Chem 1B Objective 7:
Understand equilibrium reactions (equilibrium constant, LeChatelier's principle, equilibrium calculation).

Key Ideas: Many important reactions are equilibrium reactions, e.g., many reactions in our body.
Chem 1A: Reactants form products. Reaction goes in one direction – forward.
Equilibrium reaction: Reaction goes forward and backwards ==> reversible reaction.

How far does a reaction occur? See K_{eq}
K_{eq} is constant but changes with T.

Calculate [ ] from K_{eq}. Compare to stoichiometry calculation.

LeChatelier's principle – make a reaction go forward or reverse

An Equilibrium Reaction Goes In The Forward and Reverse Directions (Reversible Reaction)

Reactants react to form products: A + B ---> C + D
Products react to re-form reactants: C + D ---> A + B

$$A + B \rightleftharpoons C + D$$

*At Equilibrium, reactants **and** products will be present.*

*At Equilibrium, reactants **and** products will be present.*

The ratio of reactants and products is quantified with an

Equilibrium Constant: $K_{eq} = \dfrac{\Pi\ [\text{products}]^n}{\Pi\ [\text{reactants}]^m}$

Example: $aA + bB \Leftrightarrow cC + dD$

$$K_{eq} = \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}$$

More reactants means K_{eq} is:

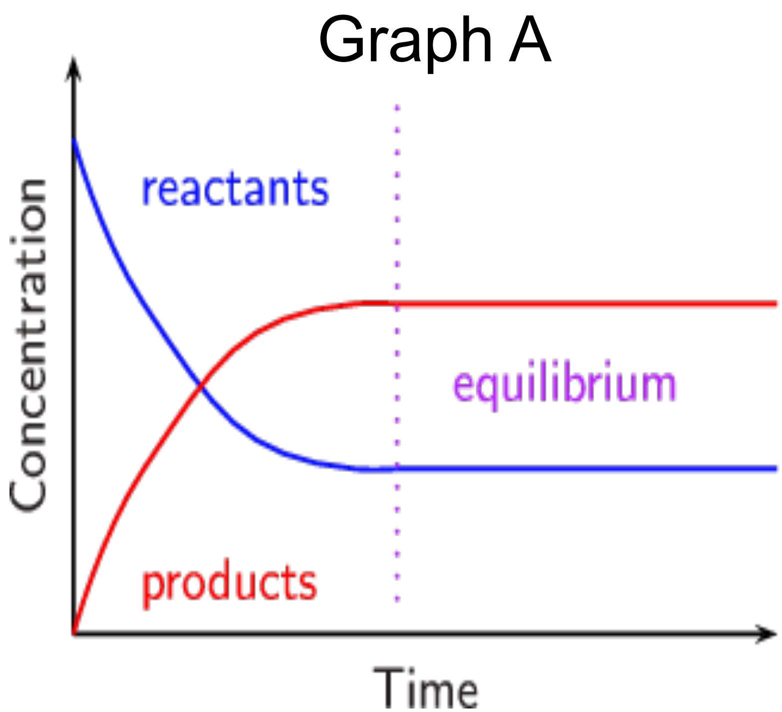
(i) > 1 (ii) = 1 (iii) < 1

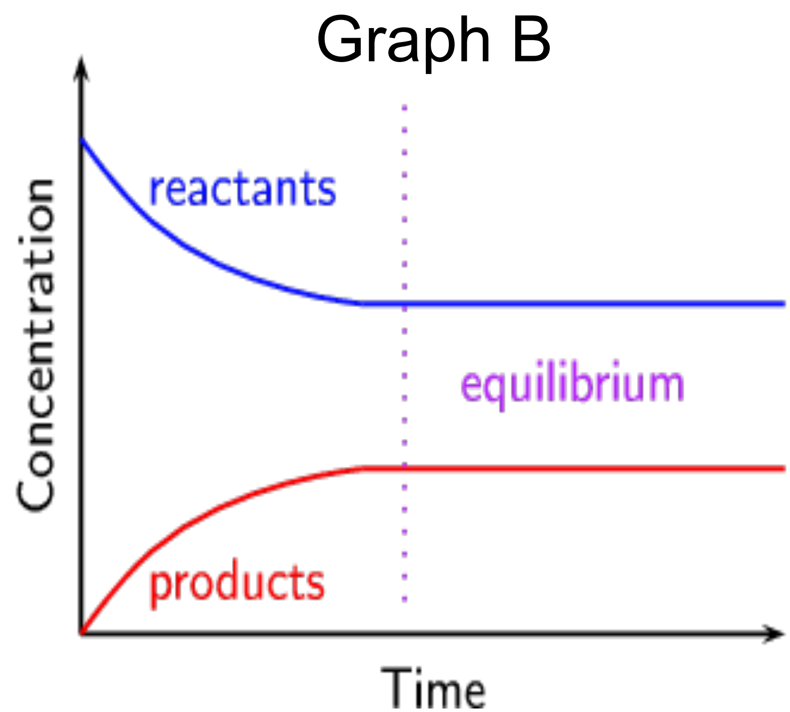
More products means K_{eq} is:

(i) > 1 (ii) = 1 (iii) < 1

Equilibrium Constant: $K_{eq} = \dfrac{\Pi\ [\text{products}]^n}{\Pi\ [\text{reactants}]^m}$

Which graph has a $K_{eq} > 1$?





https://www.everythingmaths.co.za/science/grade-12/08-chemical-equilibrium/08-chemical-equilibrium-03.cnxmlplus

Example: Acetic acid dissociates into its ions.

$$CH_3COOH + H_2O \dashrightarrow CH_3COO^- + H_3O^+ \qquad K_{eq} = 1.8\times10^{-5}$$

a. Write an equilibrium constant expression for this reaction.

K_{eq} =

Note: For a pure substance, e.g., solid or liquid, [ ] = 1.
So [H2O (l)] = 1.

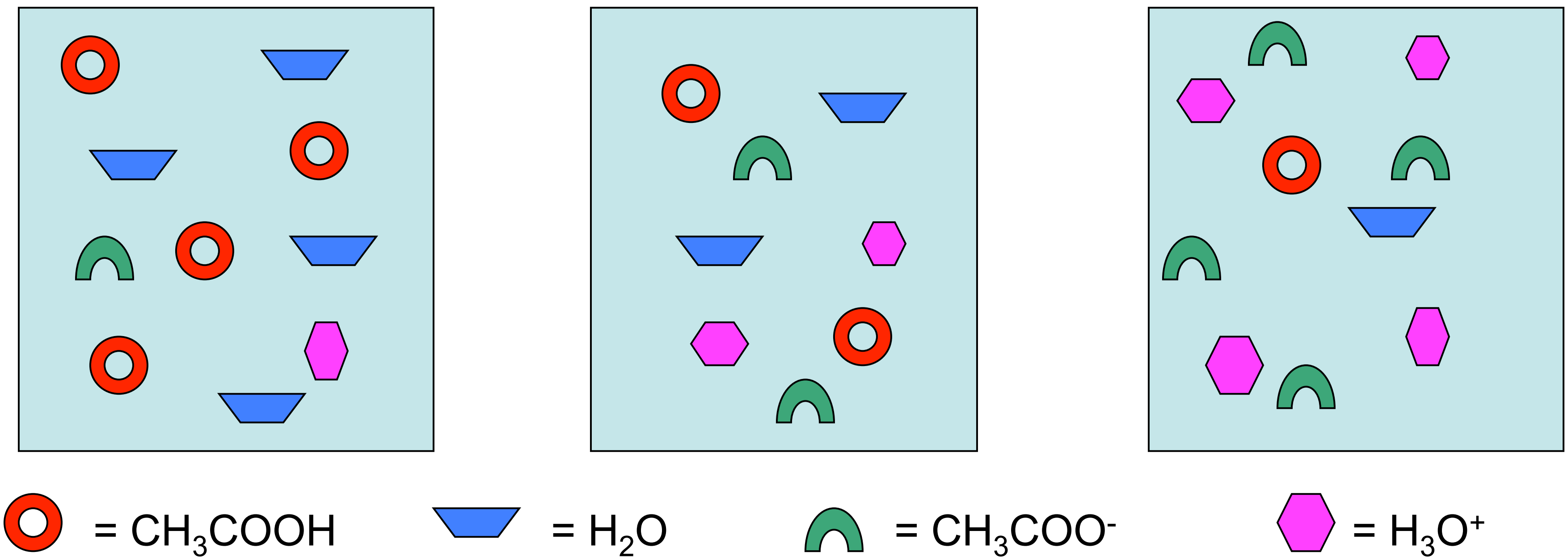
b. At equilibrium, are more reactants present or more products?

<u>Example</u>: Acetic acid dissociates into its ions.

$$CH_3COOH + H_2O \dashrightarrow CH_3COO^- + H_3O^+ \qquad K_{eq} = 1.8\times10^{-5}$$

a. Which picture represents this mixture at equilibrium?

A B C



b. Draw a concentration vs. time graph.

Objective: Use LeChatelier's Principle To Control The Direction (Forward/Backward) Of A Reaction

LeChatelier's Principle: When a stress is placed on a reaction, the reaction shifts in a direction that relieves the stress (and re-establishes equilibrium).

Stress	**Stress Relief**
Upset stomach	Rolaids
Add reactant	Rxn shifts toward products
Remove reactant	Rxn shifts toward reactants
Add product	Rxn shifts toward reactants
Remove product	Rxn shifts toward products
One minute left on the exam and two pages to go	panic
Add/remove heat	
Increase/decrease pressure	
Someone looking over your shoulder	Anxiety

*At <u>Equilibrium, reactants **and** products will be present.</u>*

The ratio of reactants and products is quantified with an

Equilibrium Constant: $K_{eq} = \dfrac{\Pi\ [\text{products}]^n}{\Pi\ [\text{reactants}]^m}$

<u>Example</u>: A + B ⇔ C + D $\qquad K_{eq} = \dfrac{[C]\ [D]}{[A]\ [B]} = 5$

If Reactant A is added, does $\dfrac{[C]\ [D]}{[A]\ [B]}$ increase or decrease?

This ratio DECREASES so reaction is no longer at equilibrium.

For reaction to get back to equilibrium, numerator [C] [D] has to increase ===> more products form ===> reaction shifts to product side.

Objective: apply Equilibrium Principles

How can you get more salt to dissolve in water?

NaCl dissolution is endothermic.

Write a chemical equation that represents this reaction.

What is the effect of T?

What is the effect of adding more salt?

What is the effect of adding more water?

http://jerpchem11.blogspot.com/2010/03/solution-chemistry-mar30.html

Aspirin Synthesis (Chem 1A Lab 4) is an Equilibrium Reaction.

Salicylic acid + acetic anhydride -- H_3PO_4 catalyst --> aspirin + acetic acid

$C_7H_6O_3$ + $C_4H_6O_3$ ----> $C_9H_8O_4$ + CH_3COOH + heat

<u>Reaction conditions affect Reaction Rate and Yield</u>:

T = 75°C, time = 20 minutes

Use excess $C_4H_6O_3$ --> reaction shifts to products --> higher yield. Reaction occurs: (i) faster (ii) slower

Use higher T --> reaction shifts to reactants --> lower yield.
Reaction occurs: (i) faster (ii) slower

Use catalyst --> no effect on equilibrium or yield
Reaction occurs: (i) faster (ii) slower

You made <u>***Esters***</u> in Lab 1 in Chem 1B lab.

Acid + Alcohol ---> Ester + Water

<u>Lab 4: How to Optimize the Yield?</u>

a. Is the reaction exothermic or endothermic?

b. What is the effect of temperature in this reaction?

c. Should an excess of one reactant be used? If so, which reactant should be the excess reactant?

d. How can the yield be increased?

e. What does the sulfuric acid catalyst do?

Apply LeChatelier's Principle to Make Drano Work Better

Drano drain cleaner consists of Al filings and NaOH pellets. When water is added, the heat produced melts and saponifies the fat that clogs a drain.

$$2\,Al\,(s) + 2\,NaOH\,(s) + 6\,H_2O\,(l) \rightarrow 2\,NaAl(OH)_4\,(aq) + 3\,H_2\,(g)$$

a. Would you expect this reaction to have a large K or small K? Explain.
b. In terms of reactants and products, explain how this reaction can be shifted to the right (toward products).
c. If an excess amount of water is added, how will the reaction be affected?
d. If hot water was added instead of cold water, would Drano work better? In other words, which direction would the reaction shift?
e. If the drain was plugged immediately after Drano was added to the clog, would Drano work better? In other words, which direction would the reaction shift?

Determine Reaction Conditions by Applying LC Principle

Under the conditions of a car engine, nitrogen and oxygen reacts to form NO_x, which is a component of smog:

$N_2 + O_2$ --> 2 NO (1)

$N_2 + 2\,O_2$ --> 2 NO_2 (2)

Under what temperature (low T or high T) and pressure (low P or high P) conditions does each reaction occur? Give reasons based on LeChatelier's principle.

ΔH_f of NO (g) = 90.4 kJ/mole ==> Hess's law ==> Rxn (1) is *endothermic*

Increase in T shifts reaction toward products ==> ***Use High T***

ΔH_f of NO_2 (g) = 33.9 kJ/mole ==> Hess's law ==> Rxn (2) is *endothermic*

Increase in T shifts reaction toward products ==> ***Use High T***

Rxn (1): 2 moles of gas reactants --> 2 moles of gas products

Changing P does not shift reaction ==> ***Use Any P***

Rxn (2): 3 moles of gas reactants --> 2 moles of gas products

Increase in P shifts reaction toward products ==> ***Use High P***

500 million tons of Nitrogen Fertilizer is Produced Annually
(as NH_3, NH_4NO_3, and urea) and Uses 1-2% of World's Energy Supply

Plants Make NH_3 from N_2 (Nitrogen Fixation)

The ***Haber process*** is the industrial process for the synthesis of ammonia from N_2 and H_2. In this process, the reaction conditions are <u>*high pressure*</u> and <u>*low temperature*</u>. A <u>*catalyst*</u> is used and <u>*product is removed*</u> from the reaction vessel during the reaction.

a. Write a chemical equation that represents the Haber process.

b. Explain why these reaction conditions are used. If a catalyst was not used, could a higher reaction temperature be used to optimize the yield? Give reasons.

Does Salt Melt Ice?

$\Delta H_{solution}$ of NaCl is close to 0. So $q \approx 0$. Melting?

Melting: H_2O (s) <==> H_2O (l)

As soon as some salt dissolves in the ice's surface film, the solute ions interfere with the H_2O (l) molecules' (leftward) ability to join the solid lattice, and the equilibrium therefore shifts to the right: toward less solid and more solution. That is, the ice dissolves in the solution.

Pardon my vernacular, but that ain't melting, and it ain't no freezing point depression phenomenon, neither.

Yes, the solution's freezing point is lower than that of pure water, but so what? Our practical concern here is with ice dissolving into the solution, not the solution freezing into ice.
CEN, 3/31/08, Newscripts, p. 56

Objective: Determine the amounts of reactants and products at _____

$CH_4\ (g) + 2\ O_2\ (g) \longrightarrow CO_2\ (g) + 2\ H_2O\ (g)$ $K = 10^{140}$

Does this reaction occur? Why?
1 mole of CH_4 (g) burns in 5 moles of O_2. Calculate the moles of products produced.

Solution (from ***Chem 1A***):

	CH_4 (g)	+ 2 O_2 (g) --->	CO_2 (g)	+ 2 H_2O (g)
Initial	1	5	0	0
Amount reacts				
Amount leftover/ produced				

Objective: Determine the amounts of reactants and products at *Equilibrium*

Haber process: Chang, 6th ed., p. 539, Problem 15.72.

N_2 (g) + 3 H_2 (g) <==> 2 NH_3 (g) $K_p = 4.31 \times 10^{-4}$ at 375°C

In a certain experiment, a student starts with 0.862 atm of N_2 and 0.373 atm of H_2 in a constant volume vessel at 375°C. Calculate the partial pressures of all species when equilibrium is reached.

Solution:

	N_2 (g) +	3 H_2 (g) <==>	2 NH_3 (g)
Initial p	0.862	0.373	0
Amount reacts	x	3x	2x
Amount at equilibrium	0.862-x	0.373-3x	2x

$$K_p = 4.31 \times 10^{-4} = \frac{(2x)^2}{(0.862-x)(0.373-3x)^3}$$

Solve for x!

Objective: Determine the amounts of reactants and products at Equilibrium

1 mole each of H_2 and I_2 are placed in a 1 l box at 490°C. What are the concentrations of reactants and products at equilibrium?

$H_2 + I_2 \Longleftrightarrow 2\,HI$ K = 45.9 at 490°C

Method: balance chemical equation
set up "initial amount",
"amount reacts",
"amount at equilibrium"
plug "equilibrium" amount into K
solve for x