .043$$

Poll: Clicker Question



Consider the previous example at equilibrium.

Add 0.5 atm of HI(g).

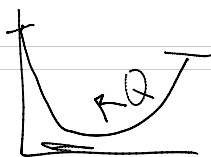
$$.914 + .5 \quad .043 \quad .043$$

What is going to happen to the reaction mixture?

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

~~$K = \frac{(.043)(.043)}{.914}$~~

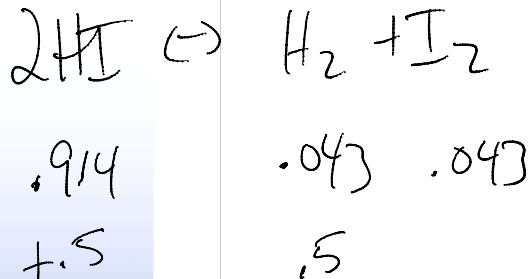
$\frac{(.043)(.043)}{(.914)}$



Poll: Clicker Question

Consider the previous example at equilibrium.

Add 0.5 atm of HI(g) and 0.5 atm of H₂ (g).



What is going to happen to the reaction mixture?

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

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

$$Q = \frac{(.543)(.043)}{(1.44)^2}$$

$$Q = 1.17 \times 10^{-2}$$

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

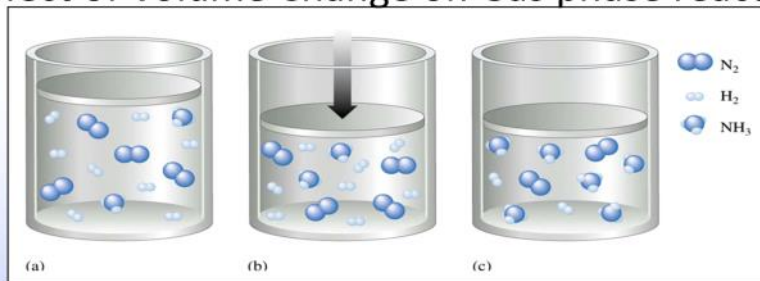
- Consider the equilibrium $\text{SO}_3(\text{g}) + \text{NO}(\text{g}) \leftrightarrow \text{SO}_2(\text{g}) + \text{NO}_2(\text{g})$.
Predict the effect on the equilibrium of

a) the addition of NO

b) the removal of SO_2

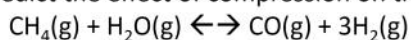
c) the addition of NO_2 .

Effect of Volume Change on Gas phase reaction



- 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 affects total pressure, does not effect partial pressure of gases, thus no effect on Q, thus no shift

Predict the effect of compression on the equilibrium composition of the reaction



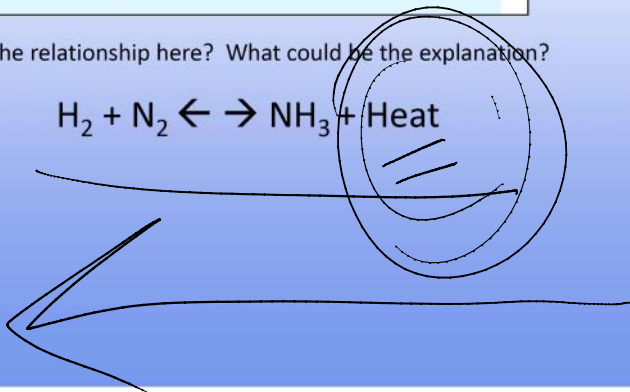
- 2 ← 4
- A) SHIFT LEFT
- B) SHIFT RIGHT

Temperature and Equilibrium

Data from an exothermic reaction

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

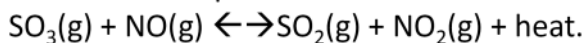
What is the relationship here? What could be the explanation?



Poll: Clicker Question

Equilibria response to change

Consider the equilibrium



Predict the effect on the equilibrium of

1. the addition of NO
2. the removal of SO₂
3. the addition of NO₂
4. Decrease the volume of reaction vessel
5. Increase the temperature

A) SHIFT RIGHT

B) SHIFT LEFT

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.

Equilibrium constant is the product of the ions in solution

Solubility is driven by Free Energy

Relationship between Solubility and Free Energy

Talk about standard states.... 1 M

What actually happens versus where would it like to be.

$$\Delta G^{\circ}_{\text{rxn}} = -RT \ln K$$

$$\Delta G^{\circ}_{\text{rxn}} > 0, K_{\text{sp}} < 1$$

$$\Delta G^{\circ}_{\text{rxn}} = 0, K_{\text{sp}} = 1$$

$$\Delta G^{\circ}_{\text{rxn}} < 0, K_{\text{sp}} > 1$$

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Example

- The standard reaction free energy for $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$ is -21.1 kJ/mol at 500K (when $RT = 4.16 \text{ kJ/mol}$). What is the value of ΔG_r at 500 K when the partial pressures of the gases are $P_{\text{H}_2}=1.5 \text{ bar}$, $P_{\text{I}_2}=.88 \text{ bar}$ and $P_{\text{HI}}=.65 \text{ bar}$? What is the spontaneous direction of the reaction?