

14 topics (13)

7-9%

Unit 7

## 7.1 Introduction to Equilibrium

### ENDURING UNDERSTANDING:

TRA-6

Some reactions can occur in both forward and reverse directions, sometimes proceeding in each direction simultaneously.

### LEARNING OBJECTIVE:

TRA-6.A

Explain the relationship between the occurrence of a reversible chemical or physical process, and the establishment of equilibrium, to experimental observations.

# REVERSIBLE REACTIONS

A reversible reaction is a reaction that can go both forwards: **acid + alcohol  $\rightarrow$  ester** (condensation)

and backwards: **ester  $\rightarrow$  acid + alcohol** (hydrolysis)

Equations for such reactions should use two-way arrows



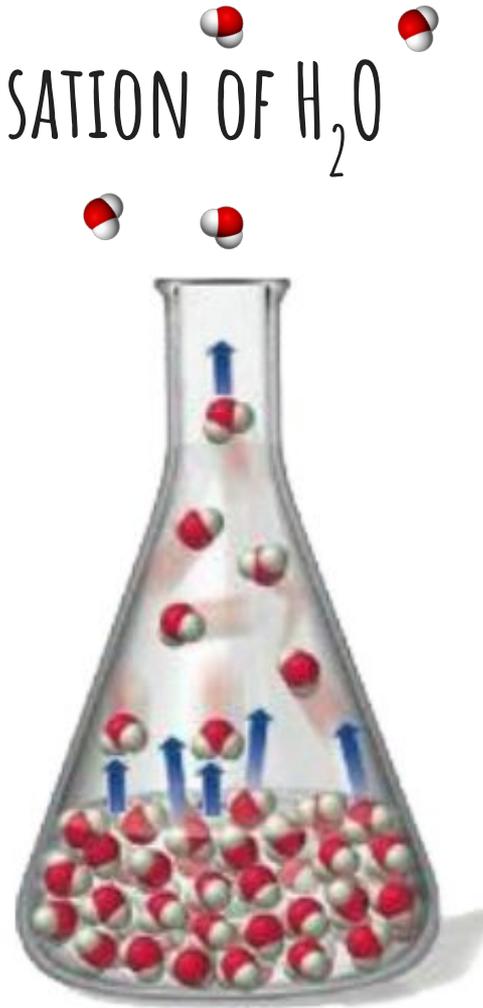
to show the reaction can go in either direction.

# LET'S LOOK AT EVAPORATION AND CONDENSATION OF H<sub>2</sub>O

If water is left in an open flask, it will start to evaporate.

The Rate of the forward reaction is as fast as it can go since the amount (concentration) of liquid water is at its highest.

Being open means that the water vapor produced can escape so it is not available for the reverse reaction (condensation).



# CLOSED FLASK

If water is left in an stoppered flask, it will start to evaporate.



However, since the water vapor cannot escape, the reverse reaction will also be possible.

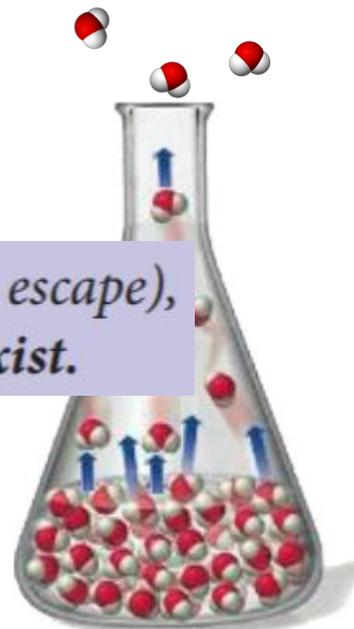


After some time, Rate of backward = Rate of forward and the amounts of liquid water and water vapor will not change

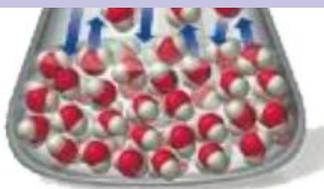


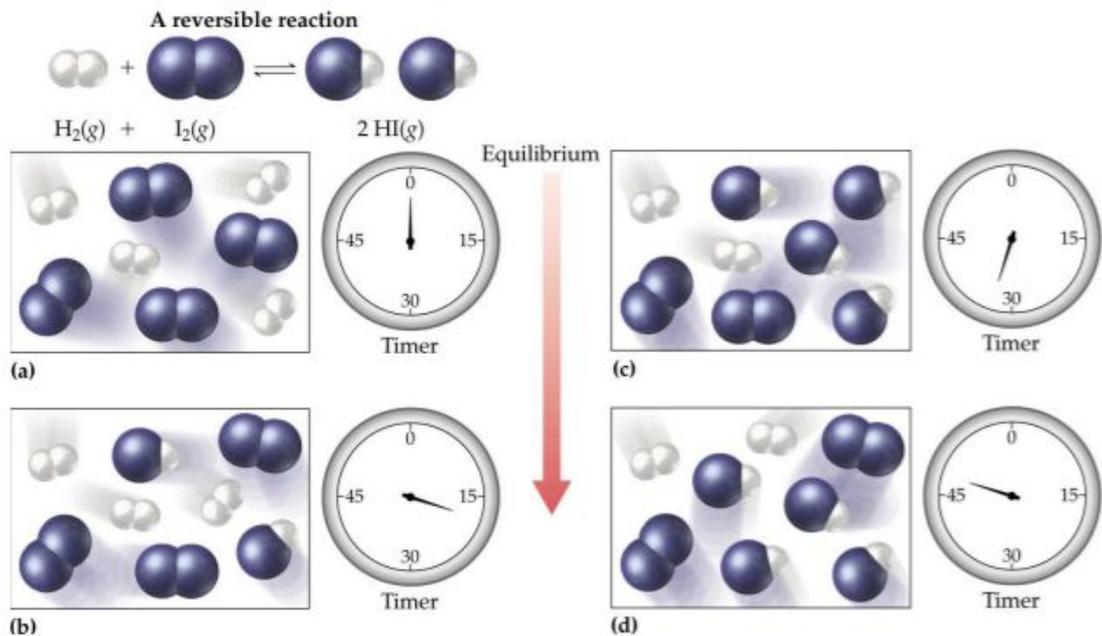
# OPEN SYSTEM VS. CLOSED SYSTEM

*In an open system, (one in which one or more of the chemicals can escape), reversible reactions will not occur and an equilibrium will not exist.*



*In a closed system, (one in which none of the chemicals can escape), reversible reactions will occur and an equilibrium mixture will exist.*





a) - at  $t = 0$ , mixture is 100% reactants

$$\text{Rate}_{\text{forw}} = \text{fast} \quad \text{Rate}_{\text{back}} = 0$$

b) - at  $t = 15$ , mixture mainly reactants

$$\text{Rate}_{\text{forw}} = \downarrow \quad \text{Rate}_{\text{back}} = \uparrow$$

c) - at  $t = 30$ , mixture establishes

$$\text{Rate}_{\text{forw}} = \downarrow \quad \text{Rate}_{\text{back}} = \uparrow$$

d) - at  $t = 45$ , mixture established

$$\text{Rate}_{\text{forw}} = \text{Rate}_{\text{back}}$$

*At Equilibrium,*

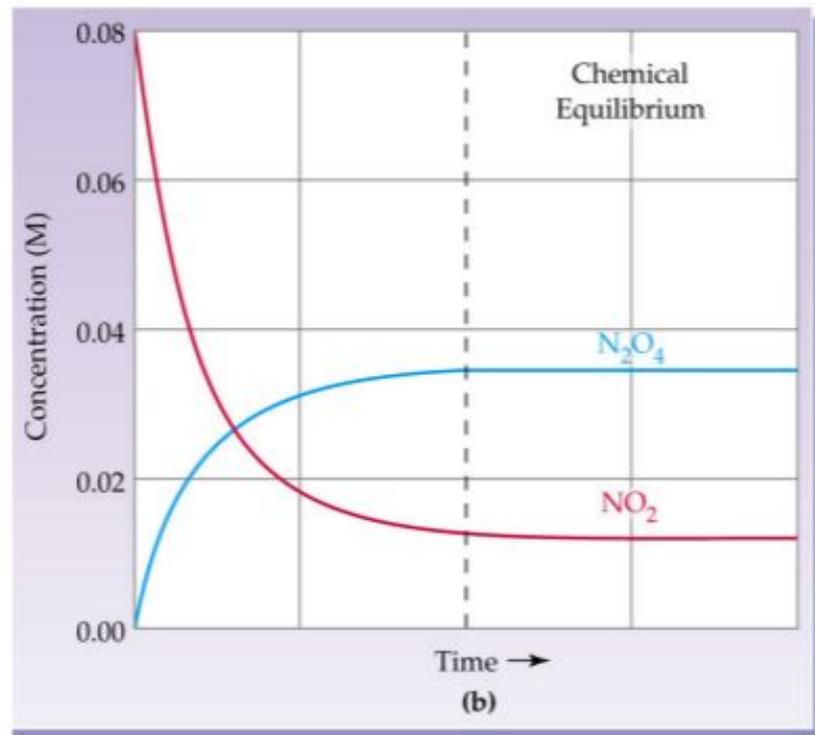
*concentrations of reactants and products no longer change  
forward and backward reactions continue (dynamic)  
rate of forward reaction = rate of backward reaction*

# GRAPHING EQUILIBRIUM

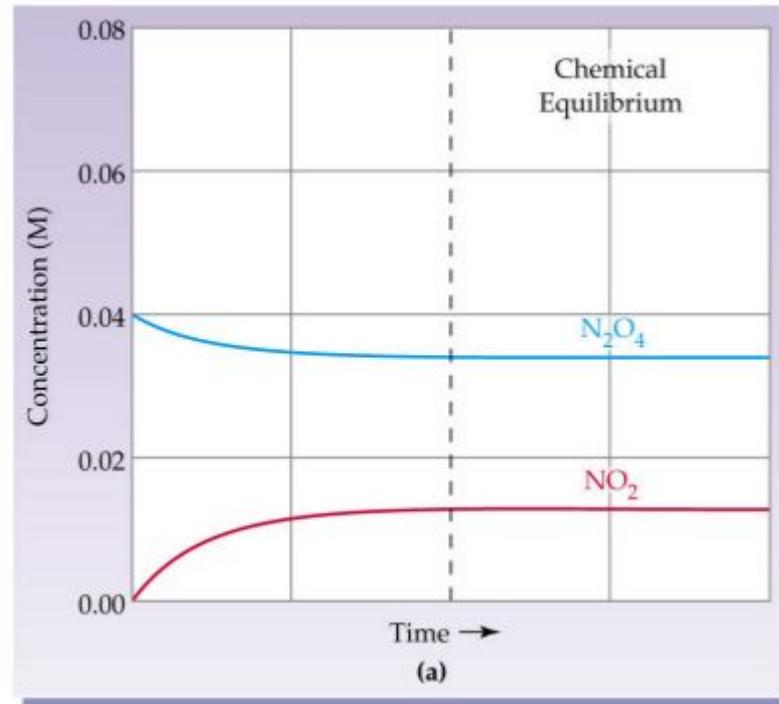
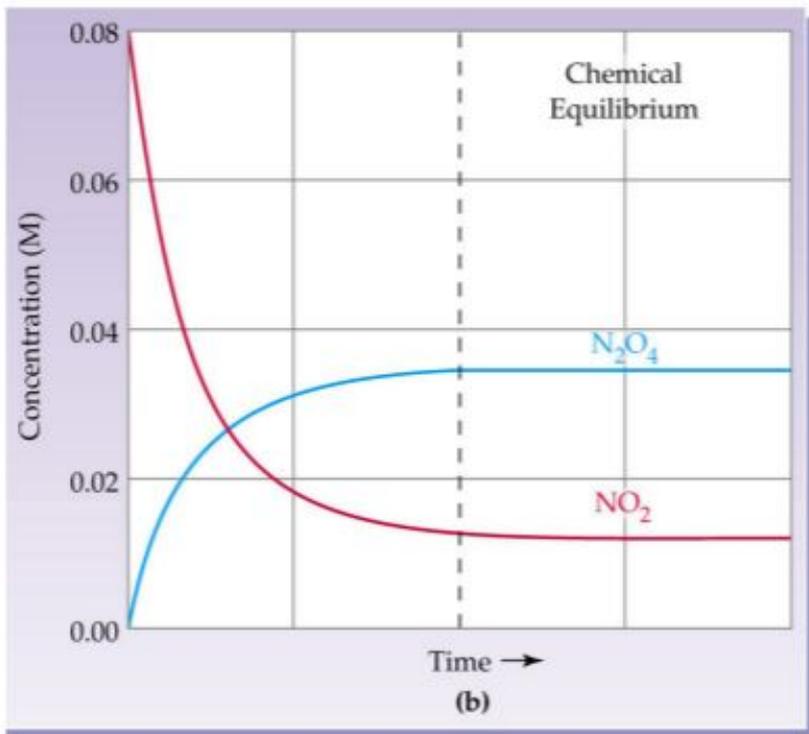
We can graph the changes to the concentration of the reactants and products as a reaction proceeds to equilibrium.

Reactants and products change rapidly at the beginning and then the rate of the reaction decreases until the reaction reaches equilibrium.

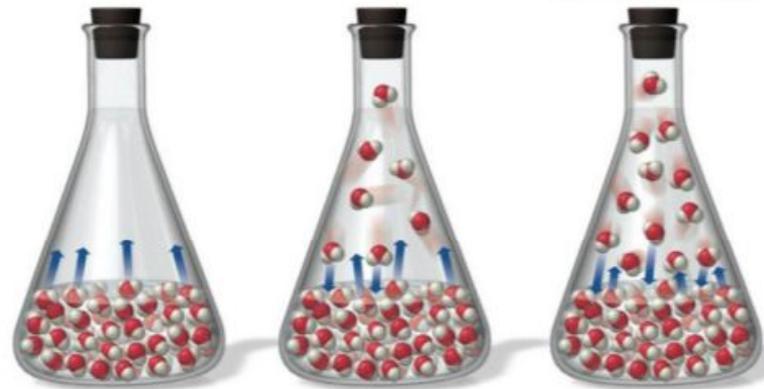
When the reaction reaches equilibrium there is no change to the amount of reactants and products.



The *equilibrium position* is same if the reaction starts off with **100% reactants** or with **100% products**.



# VAPOR PRESSURE AND EQUILIBRIUM

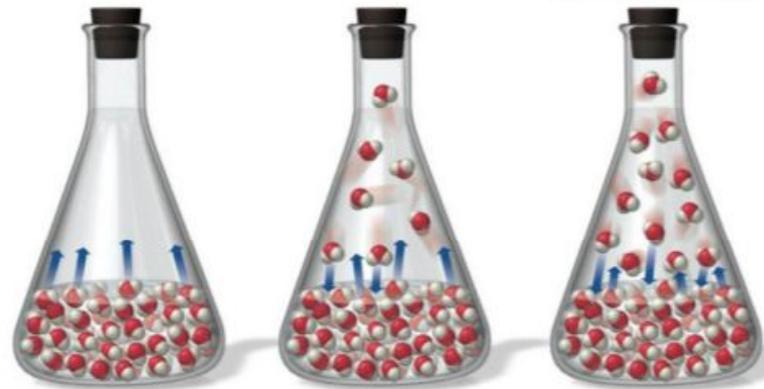


Vapor pressure builds up inside a closed container due to an increase in gas particles striking the walls of the container.

## Vapor pressure & Temperature

- To escape the liquid and form vapor, the particles must have the minimum amount of kinetic energy needed to overcome the intermolecular forces that exist between the particles.
- At higher temperatures a larger proportion of the molecules will have this energy, or above, and vapor pressure will increase.

# VAPOR PRESSURE AND EQUILIBRIUM



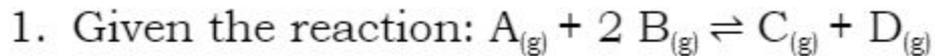
## Vapor Pressure & Intermolecular Forces

- Diethyl ether with dipole-dipole attractions will have a higher vapour pressure than ethanol and water which both have hydrogen bonding

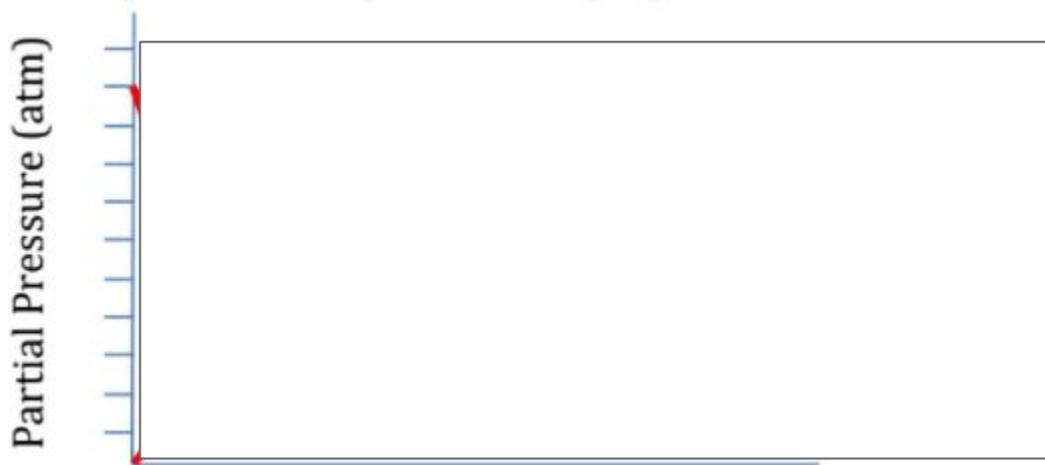
## Other Factors

- Volume and surface area may have an effect on how quickly equilibrium is established but will have no effect on the final vapour pressure.

# TOGETHER



The reaction starts with only 1.00 atm of A and 1.00 atm of B, there is no C or D in the flask. Sketch a graph to show the reaction as it proceeds to equilibrium. Upon reaching equilibrium there is 0.80 atm of A.



# YOU DO, WE REVIEW

2. Write an equilibrium reaction for the following processes:
- Freezing/melting of benzene,  $C_6H_6$
  - Dissolution of the weak acid,  $HCN_{(aq)}$
  - The proton transfer between the weak base,  $HS^-_{(aq)}$  and the weak acid,  $H_2PO_4^-_{(aq)}$

## 7.2 Direction of Reversible Reactions

### ENDURING UNDERSTANDING:

TRA-6

Some reactions can occur in both forward and reverse directions, sometimes proceeding in each direction simultaneously.

### LEARNING OBJECTIVE:

TRA-6.B

Explain the relationship between the direction in which a reversible reaction proceeds and the relative rates of the forward and reverse reactions.

# REVERSIBLE REACTIONS

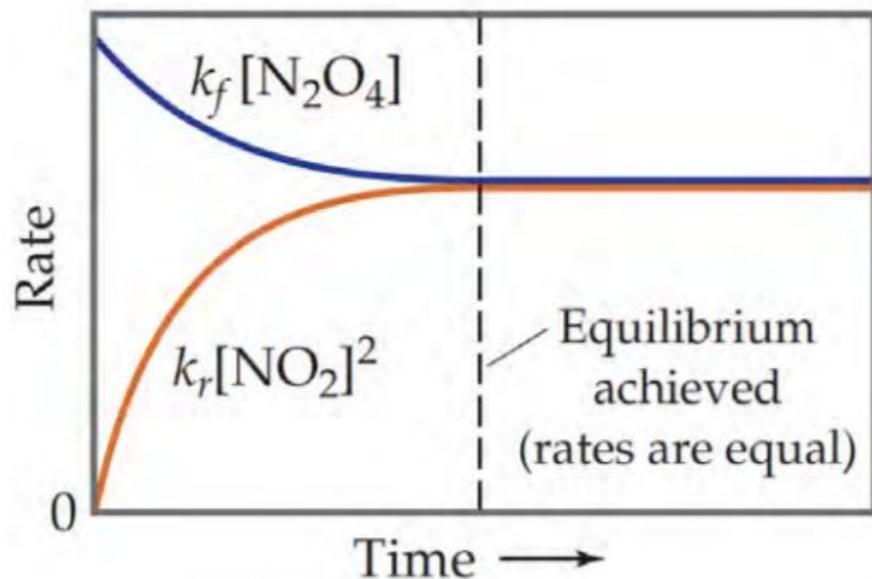
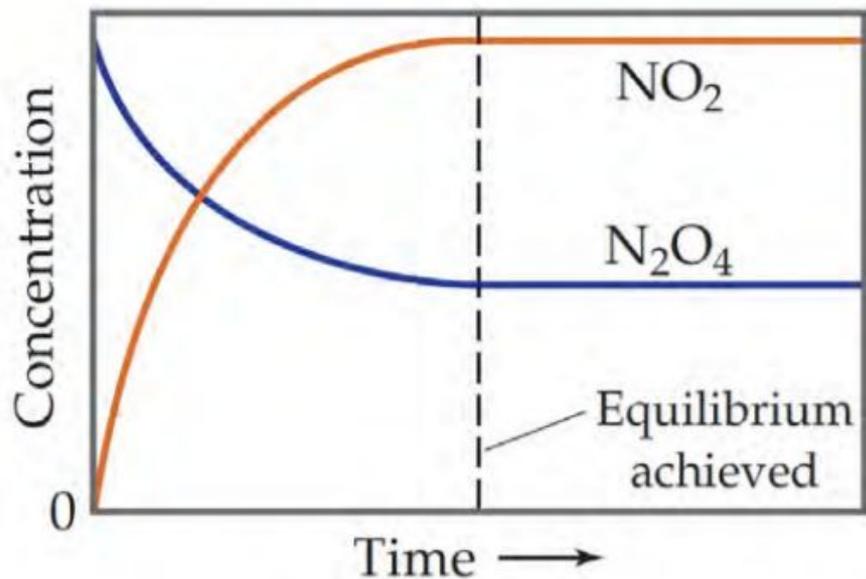
During a reversible reaction, the rate of one reaction will be decreasing, while the rate of the other reaction increases until both reactions are proceeding at **equal rates**.

$$\text{Rate}_f = k_f [\text{reactants}] \text{ and } \text{Rate}_b = k_b [\text{products}]$$

$$\text{until } \text{Rate}_f = \text{Rate}_b$$

$$\text{but } [\text{reactants}] \neq [\text{products}]$$

# RATES ARE EQUAL, CONCENTRATIONS ARE NOT



As the diagrams above illustrate,

$Rate_f = Rate_b$  at equilibrium, but  $[reactants] \neq [products]$

# ALMOST ALWAYS, ONE DIRECTION IS FAVORED

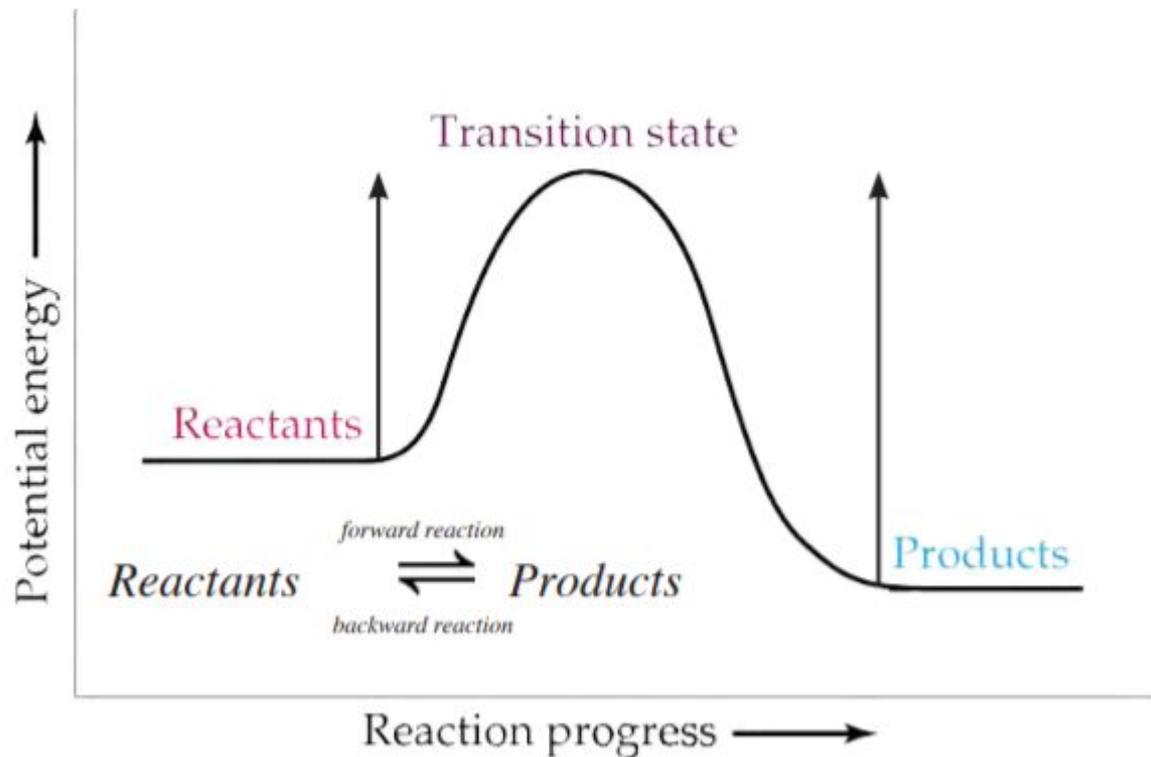
$k_f > k_b$     *forward reaction favoured*     $[products] > [reactants]$  at equilibrium

$k_b > k_f$     *backward reaction favoured*     $[products] < [reactants]$  at equilibrium

*Very rarely, but one example is esterification/hydrolysis,*

$k_b = k_f$     *both reactions equally favoured*     $[products] = [reactants]$  at equilibrium

# FAVORED REACTIONS



If the forward reaction is **exothermic**, then the forward reaction will be **favored**.

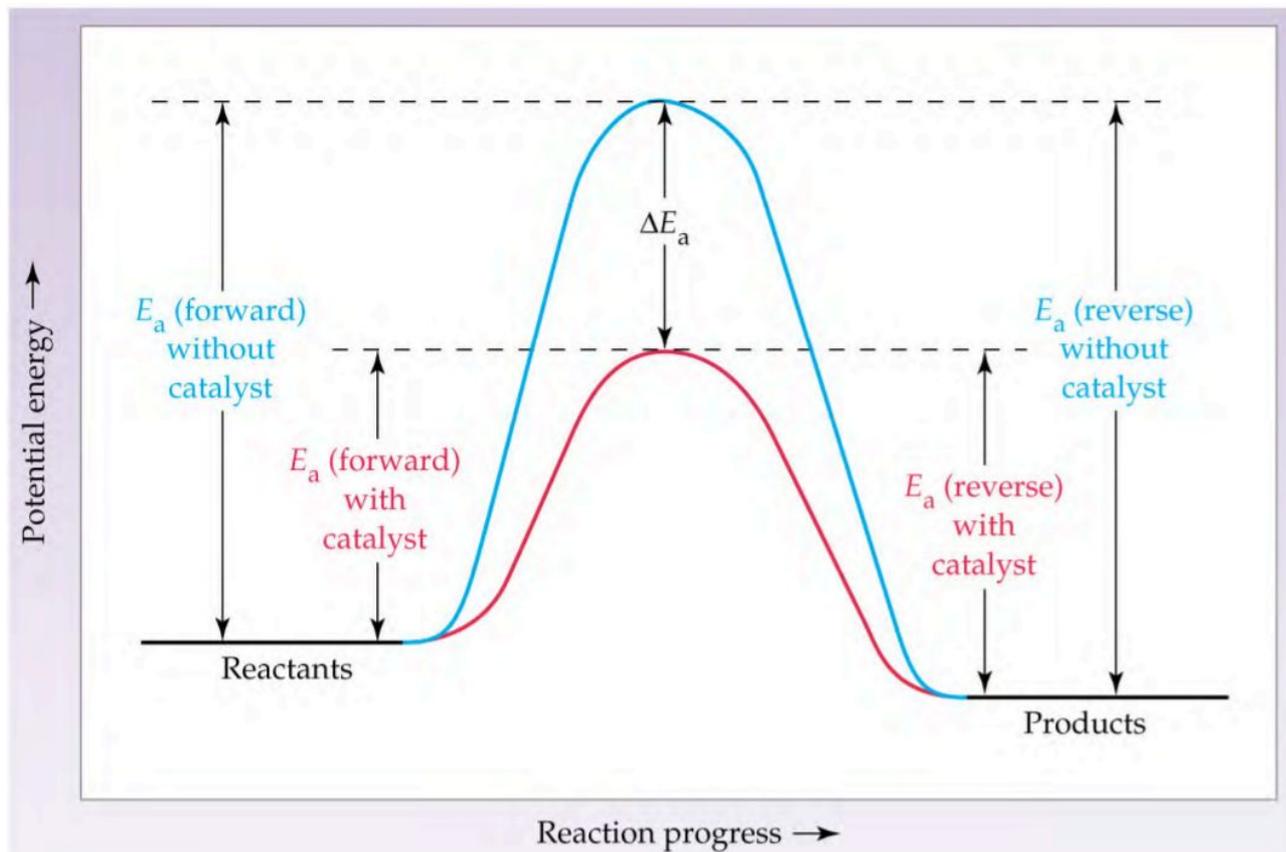
Why?

**Activation energy** for the **forward reaction is smaller** than the activation energy for the backward reaction, so equilibrium mixture will be mainly products

# WHAT ABOUT CATALYSTS?

Use of a catalyst in a reversible reaction has a **neutral effect**.

Activation energy of both reactions are different, the  $\Delta E_a$  for both reactions is the same - **both reactions benefit by the same amount**.



WHAT DOES  
CAUSE MORE  
REACTANTS OR  
MORE  
PRODUCTS TO  
FORM?

stress	$A_{(s)} + 2B_{(g)} \rightleftharpoons C_{(s)} + D_{(g)} + \text{heat}$					
increase conc. of A	↑	↓	↔	↑	↑	
increase conc. of D	↑	↑	↔	↓	↑	
decrease conc. of B	↑	↓	↔	↓	↓	
decrease conc. of C	↓	↓	↔	↓	↑	
increase pressure	↓	↓	↔	↑	↑	volume of gas must decrease
decrease pressure	↑	↑	↔	↓	↓	volume of gas must increase
increase temp.	↑	↑	↔	↓	↓	↑
decrease temp.	↓	↓	↔	↑	↑	↓
catalyst	NO SHIFT		↔	NO SHIFT		

# TOGETHER

1. The reaction  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$  is at equilibrium 500 K. What happens to the rates of the forward and reverse reactions if some  $\text{NH}_3$  is added at time,  $t$ .

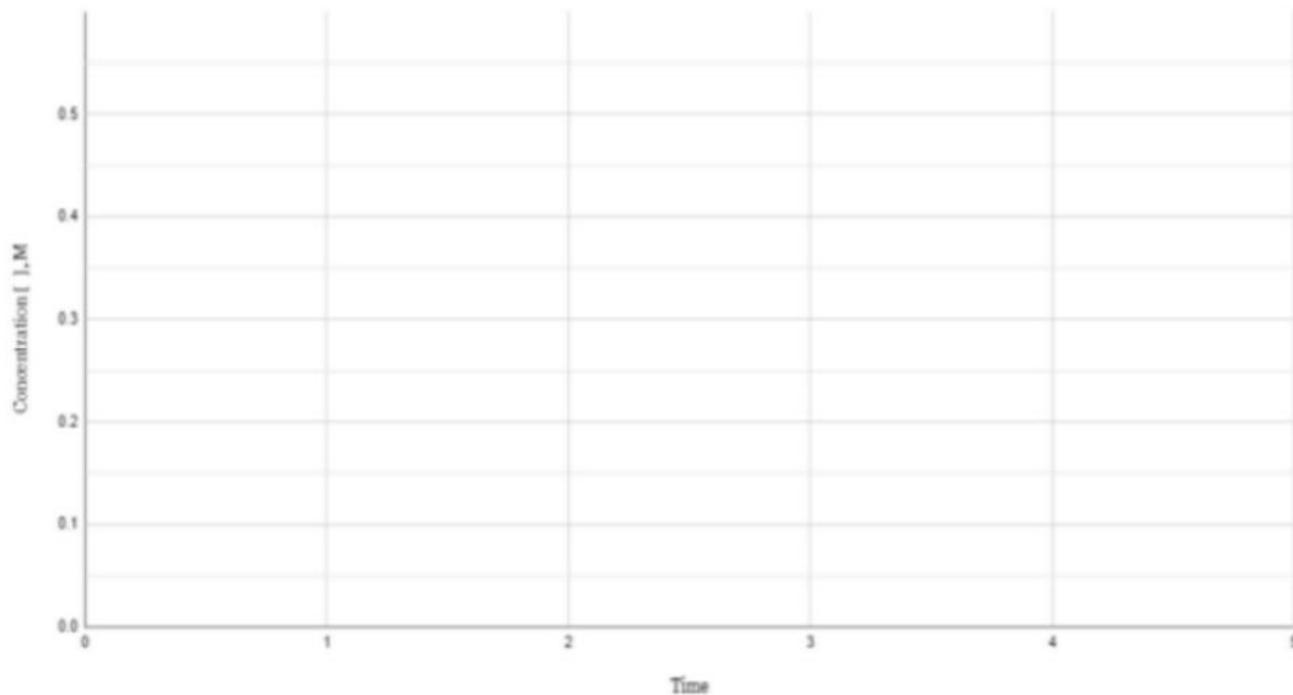
# YOU DO, WE REVIEW

2. In a previously evacuated 1.00 L flask, 0.40 moles of A and 0.50 moles of B were added and allowed to come to equilibrium.

At equilibrium, there were 0.15 moles of C. The equation for the reaction is:



Sketch three curves on the graph below to show the reaction as it reaches equilibrium.



## 7.3 & 7.4 Reaction Quotient and Equilibrium Constant & Calculating the Equilibrium Constant

### ENDURING UNDERSTANDING:

TRA-7

A system at equilibrium depends on the relationships between concentrations, partial pressures of chemical species, and equilibrium constant  $K$ .

### LEARNING OBJECTIVES:

TRA-7.A

Represent the reaction quotient  $Q_c$  or  $Q_p$ , for a reversible reaction, and the corresponding equilibrium expressions  $K_c = Q_c$  or  $K_p = Q_p$ .

TRA-7.B

Calculate  $K_c$  or  $K_p$  based on experimental observations of concentrations or pressures at equilibrium.

# LAW OF MASS ACTION



At equilibrium, we have some mixture of reactants and products.

The law of mass action states: for a reversible reaction at equilibrium and a constant temperature, a certain ratio of reactant and product concentrations has a constant value,

**K (the equilibrium constant).**

# EQUILIBRIUM EQUATION

For the following general reaction at equilibrium:



where  $a$ ,  $b$ ,  $c$ , and  $d$  are the stoichiometric coefficients for the reacting species A, B, C, and D. At a particular temperature:

**Equilibrium equation:**

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

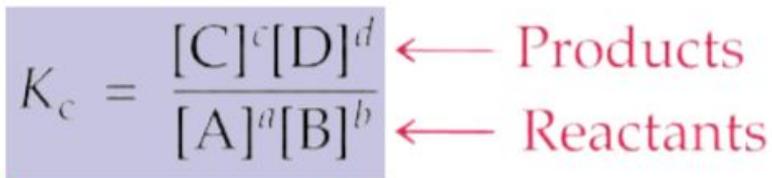
← Products  
← Reactants

Equilibrium constant

Equilibrium constant expression

# EQUILIBRIUM CONSTANTS

Equilibrium equation:



Equilibrium constant

Equilibrium constant expression

$K_c$  - the subscript "c" lets us know this is based on concentrations, usually Molarity (mol/L).

Equilibrium constants have NO UNITS!

# EQUILIBRIA OF GASES

Take the chemical equation:  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

We can substitute partial pressures for concentration.

$$\text{So, } K_p = (P_{\text{NO}_2})^2 / (P_{\text{N}_2\text{O}_4})$$

The subscript “p” tells us the equilibrium constant is based on partial pressures. Equilibrium constants of gases can also be calculated from concentrations.

# PURE LIQUIDS AND SOLIDS

Solids are NOT included in equilibrium equations (get a value of “1”).



$$\mathbf{K_c = [HI]^2/[H_2]}$$

Pure liquids are NOT included in equilibrium equations.



$$\mathbf{K_c = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}}$$

# REACTION QUOTIENT, Q

The idea of describing a mixture of reacting chemicals by calculating  $[\text{products}]/[\text{reactants}]$  (a quotient), can be extended to mixtures that have not yet reached equilibrium.

It is defined in exactly the same way as the Equilibrium Constant.

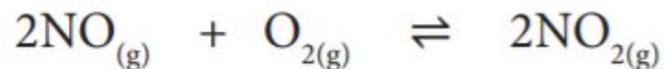
$$K_c = \frac{[C_{\text{equi}}]^c [D_{\text{equi}}]^d}{[A_{\text{equi}}]^a [B_{\text{equi}}]^b} \quad Q_c = \frac{[C_{\text{any}}]^c [D_{\text{any}}]^d}{[A_{\text{any}}]^a [B_{\text{any}}]^b} \quad \text{or} \quad Q_c = \frac{[C_{\text{initial}}]^c [D_{\text{initial}}]^d}{[A_{\text{initial}}]^a [B_{\text{initial}}]^b}$$

$$K_p = \frac{[P_{C \text{ equi}}]^c [P_{D \text{ equi}}]^d}{[P_{A \text{ equi}}]^a [P_{B \text{ equi}}]^b} \quad Q_p = \frac{[P_{C \text{ any}}]^c [P_{D \text{ any}}]^d}{[P_{A \text{ any}}]^a [P_{B \text{ any}}]^b} \quad \text{or} \quad Q_p = \frac{[P_{C \text{ initial}}]^c [P_{D \text{ initial}}]^d}{[P_{A \text{ initial}}]^a [P_{B \text{ initial}}]^b}$$

# CALCULATING EQUILIBRIUM CONSTANT

You can calculate the value for these by plugging the experimental concentrations or partial pressures and the coefficients from the balanced equation.

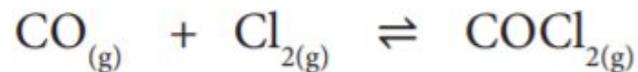
*Example 1:* The following equilibrium process has been studied at 230°C:



In one experiment, the concentrations of the reacting species at equilibrium are found to be  $[\text{NO}] = 0.0542 \text{ M}$ ,  $[\text{O}_2] = 0.127 \text{ M}$ , and  $[\text{NO}_2] = 15.5 \text{ M}$ .

Calculate the equilibrium constant ( $K_c$ ) of the reaction at this temperature.

*Example 2:* Carbonyl chloride ( $\text{COCl}_2$ ), also called phosgene, was used in World War I as a poisonous gas. The equilibrium concentrations for the reaction between carbon monoxide and molecular chlorine to form carbonyl chloride



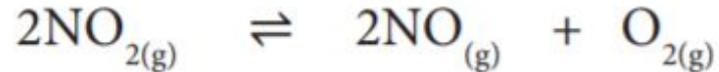
at  $74^\circ\text{C}$  are  $[\text{CO}] = 1.2 \times 10^{-2} \text{ M}$ ,  $[\text{Cl}_2] = 0.054 \text{ M}$ , and  $[\text{COCl}_2] = 0.14 \text{ M}$ . Calculate the equilibrium constant ( $K_c$ ).

*Example 3:* At 250 °C Phosphorus pentachloride decomposes to form phosphorus trichloride and molecular chlorine



If the equilibrium partial pressures of  $\text{PCl}_5$  and  $\text{PCl}_3$  and  $\text{Cl}_2$  are 0.875 atm, 0.463 atm and 1.98 atm , respectively, what is the equilibrium constant ( $K_p$ ) at 250°C?

*Example 4:* The equilibrium constant  $K_p$  for the reaction



is 158 at 1000 K. Calculate  $P_{\text{O}_2}$  if  $P_{\text{NO}_2} = 0.400$  atm and  $P_{\text{NO}} = 0.270$  atm.

# AGENDA

- Bellwork
- Expectations lecture
- 7.5, 7.6, 7.7 notes
- Group (BR)ICE Problems
- Groups present
- Students go home and do their homework **AND WATCH THE AP DAILY VIDEOS**



# VIDEOS

- You were supposed to watch four videos
- Longest video: 8:22
- Shortest video: 6:21

## 7.5 & 7.6 Magnitude and Properties of the Equilibrium Constant

### ENDURING UNDERSTANDING:

TRA-7

A system at equilibrium depends on the relationships between concentrations, partial pressures of chemical species, and equilibrium constant  $K$ .

### LEARNING OBJECTIVES:

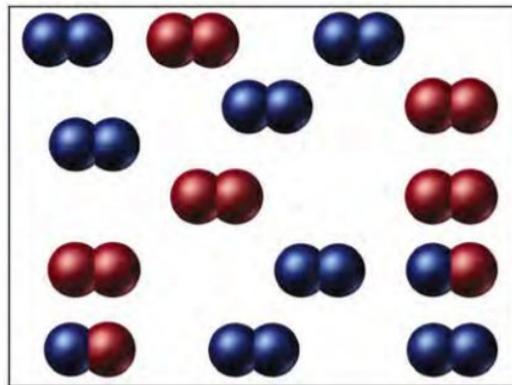
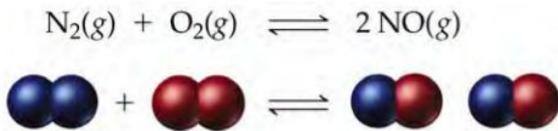
TRA-7.C

Explain the relationship between very large or very small values of  $K$  and the relative concentrations of chemical species at equilibrium.

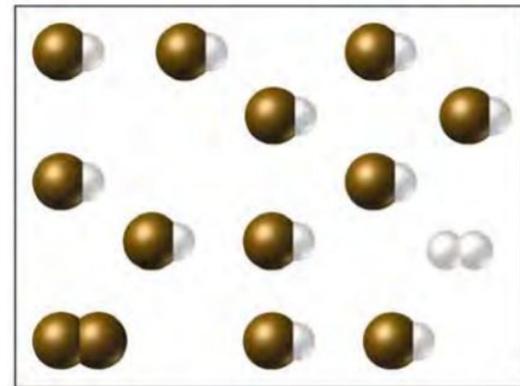
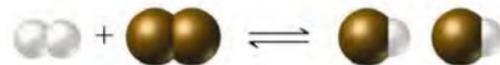
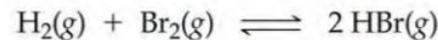
TRA-7.D

Represent a multistep process with an overall equilibrium expression, using the constituent  $K$  expressions for each individual reaction.

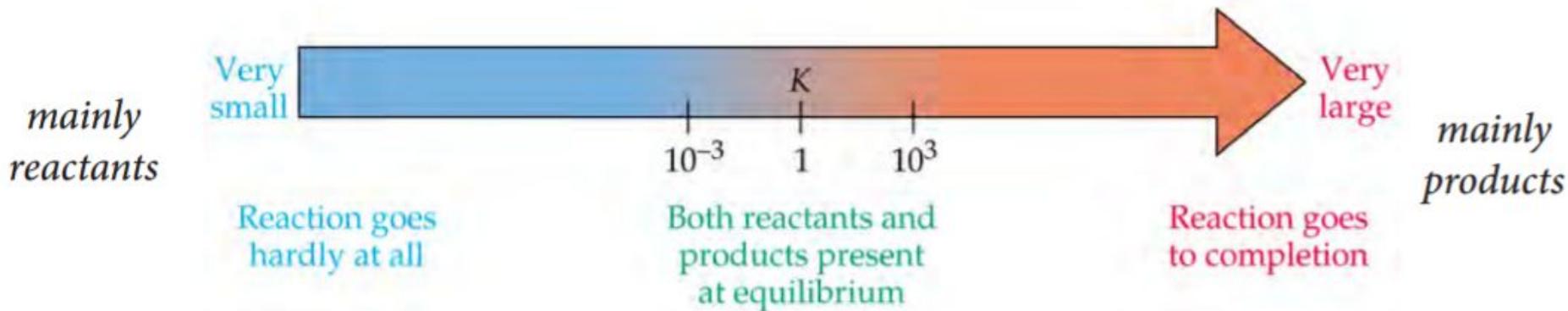
- LARGE K MEANS MOSTLY PRODUCTS
- SMALL K MEANS MOSTLY REACTANT



$$K = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \text{Small Number}$$



$$K = \frac{[\text{HBr}]^2}{[\text{H}_2][\text{Br}_2]} = \text{Large Number}$$



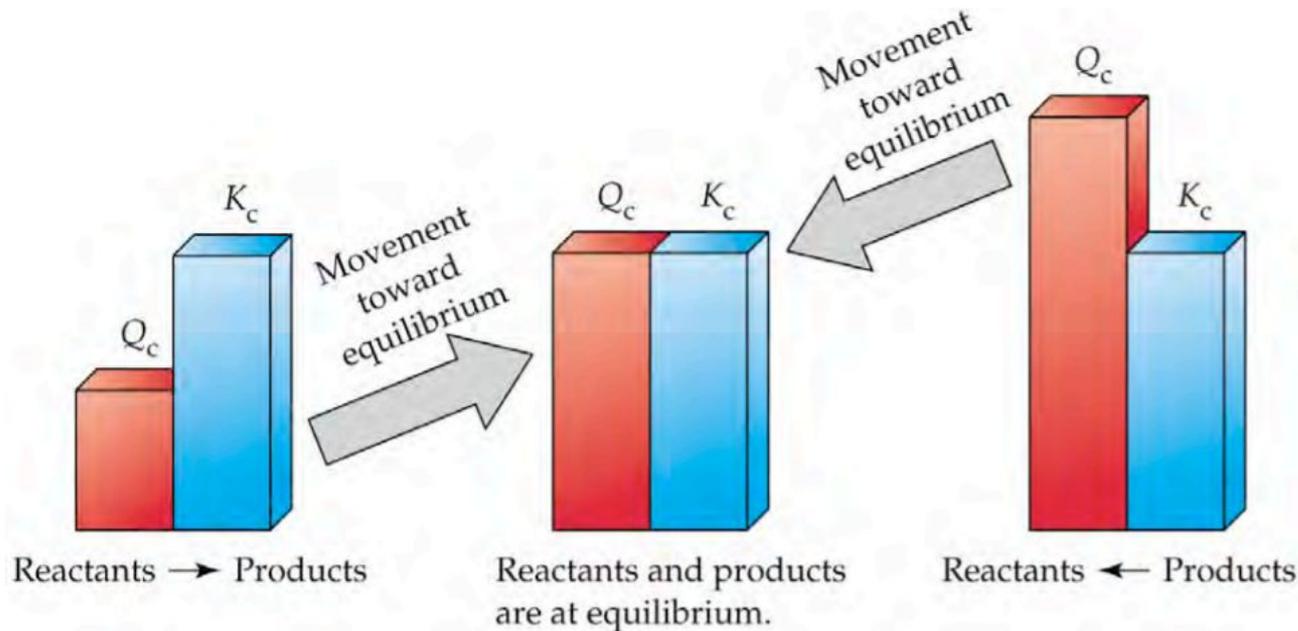
# COMPARING Q TO K

$$K_c = \frac{[\text{products}]}{[\text{reactants}]}$$

*at equilibrium*

$$Q_c = \frac{[\text{products}]}{[\text{reactants}]}$$

*at that moment*



# COMPARING Q TO K

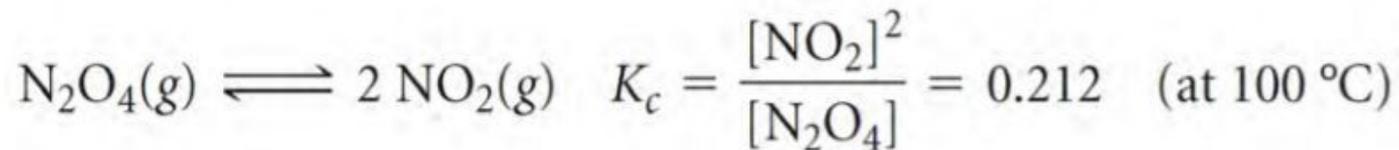
- $Q_c < K_c$  - The ratio of concentrations of products to reactants is too small. To reach equilibrium, reactants must be converted to products. The system proceeds from left to right (consuming reactants, forming products) to reach equilibrium.
- $Q_c = K_c$  - The initial concentrations are equilibrium concentrations. The system is at equilibrium.
- $Q_c > K_c$  - The ratio of concentrations of products to reactants is too large. To reach equilibrium, products must be converted to reactants. The system proceeds from right to left (consuming products, forming reactants) to reach equilibrium.

# PROPERTIES OF THE EQUILIBRIUM CONSTANT

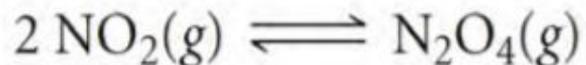
Three Relationships:

1. Reversing the Reaction
2. Multiplying an Equation
3. Combining the Reactions

# REVERSING THE REACTION



We could equally well consider this equilibrium in terms of the reverse reaction:



The equilibrium expression is then:

$$K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{1}{0.212} = 4.72 \quad (\text{at } 100 \text{ }^\circ\text{C})$$

This equation is simply the **reciprocal** of the original equation.

# MULTIPLYING AN EQUATION

The form in which a chemical equation is written affects its  $K_c$  expression and constant. To avoid possible ambiguity, chemists **must** provide the chemical equation with the  $K_c$  value.

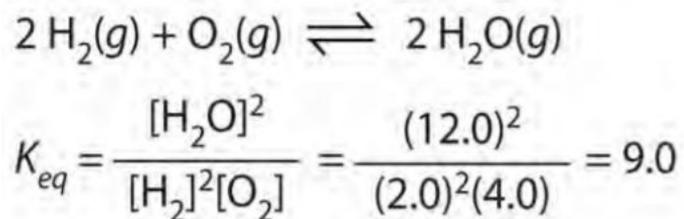
Consider:  $\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \text{H}_2\text{O}(g)$

At a particular temperature, 2.0 mol  $\text{H}_2$ , 4.0 mol  $\text{O}_2$ , and 12.0 mol  $\text{H}_2\text{O}$  are discovered at equilibrium in a 1.0 L flask.

$$K_{eq} = \frac{[\text{H}_2\text{O}]}{[\text{H}_2][\text{O}_2]^{1/2}} = \frac{12.0}{(2.0)(4.0)^{1/2}} = 3.0$$

# MULTIPLYING AN EQUATION

The same reaction has a different equilibrium expression and a different constant when the coefficients in its equation are doubled:

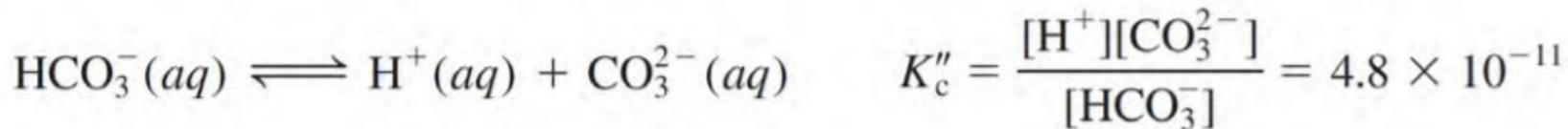
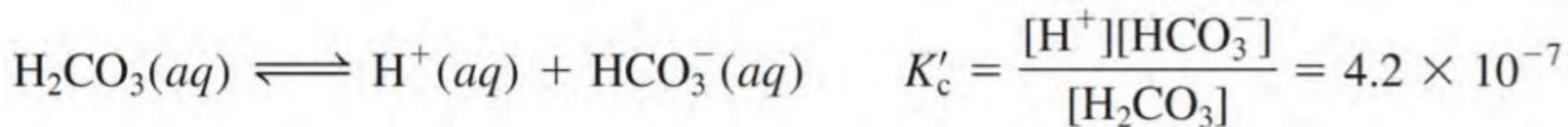


Doubling a chemical equation's coefficients has the effect of squaring its  $K_c$ .

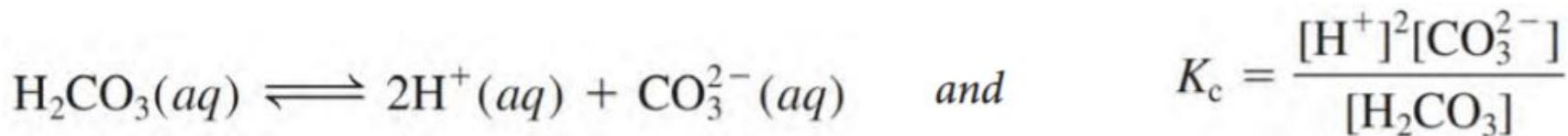
Tripling a chemical equation's coefficients has the effect of cubing its  $K_c$ , and so on.

# COMBINING REACTIONS

A more complicated situation is one in which the product molecules in one equilibrium system are involved in a second equilibrium process:



We can represent the overall reaction as:



# COMBINING REACTIONS

Multiplying and cancelling the original equilibrium expressions,  $K'_c$  and  $K''_c$ :

$$\frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \times \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{[\text{H}^+]^2[\text{CO}_3^{2-}]}{[\text{H}_2\text{CO}_3]}$$

$$\begin{aligned} K_c &= K'_c K''_c \\ &= (4.2 \times 10^{-7})(4.8 \times 10^{-11}) \\ &= 2.0 \times 10^{-17} \end{aligned}$$

If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.

# FINALLY, Q

Since  $Q$  and  $K_c$  and  $K_p$  are all calculated using exactly the same mathematical equations, the relationships described previously will apply equally to all.

*reverse reaction*

$$K_c \rightarrow K_c^{-1}$$

$$Q \rightarrow Q^{-1}$$

$$K_p \rightarrow K_p^{-1}$$

*multiply reaction by  $n$*

$$K_c \rightarrow K_c^n$$

$$Q \rightarrow Q^n$$

$$K_p \rightarrow K_p^n$$

*combine reactions*

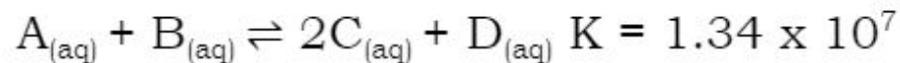
$$K_c \rightarrow K_c' K_c''$$

$$Q \rightarrow Q' Q''$$

$$K_p \rightarrow K_p' K_p''$$

## TOGETHER 7.5

1. Given the following reaction, what can be said about the relative amounts of the reactants and products when you reach equilibrium? Explain.



## TOGETHER 7.6

1. Given the following reactions, calculate the value for K for the overall reaction.

$A + B \rightleftharpoons C + 2 D$	$K_1 = 5$
$D + B \rightleftharpoons E$	$K_2 = 15$
$A + 3 B \rightleftharpoons C + 2 E$	$K = ?$

## 7.7 Calculating Equilibrium Concentrations

### ENDURING UNDERSTANDING:

TRA-7

A system at equilibrium depends on the relationships between concentrations, partial pressures of chemical species, and equilibrium constant  $K$ .

### LEARNING OBJECTIVE:

TRA-7.E

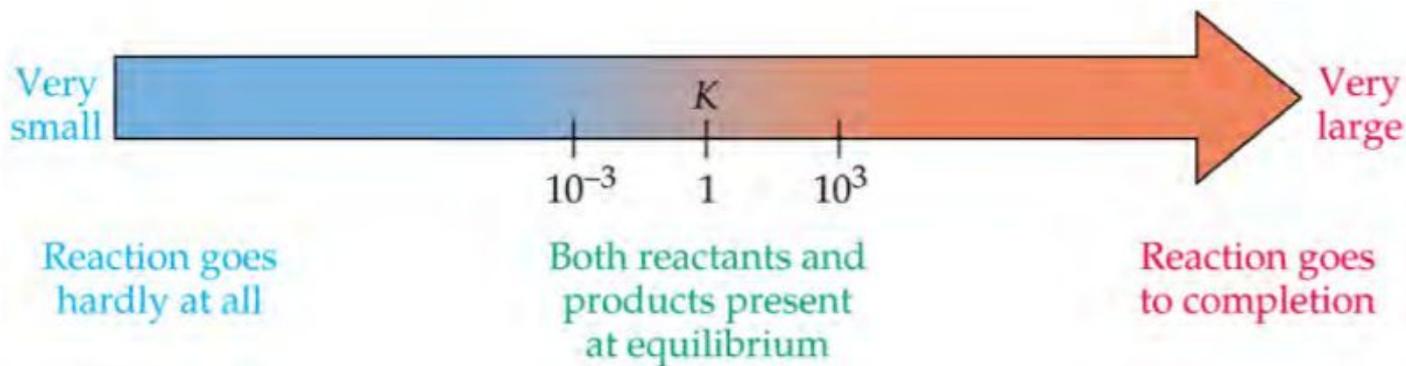
Identify the concentrations or partial pressures of chemical species at equilibrium based on the initial conditions and the equilibrium constant.

# PREVIOUSLY

We learned how when the equilibrium constant is very large or very small, we can make assumptions about the amounts of products and reactants.

**Equilibrium Constant:**  $K = [\text{products}] / [\text{reactants}]$  and

$K > 1$  means  $[\text{products}] > [\text{reactants}]$  and  $K < 1$  means  $[\text{reactants}] > [\text{products}]$



# WHAT ABOUT EQUILIBRIUM CONSTANTS BETWEEN THE EXTREMES?

We can use stoichiometry!

Though chemicals will not necessarily be mixed in stoichiometric proportions initially, reactions will still obey the stoichiometric relationships.



**Does not mean:** mixture will have ratios of 2:1:1:4

**It does mean:** If  $\text{CH}_{4\text{(g)}}$  decreases by  $x$

$\text{H}_{2\text{(g)}}\text{S}$  decreases by  $2x$

$\text{CS}_{2\text{(g)}}$  increases by  $x$

$\text{H}_{2\text{(g)}}$  increases by  $4x$

# (BR)ICE TABLES

A common procedure for solving equilibrium concentrations is sometimes referred to as the ICE method, where the acronym stands for **I**nitial, **C**hange, and **E**quilibrium.

	A	+	2B	⇌	C
I					
C					
E					

*Example 1:* The following gases were placed in a 4.00 L flask: 8.00 mol  $\text{N}_2$  and 10.00 mol  $\text{H}_2$ .

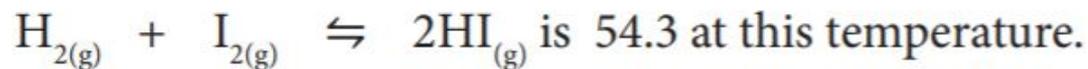
After equilibrium was achieved, 1.20 M  $\text{NH}_3$  was found in the flask. Complete the ICE table below and determine the equilibrium constant,  $K_{\text{eq}}$ .

	$\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$		
I			
C			
E			

\*Pay attention to UNITS! We first have to solve for molarity of  $\text{N}_2$  and  $\text{H}_2$ .

$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(\quad)^2}{(\quad)(\quad)^3} = \underline{\hspace{2cm}} =$$

*Example 2:* A mixture of 0.500 mol  $\text{H}_2$  and 0.500 mol  $\text{I}_2$  was placed in a 1.00-L stainless-steel flask at 430 °C. The equilibrium constant  $K_c$  for the reaction



Calculate the concentrations of  $\text{H}_2$ ,  $\text{I}_2$ , and  $\text{HI}$  at equilibrium.

	$\text{H}_{2(g)}$	+	$\text{I}_{2(g)}$	$\rightleftharpoons$	$2\text{HI}_{(g)}$
<i>Initial</i>	0.500		0.500		
<i>Change</i>					
<i>Equilibrium</i>					

$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(\quad)^2}{(\quad)(\quad)} = 54.3$$

# 5% ASSUMPTION (FOR A VERY SMALL K)

Given,  $A_{(aq)} + B_{(aq)} \rightleftharpoons AB_{(aq)}$ , with an equilibrium constant of  $3.4 \times 10^{-5}$  at  $50^\circ\text{C}$ . If  $1.00\text{ M}$  of A and  $2.00\text{ M}$  of B are allowed to reach equilibrium, what are the equilibrium values?

	<b>A</b>	<b>B</b>	<b>AB</b>
<b>I</b>			
<b>C</b>			
<b>E</b>			

$$K_c = \quad \quad \quad = 3.4 \times 10^{-5}$$

# 5% ASSUMPTION

$$K_c = \frac{(x)}{(1.00-x)(2.00-x)} = 3.4 \times 10^{-5}$$

Difficult to solve without a graphing calculator...

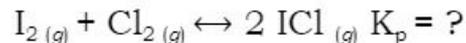
BUT:  $K$  is very small, meaning VERY few products are forming. We can assume  $x$  is negligible compared to 1.00 or 2.00.

Therefore we can rewrite the equation:  $K_c = \frac{x}{(1.00)(2.00)} = 3.4 \times 10^{-5}$

$$X = 6.8 \times 10^{-5}$$

# TOGETHER

1. Consider the reaction:



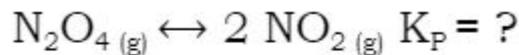
Enough ICl was added to reach a partial pressure of 2.45 atm in a previously evacuated vessel. After the reaction reached equilibrium, the pressure of the  $\text{I}_2$  was 0.30 atm.

Complete an ICE diagram to find the equilibrium pressures of each species and then use those values to calculate the value of the equilibrium constant.

	$\text{I}_2$	$\text{Cl}_2$	$2\text{ICl}$
<b>I</b>			
<b>C</b>			
<b>E</b>			

# YOU DO, WE REVIEW

2. Consider the reaction:



The reaction mixture initially contains a partial pressure of  $\text{NO}_2$  of 0.100 atm, when the reaction reached equilibrium the partial pressure of  $\text{NO}_2$  was 0.080 atm. Find the equilibrium concentrations of  $\text{N}_2\text{O}_4$  at this temperature and use it to find the value for the equilibrium constant.

# AGENDA

Bellwork

Finish presenting

7.8 and 7.9

Lab



## 7.8 Representations of Equilibrium

### ENDURING UNDERSTANDING:

TRA-7

A system at equilibrium depends on the relationships between concentrations, partial pressures of chemical species, and equilibrium constant  $K$ .

### LEARNING OBJECTIVE:

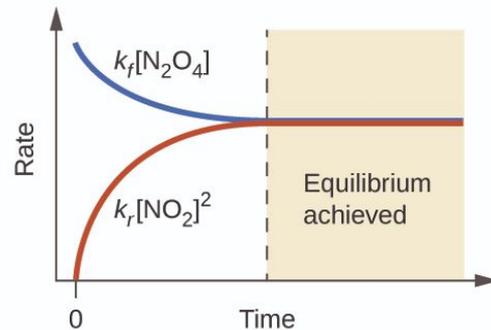
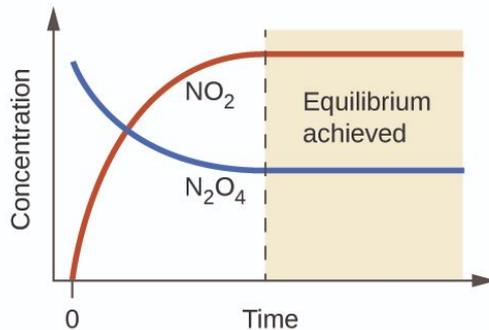
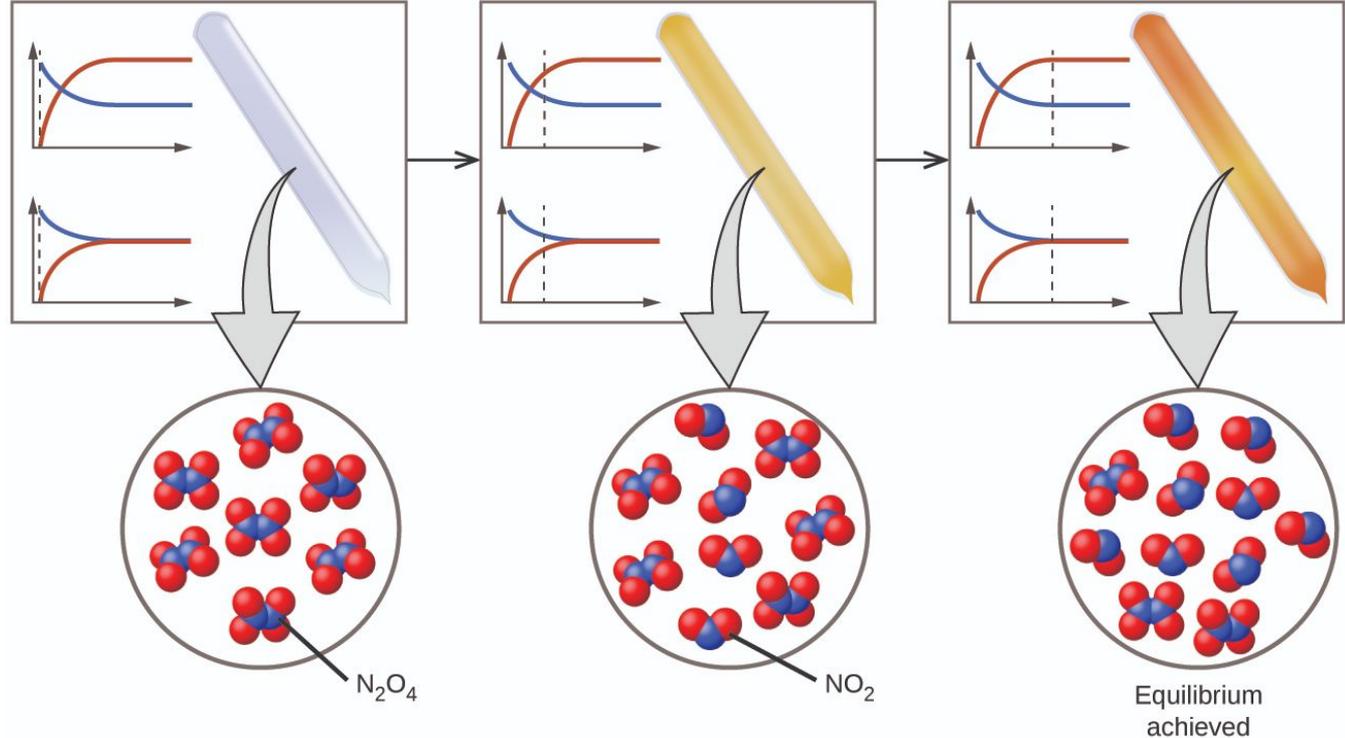
TRA-7.F

Represent a system undergoing a reversible reaction with a particulate model.

# EQUILIBRIUM MODELS

We can model the reactions to show the relative numbers of particles before and after equilibrium.

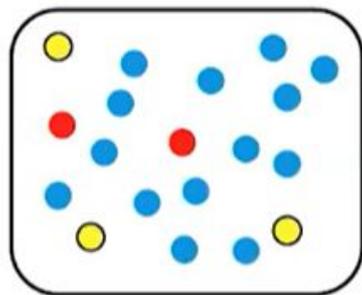
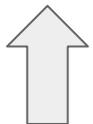
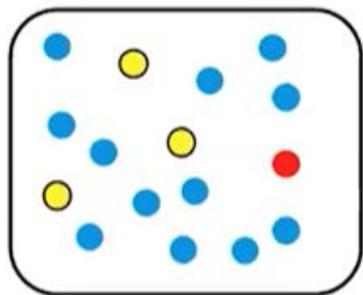
We can deduce the value of the equilibrium constant from the models.



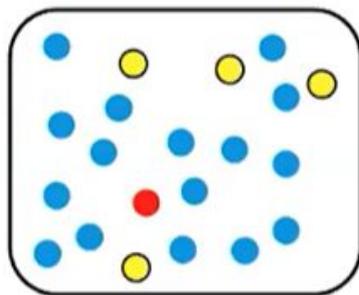
# EXAMPLE (IF YOU WATCHED THE DAILY VIDEO THIS WILL BE FAMILIAR!)



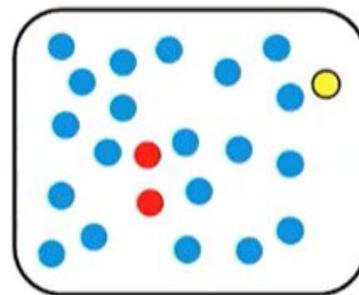
At equilibrium



Reaction  
Vessel A



Reaction  
Vessel B



Reaction  
Vessel C

$$K = \frac{[Z]}{[Q][Y]^2}$$

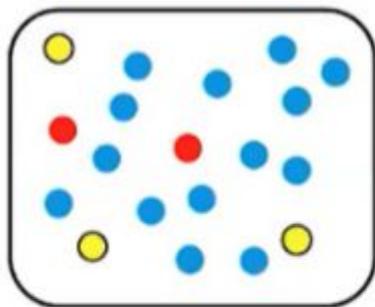
# EXAMPLE



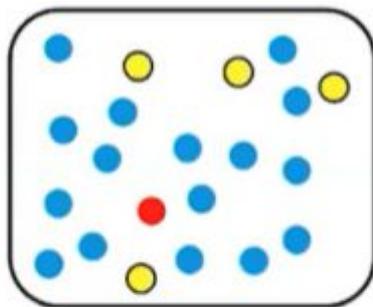
$K_{eq} = 4$   
(from last slide)

**Vessel A:**

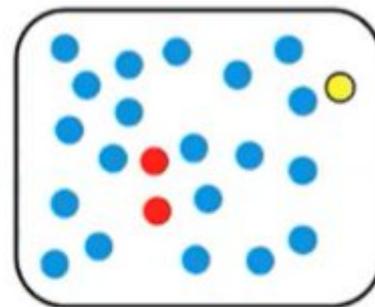
$$Q = \frac{[Z]}{[Q][Y]^2}$$



**Reaction Vessel A**



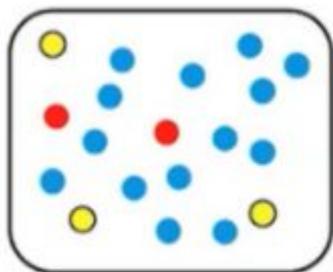
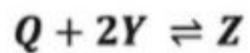
**Reaction Vessel B**



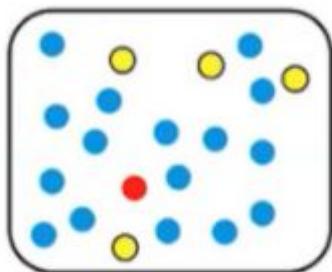
**Reaction Vessel C**

How does  $Q$  compare to  $K_{eq}$ ?

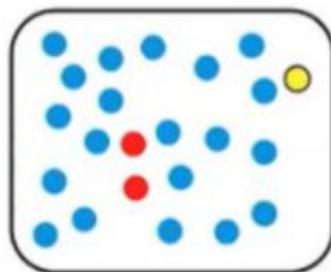
FIND Q FOR VESSELS B & C AND REACTION DIRECTION



Reaction  
Vessel A

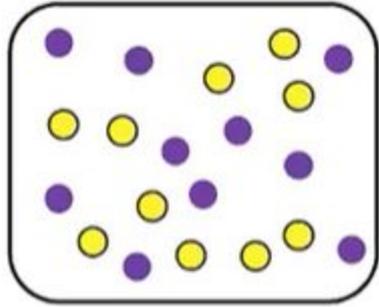


Reaction  
Vessel B

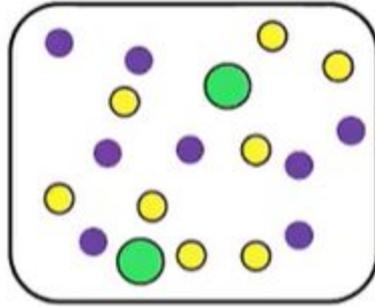


Reaction  
Vessel C

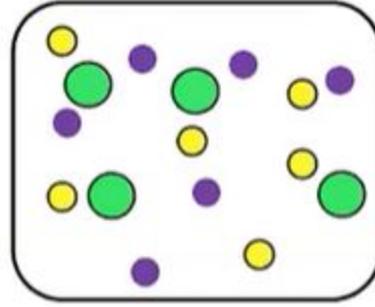
WHAT TIME IS EQUILIBRIUM REACHED? JUSTIFY YOUR ANSWER.



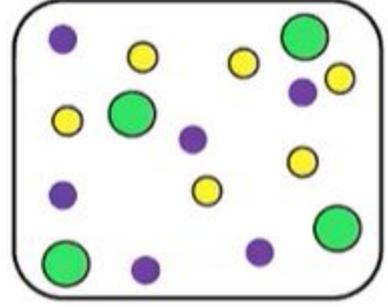
0 minutes



10 minutes

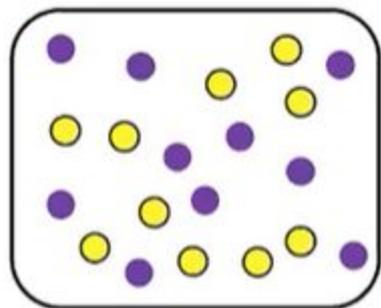


20 minutes

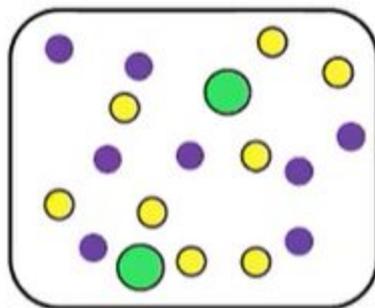


30 minutes

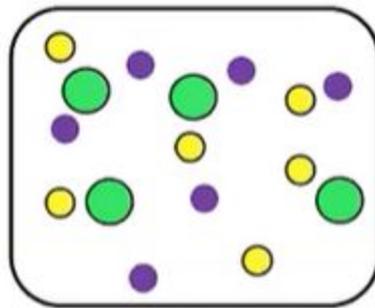
# WHAT TIME IS EQUILIBRIUM REACHED? JUSTIFY YOUR ANSWER.



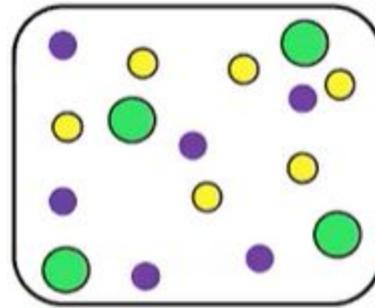
0 minutes



10 minutes



20 minutes

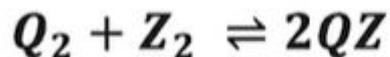


30 minutes

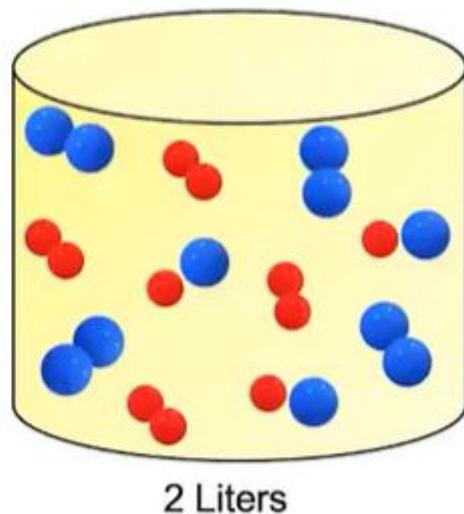
<b>Claim:</b>	<b><i>20 minutes</i></b>
<b>Evidence:</b>	<b><i>From 20 to 30 minutes the number of reactants and products is constant</i></b>
<b>Reasoning:</b>	<b><i>Dynamic equilibrium is reached when rate forward = rate reverse. Reactant is still forming product and vice versa, the amounts remain constant</i></b>

# QUICK CHECK

The diagram shows the following reaction at equilibrium in a two-liter reaction vessel. Each particle represents 0.020 moles.

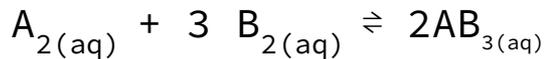


- (a) Determine the molarity of  $Q_2$ ,  $Z_2$ , and  $QZ$  at equilibrium.
- (b) Write the equilibrium constant expression in terms of molarity and calculate the equilibrium constant

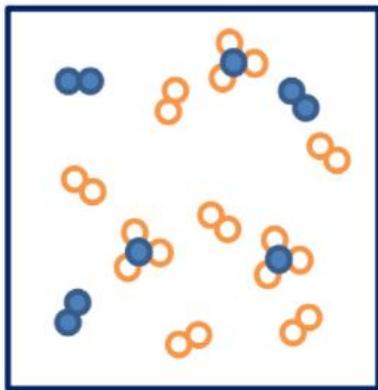


# ONE LAST THING...

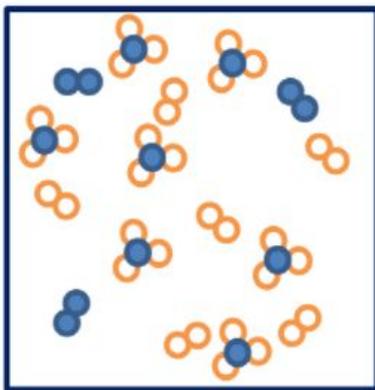
Consider this set of images for this reaction:



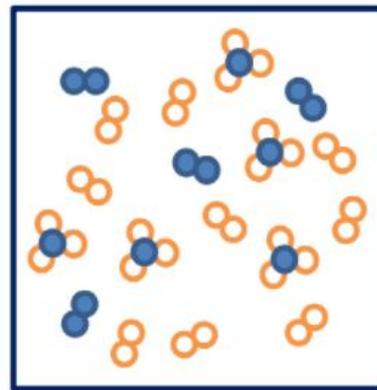
The system is initially at equilibrium, then some  $AB_3$  is added. The reaction then moves to a new equilibrium.



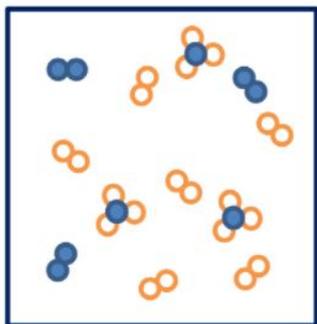
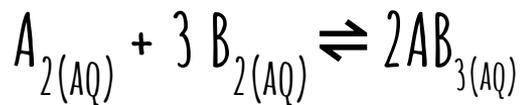
Initial Equilibrium



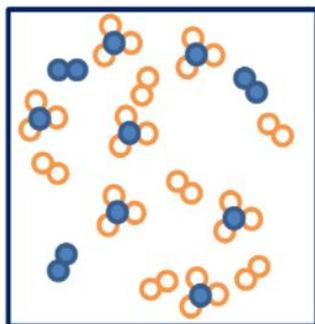
Addition of  $AB_3$   
(Not at equilibrium)



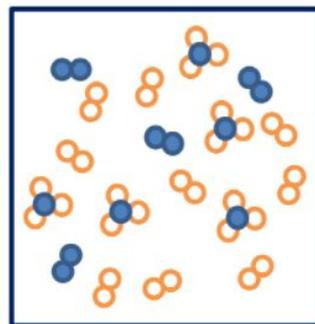
Possible New Equilibrium



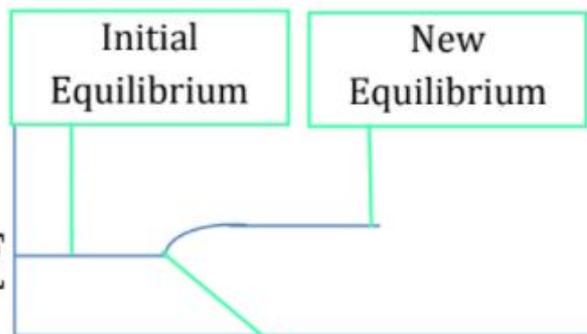
Initial Equilibrium



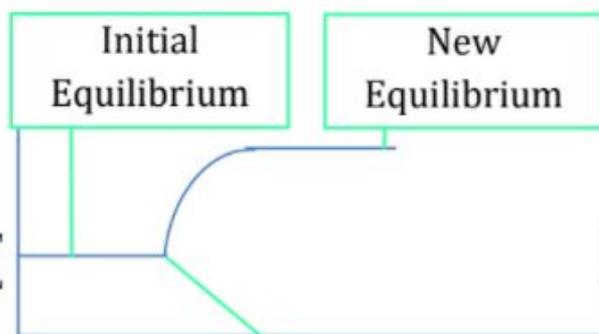
Addition of AB<sub>3</sub>  
(Not at equilibrium)



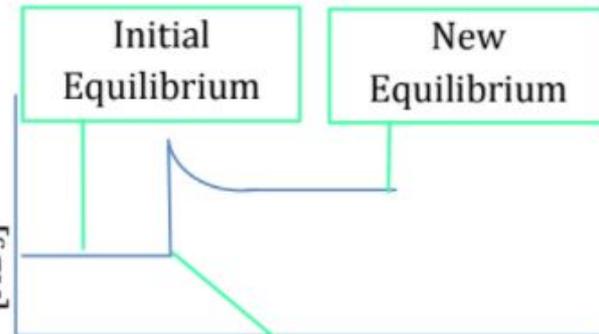
Possible New Equilibrium



Time when AB<sub>3</sub>  
was added



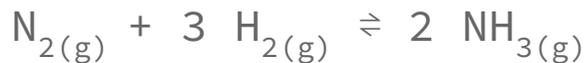
Time when AB<sub>3</sub>  
was added



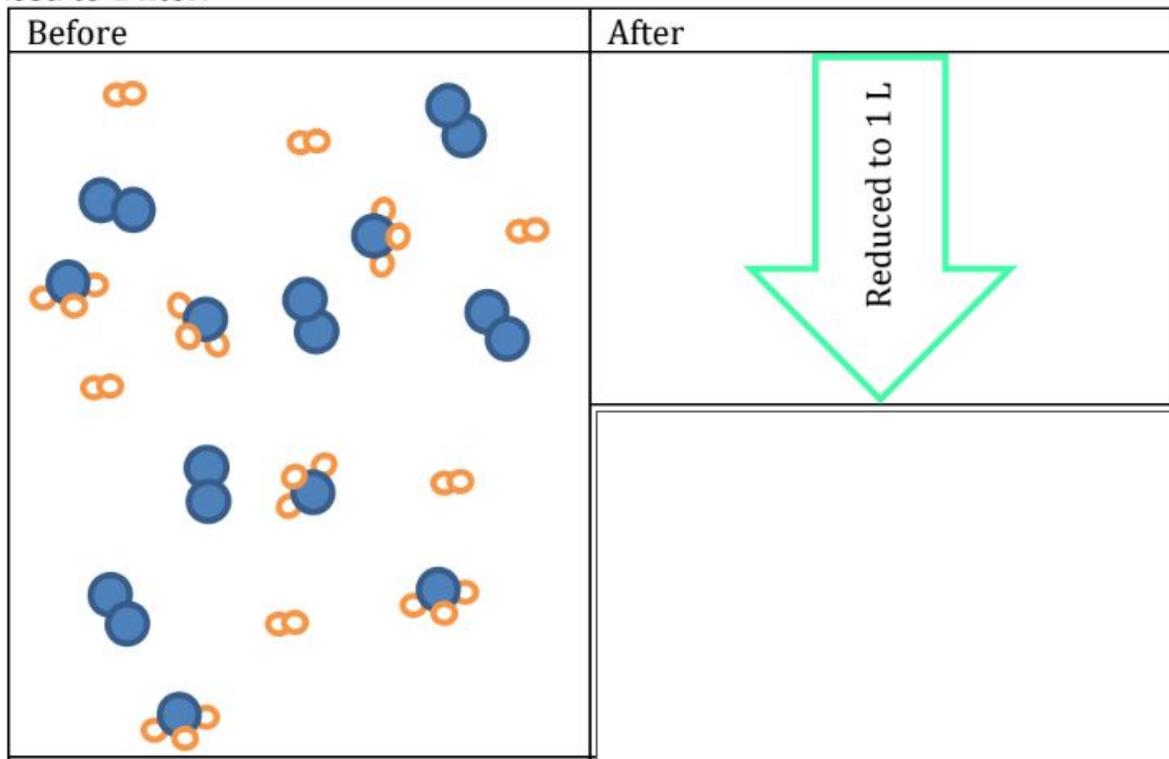
Time when AB<sub>3</sub>  
was added

# TOGETHER

Consider the reaction:



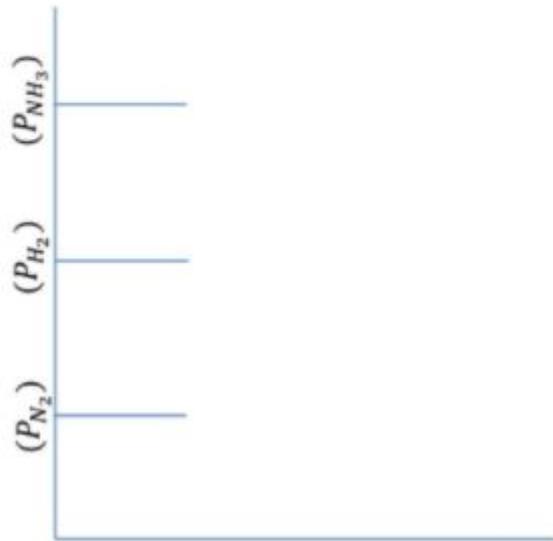
Given 6 moles of nitrogen, 6 moles of hydrogen and 6 moles of ammonia at equilibrium in a 2 liter container, draw a possible equilibrium showing how the number of reactants and products might change if the volume of the container was reduced to 1 liter.



# YOU DO, WE REVIEW

Consider the reaction:  $\text{N}_{2(g)} + 3 \text{H}_{2(g)} \rightleftharpoons 2 \text{NH}_{3(g)}$

Given 6 moles of nitrogen, 6 moles of hydrogen and 6 moles of ammonia at equilibrium in a 2 liter container, sketch a graph showing how the amount of reactants and products will change if the volume of the container was reduced to 1 liter.



## 7.9 Le Chatelier's Principle

### ENDURING UNDERSTANDING:

TRA-8	Systems at equilibrium respond to external stresses to offset the effect of the stress.
-------	---

### LEARNING OBJECTIVE:

TRA-8.A	Identify the response of a system at equilibrium to an external stress, using Le Châtelier's principle.
---------	---

TRA-8.B	Explain the relationships between $Q$ , $K$ , and the direction in which a reversible reaction will proceed to reach equilibrium.
---------	---

# DYNAMIC EQUILIBRIUM VS STATIC

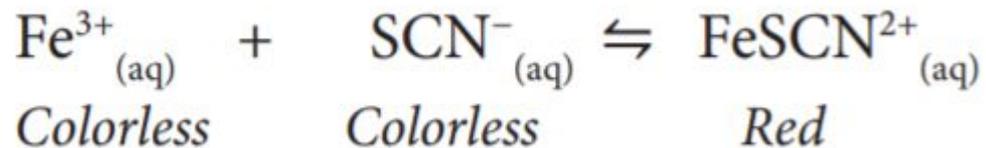
---

REPEAT TO YOURSELF EVERYDAY:

THE ONLY THING THAT  
CAN CHANGE THE VALUE  
OF  $k$  IS **TEMPERATURE**

# PREDICTING AND EXPLAINING CHANGES TO A SYSTEM AT EQUILIBRIUM

What happens if we add more  $\text{Fe}^{3+}$  to the following system at equilibrium?



# PREDICTION AND EXPLANATION EXAMPLES FOR FRQS

**Prediction:** increasing  $[\text{Fe}^{3+}]$  favor the forward reaction creating more products.

**Explanation:** if we increase  $[\text{Fe}^{3+}]$  then we increase number of collisions between  $\text{Fe}^{3+}(\text{aq})$  and  $\text{SCN}^{-}(\text{aq})$  and so we increase the rate of the forward reaction.

$\text{Rate}_{\text{forward}} > \text{Rate}_{\text{reverse}}$ , so more products and less reactants until new equilibrium mixture forms and  $\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$  again.

# HENRI-LOUIS LE CHÂTELIER (1850-1936)

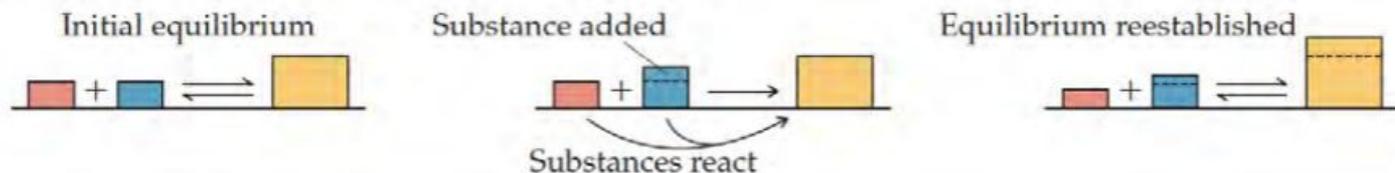
- Le Châtelier's Principle: if a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium shifts to counteract the change to reestablish an equilibrium.
- Using Le Châtelier's Principle to **Explain**: if we increase  $[\text{Fe}^{3+}]$  then the equilibrium will respond in order to counter this disturbance, it will remove  $\text{Fe}^{3+}$  ions by converting them into  $\text{FeSCN}^{2+}$ .
- The prediction is the same! More products produced, rate of the forward reaction is faster than the rate of reverse reaction until equilibrium is reached again...

## Le Chatelier's Principle

If a system at equilibrium is disturbed by a change in **concentration**, **pressure**, or **temperature**, the system will shift its equilibrium position so as to counter the effect of the disturbance.

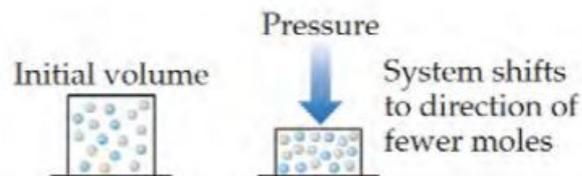
**Concentration:** adding or removing a reactant or product

*If a substance is added to a system at equilibrium, the system reacts to consume some of the substance. If a substance is removed from a system, the system reacts to produce more of substance.*



**Pressure:** changing the pressure by changing the volume

*At constant temperature, reducing the volume of a gaseous equilibrium mixture causes the system to shift in the direction that reduces the number of moles of gas.*



**Temperature:**

*If the temperature of a system at equilibrium is increased, the system reacts as if we added a reactant to an endothermic reaction or a product to an exothermic reaction. The equilibrium shifts in the direction that consumes the "excess reactant," namely heat.*



## QUICK CHECK



A sealed rigid vessel contains  $\text{BaO}_{2(s)}$  in equilibrium with  $\text{BaO}_{(s)}$  and  $\text{O}_{2(g)}$  as represented by the equation above. Which of the following changes will increase the amount of  $\text{BaO}_{2(s)}$  in the vessel?

- A** Removing a small amount of  $\text{O}_{2(g)}$       **B** Removing a small amount of  $\text{BaO}_{(s)}$
- C** Adding He gas to the vessel      **D** Lowering the temperature

# APPLYING LE CHÂTELIER'S TO K & Q

At equilibrium:  $Q = K$

When a stress is applied:  $Q \neq K$

Meaning: If an equilibrium system is subjected to a stress (resulting in  $K_c \neq Q_c$ ), the system will respond in such a way as to reduce the stress (and ensure that  $K_c = Q_c$ ).

# STRESS I: CHANGING CONCENTRATION

Concentrations can be changed by:

- Adding or removing a reactant or product
- Adding water to dilute (reduce concentration)

**K does not change! K ONLY changes with Temperature change.**

However, there will be a new  $Q$ . The reaction will shift until  $Q_{\text{new}} = K$

# LAB

- Typo for activity 2
- Iodine demonstration
- You must determine the time needed for each activity
- Safety: goggles
- If you finish early: you are challenged with returning all of your test tubes to the original equilibrium
- Cleanup!!!!

## EXAMPLE 1

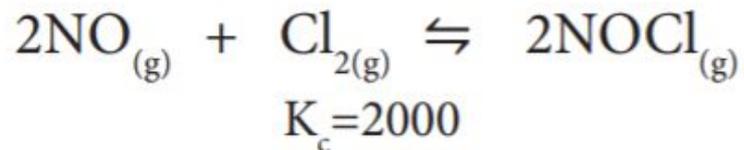


$$K_c = \frac{[\text{H}_3\text{O}^+][\text{Cl}^-][\text{HOCl}]}{[\text{Cl}_2]} = 4.8 \times 10^{-4}$$

The equilibrium reaction between  $\text{Cl}_{2(aq)}$  and  $\text{H}_2\text{O}_{(l)}$  at  $25^\circ\text{C}$  is represented by the chemical equation shown above. If a solution at equilibrium at  $25^\circ\text{C}$  is diluted with distilled water to twice its original volume, *what would be the new value for  $Q_c$  and what would be the response by the system immediately after dilution?*

\*If a system is diluted to twice the volume (with the same number of moles of each solute) the new concentrations are half the original. Use  $\frac{1}{2}$  the original coefficients for all concentrations.

## EXAMPLE 2



Species	Concentration (M)
$\text{NO}(g)$	0.050
$\text{Cl}_2(g)$	0.050
$\text{NOCl}(g)$	0.50

A mixture of  $\text{NO}_{(g)}$  and  $\text{Cl}_{2(g)}$  is placed in a previously evacuated container and allowed to reach equilibrium according to the chemical equation shown above.

When the system reaches equilibrium, the reactants and products have the concentrations listed in the table above.

The volume of the container is decreased by one half. *What would be the new value for  $Q_c$  and what would be the response by the system immediately after reducing the volume?*

\*What does halving the volume do to concentrations?

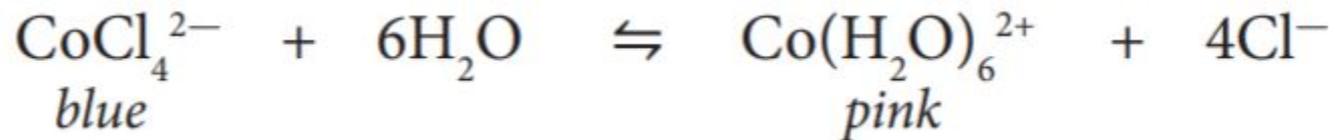
# STRESS 2: TEMPERATURE CHANGE

**Temperature change changes K! Q will follow.**

Treat temperature as a reactant for endothermic reactions and a product for exothermic reactions.

<i>forward reaction exothermic</i>	<i>temperature decreases</i>	<i>reactants</i> $\Rightarrow$ <i>products</i>	$K_c \nearrow$	$Q_c \nearrow$
	<i>temperature increases</i>	<i>products</i> $\Rightarrow$ <i>reactants</i>	$K_c \searrow$	$Q_c \searrow$
<i>forward reaction endothermic</i>	<i>temperature decreases</i>	<i>products</i> $\Rightarrow$ <i>reactants</i>	$K_c \searrow$	$Q_c \searrow$
	<i>temperature increases</i>	<i>reactants</i> $\Rightarrow$ <i>products</i>	$K_c \nearrow$	$Q_c \nearrow$

## EXAMPLE



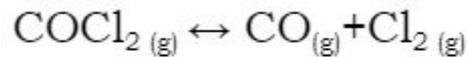
The reaction above is exothermic.

What color will the solution be when placed in an ice bath?

What color will the solution be when placed on a hot plate?

## TOGETHER (7.9)

1. In an endothermic process, phosgene gas,  $\text{COCl}_2$ , decomposes into carbon monoxide gas,  $\text{CO}$ , and chlorine gas,  $\text{Cl}_2$ . The  $K_{\text{eq}}$  for the reaction is 0.0071. Using Le Châtelier's principle, predict how the reaction will respond to each of the following stressors:



- Adding more  $\text{COCl}_{2(g)}$
- Removing  $\text{CO}_{(g)}$
- Increasing the pressure.
- Decreasing the temperature.

# AGENDA

Bellwork

7.10 notes

7.10 practice problems

7.11 notes

7.11 practice problems

Lab project

## 7.10 Le Chatelier's Principle and Q

### ENDURING UNDERSTANDING:

TRA-8	Systems at equilibrium respond to external stresses to offset the effect of the stress.
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### LEARNING OBJECTIVE:

TRA-8.A	Identify the response of a system at equilibrium to an external stress, using Le Châtelier's principle.
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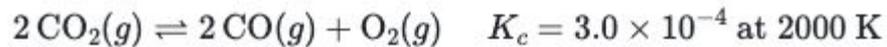
TRA-8.B	Explain the relationships between Q, K, and the direction in which a reversible reaction will proceed to reach equilibrium.
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IF ALL OF OUR COMPOUNDS HAVE AN INITIAL CONCENTRATION

We must determine the direction the reaction is moving in

How could we do this?

# EXAMPLE

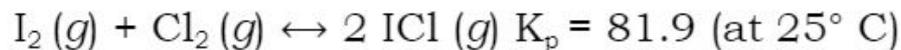


At high temperatures,  $\text{CO}_2(g)$  decomposes into  $\text{CO}(g)$  and  $\text{O}_2(g)$  according to the equation above. A sample of each gas is injected into a rigid, evacuated container at 2000 K. The initial concentrations of the gases are listed in the table below.

Gas	Initial concentration ( $M$ )
$\text{CO}_2$	1.0
$\text{CO}$	0.30
$\text{O}_2$	0.30

# TOGETHER (7.10)

Consider the reaction:



A reaction mixture at  $25^\circ \text{ C}$  initially contains  $P_{\text{I}_2} = 0.100 \text{ atm}$ ,  $P_{\text{Cl}_2} = 0.100 \text{ atm}$ , and  $P_{\text{ICl}} = 0.100 \text{ atm}$ .

- Find  $Q_{\text{initial}}$
- Will the forward or reverse reaction be favored?
- Find the equilibrium partial pressures of  $\text{I}_2$ ,  $\text{Cl}_2$  and  $\text{ICl}$  at this temperature.

## 7.11 Introduction to Solubility Equilibria

### ENDURING UNDERSTANDING:

SPQ-5

The dissolution of a salt is a reversible process that can be influenced by environmental factors such as pH or other dissolved ions.

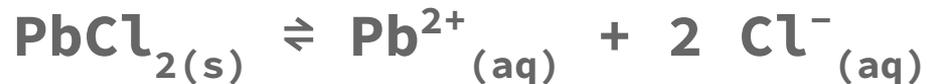
### LEARNING OBJECTIVE:

SPQ-5.A

Calculate the solubility of a salt based on the value of  $K_{sp}$  for the salt.

$K_{sp}$ 

Since solids are not included in a K expression,  $K_{sp}$  **never** have denominators.



The  $K_{sp}$  expression is:

$$K_{sp} = 1.7 \times 10^{-5} = [\text{Pb}^{2+}][\text{Cl}^{-}]^2$$

# MOLAR SOLUBILITY & SOLUBILITY

- Molar solubility (mol/L)- the number of moles of solute in 1 L of a saturated solution
- Solubility (g/L)- the number of grams of solute in 1 L of a saturated solution

But what does saturated mean?

# UNSATURATED, SATURATED, & SUPERSATURATED

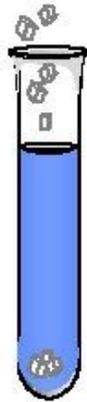
## UNSATURATED SOLUTION

more solute  
dissolves



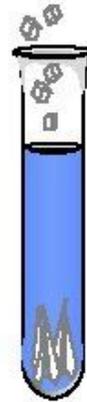
## SATURATED SOLUTION

no more solute  
dissolves



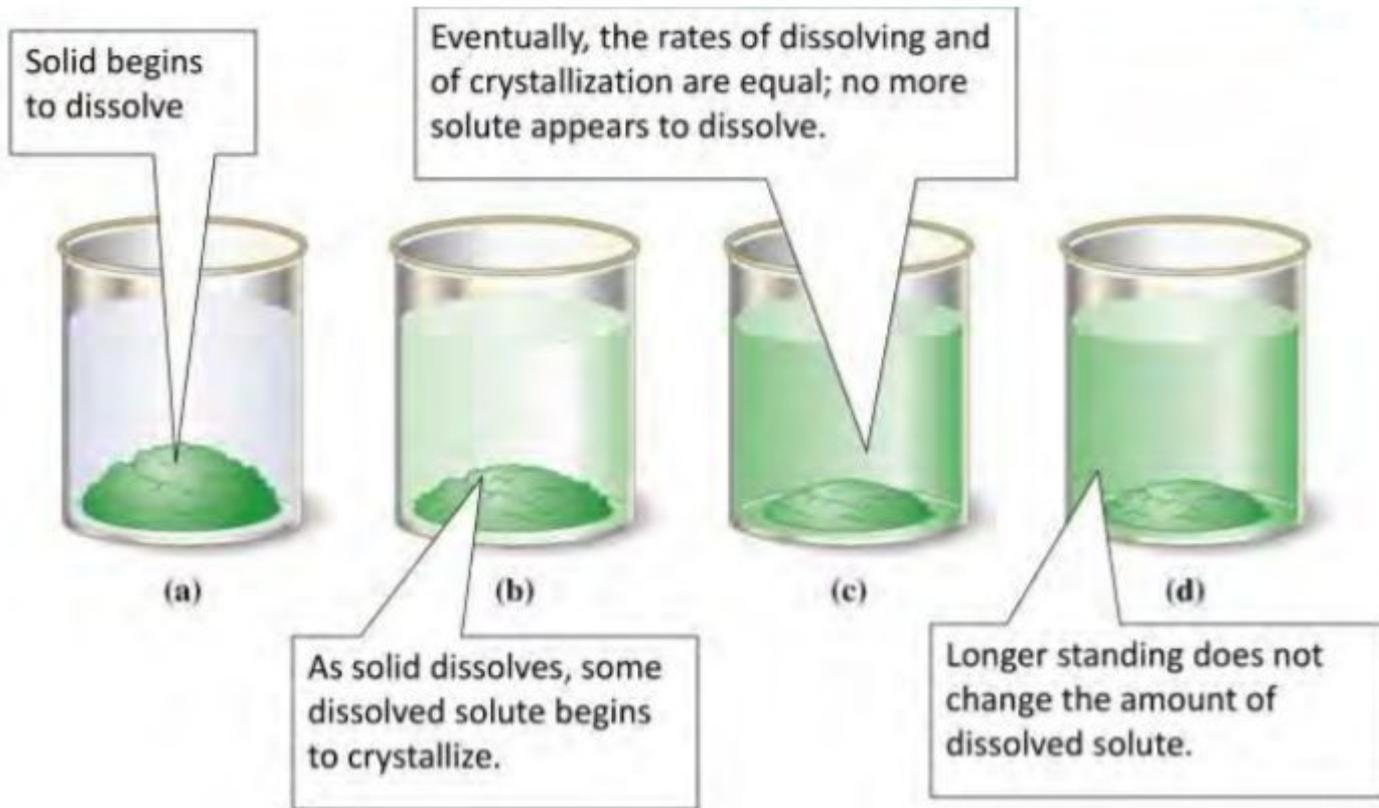
## SUPERSATURATED SOLUTION

becomes unstable,  
crystals form



increasing concentration

# SATURATED = EQUILIBRIUM



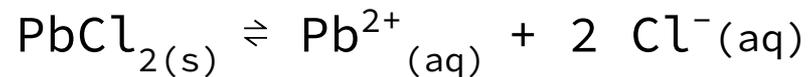
$$K_{sp} > 1 = \text{SOLUBLE}$$

So the closer the  $K_{sp}$  is to 1, the more soluble the solid is.

Compound	$K_{sp}$
Aluminum hydroxide $[\text{Al}(\text{OH})_3]$	$1.8 \times 10^{-33}$
Barium carbonate ( $\text{BaCO}_3$ )	$8.1 \times 10^{-9}$
Barium fluoride ( $\text{BaF}_2$ )	$1.7 \times 10^{-6}$
Barium sulfate ( $\text{BaSO}_4$ )	$1.1 \times 10^{-10}$
Bismuth sulfide ( $\text{Bi}_2\text{S}_3$ )	$1.6 \times 10^{-72}$
Cadmium sulfide ( $\text{CdS}$ )	$8.0 \times 10^{-28}$
Calcium carbonate ( $\text{CaCO}_3$ )	$8.7 \times 10^{-9}$
Calcium fluoride ( $\text{CaF}_2$ )	$4.0 \times 10^{-11}$
Calcium hydroxide $[\text{Ca}(\text{OH})_2]$	$8.0 \times 10^{-6}$
Calcium phosphate $[\text{Ca}_3(\text{PO}_4)_2]$	$1.2 \times 10^{-26}$
Chromium(III) hydroxide $[\text{Cr}(\text{OH})_3]$	$3.0 \times 10^{-29}$
Cobalt(II) sulfide ( $\text{CoS}$ )	$4.0 \times 10^{-21}$
Copper(I) bromide ( $\text{CuBr}$ )	$4.2 \times 10^{-8}$
Copper(I) iodide ( $\text{CuI}$ )	$5.1 \times 10^{-12}$
Copper(II) hydroxide $[\text{Cu}(\text{OH})_2]$	$2.2 \times 10^{-20}$
Copper(II) sulfide ( $\text{CuS}$ )	$6.0 \times 10^{-37}$
Iron(II) hydroxide $[\text{Fe}(\text{OH})_2]$	$1.6 \times 10^{-14}$
Iron(III) hydroxide $[\text{Fe}(\text{OH})_3]$	$1.1 \times 10^{-36}$
Iron(II) sulfide ( $\text{FeS}$ )	$6.0 \times 10^{-19}$
Lead(II) carbonate ( $\text{PbCO}_3$ )	$3.3 \times 10^{-14}$
Lead(II) chloride ( $\text{PbCl}_2$ )	$2.4 \times 10^{-4}$

## EXAMPLE 1

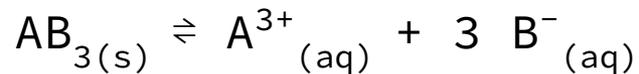
$$K_{\text{SP}} = 1.7 \times 10^{-5} = [\text{Pb}^{2+}][\text{Cl}^{-}]^2$$



What are the concentrations of  $\text{Pb}^{2+}$  and  $\text{Cl}^{-}$  in a saturated solution?

## EXAMPLE 2

The compound  $AB_3$  was dissolved in water. The molarity of ion  $A^{3+}$  is found to be 0.00213M, what is the value for the  $K_{SP}$  of  $AB_3$ ?



$$K_{SP} = [A^{3+}][B^{-}]^3$$

## YOU DO, WE REVIEW

The compound  $XBr_3$  has a  $K_{sp}$  value of  $4.52 \times 10^{-8}$ , when  $XBr_3$  is added to water, what is the concentration of the  $X^{3+}$  and  $Br^-$  ions?

## 7.12 Common-Ions

### ENDURING UNDERSTANDING:

SPQ-5

The dissolution of a salt is a reversible process that can be influenced by environmental factors such as pH or other dissolved ions.

### LEARNING OBJECTIVE:

SPQ-5.B

Identify the solubility of a salt, and/or the value of  $K_{sp}$  for the salt, based on the concentration of a common ion already present in solution.

SPQ-5.C

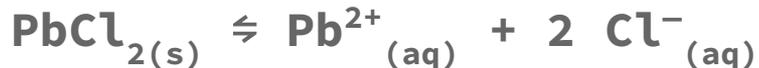
Identify the qualitative effect of changes in pH on the solubility of a salt.

# COMMON IONS - APPLYING LE CHATELIER'S TO SOLUTIONS

So far, all the dissolved ions have come from the original solid.

However, sometimes other substances are present and may share a COMMON ION with the original solid.

Example: addition of **NaCl** solution to

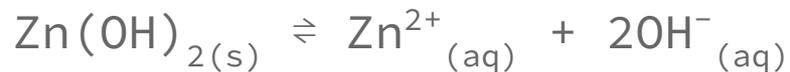


Because there is a common ion ( $\text{Cl}^{-}$ ) we have added more of one of the products and the formation of reactant (solid) will be favored.

## EXAMPLE:

What is the molar solubility of  $\text{Zn(OH)}_2$  in a solution of  $0.10\text{M NaOH}$ ?  $K_{\text{sp}}$  of  $\text{Zn(OH)}_2 = 3.0 \times 10^{-17}$

1. Write the dissociation equation (solid  $\rightleftharpoons$  ions) and the  $K_{\text{sp}}$  expression.



$$K_{\text{sp}} = [\text{Zn}^{2+}][\text{OH}^{-}]^2 = 3.0 \times 10^{-17}$$

# EXAMPLE

## 2. Create an ICE table

	$\text{Zn(OH)}_{2(s)}$	$\text{Zn}^{2+}_{(aq)}$	$2 \text{OH}^{-}_{(aq)}$
Initial	Some amount of solid	0	0.10 M
Change/Coefficient	-x	+x	+2x
Equilibrium		x	$0.10 + 2x$

Since this is a solid, we don't need to pay attention to this part!

We start by assuming that no solid has dissolved yet; the reaction will proceed forwards.

Since NaOH contains a soluble ion,  $\text{Na}^+$ , we know that the  $[\text{OH}^-]$  will be the same as the NaOH concentration.

# EXAMPLE

3. Plug in, assume  $x$  is super small, and solve!

$$K_{sp} = 3.0 \times 10^{-17} = (x)(.1 + 2x)^2$$



VERY  
SMALL  
compared  
to .1!

$$3.0 \times 10^{-17} = (x)(.01)$$

$$x = 3.0 \times 10^{-15} \text{M} = [\text{Zn}^{2+}] = \text{molar solubility of } \text{Zn}(\text{OH})_2$$

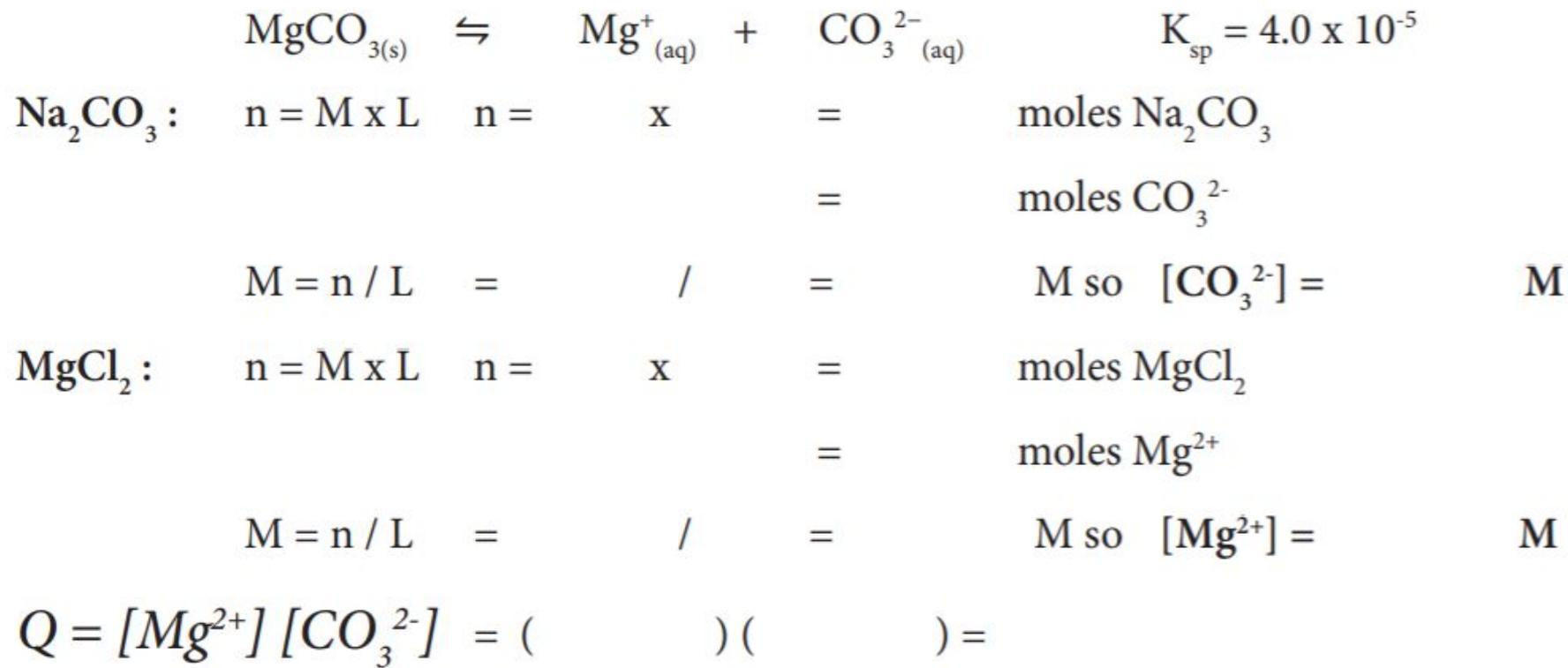
# PRECIPITATION RXNS

Alternatively, two solutions may be mixed, and only then does the possibility of forming a solid exist as between them they both have ions that belong to a potential precipitation reaction.

Example: Will a precipitate form when 23 mL of 0.020M  $\text{Na}_2\text{CO}_3$  is added to 12 mL of 0.010M  $\text{MgCl}_2$ ?



*Example 1:* Will a precipitate form when 23 mL of 0.020 M  $\text{Na}_2\text{CO}_3$  is added to 12 mL of 0.010 M  $\text{MgCl}_2$ ?



## TOGETHER (7.12)

1. Write a balanced chemical equation for the dissolution of calcium hydroxide,  $\text{Ca(OH)}_{2(s)}$  in pure water. Calculate the molar solubility of  $\text{Ca(OH)}_2$  when it is dissolved in a 0.20 M calcium nitrate,  $\text{Ca(NO}_3)_2$ , solution. The  $K_{sp}$  of  $\text{Ca(OH)}_2$  is  $1.3 \times 10^{-6}$

## 7.14 Free Energy of Dissolution

### ENDURING UNDERSTANDING:

SPQ-5

The dissolution of a salt is a reversible process that can be influenced by environmental factors such as pH or other dissolved ions.

### LEARNING OBJECTIVE:

SPQ-5.D

Explain the relationship between the solubility of a salt and changes in the enthalpy and entropy that occur in the dissolution process.

# FACTORS THAT CAN HAVE AN EFFECT ON DISSOLUTION

**Enthalpy ( $\Delta H$ )** - measures potential energy (heat content)

- Energy will be needed to break the solvent-solvent attractions
- Energy will be needed to break the solute-solute attractions
- Energy will be released when solute-solvent attractions form

Energy will be released to or taken in from the surroundings

# FACTORS THAT CAN HAVE AN EFFECT ON DISSOLUTION

**Entropy ( $\Delta S$ )** - measures randomness or disorder

- solute will be more ordered before dissolution
- solvent will be more ordered before dissolution
- dissolution leads to an increase in disorder ( $+\Delta S$ )
- surroundings can also increase in disorder

One way to think about entropy is the probability of the particles or energy being distributed into all the tiny places within a container (microstates).

Salts, like  $\text{NaCl}_{(s)}$  exist as *very ordered crystal lattices*.

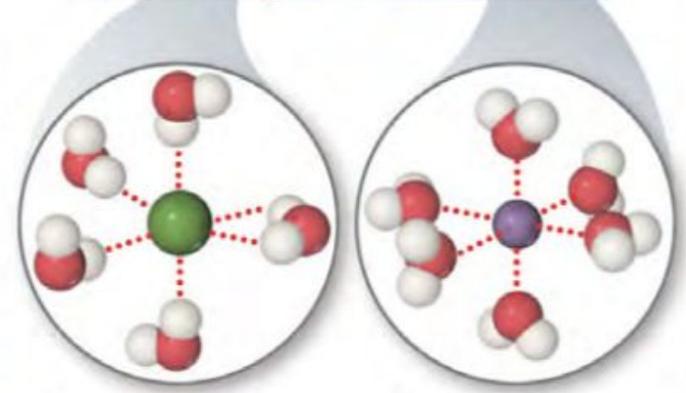
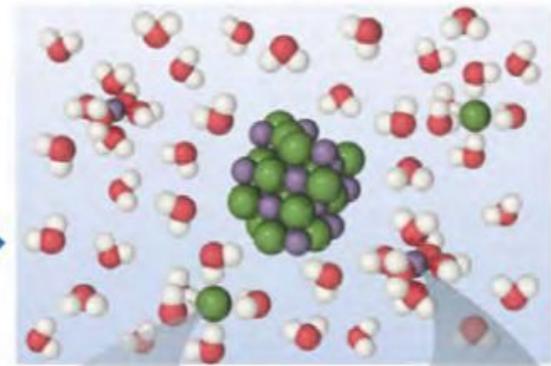
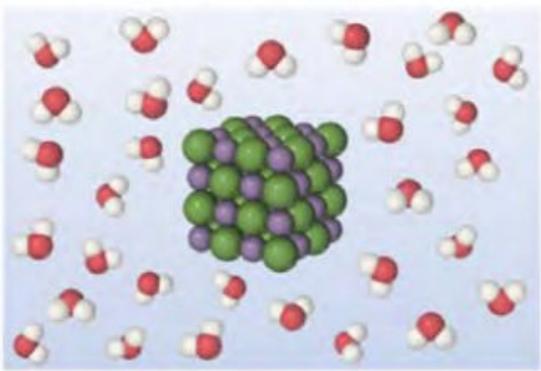
The high level of *hydrogen bonding* makes water a *more ordered liquid* - particularly at lower temperatures.

Solvent-solute interactions between water molecules and  $\text{NaCl}$  allow solid to dissolve

The  $\text{NaCl}$  experiences a *large increase in disorder, Entropy*.

The water molecules that form 'cages' around the ions are *more ordered*, but the surrounding water molecules are *more disordered*. Overall,  $\Delta S +ve$ .

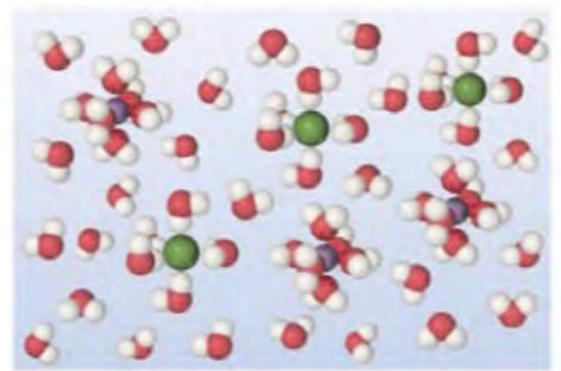
Crystal of  $\text{NaCl}$  in water



Hydrated  $\text{Cl}^-$  ion

Hydrated  $\text{Na}^+$  ion

Ions hydrated in solution



+ve is shorthand for "positive", -ve is shorthand for "negative"

# ENTROPY DRIVES DISSOLUTION

As we've seen, dissolution can be exothermic or endothermic.

Many salts dissolve easily despite being endothermic.

**Entropy is the driving force behind dissolution** due to the large increase in disorder ( $+\Delta S$ ) associated with most dissolutions.

Temperature also has an effect.

# GIBBS FREE ENERGY, $\Delta G$

Enthalpy, entropy, and temperature are all used to determine Gibbs Free Energy.

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

We will learn how to calculate Gibbs free energy in Unit 9, but for now, we can use qualitative analysis to determine if a reaction will occur spontaneously. **The larger the negative value for Gibbs free energy the more the reaction will favor the products.**

### 3 PROCESSES OF DISSOLUTION

	$\Delta H$	$\Delta S$
The intermolecular forces between solvent particles are overcome.	+	+
The intermolecular forces between solute particles are overcome.	+	+
The intermolecular forces between solvent and solute particles must reform.	-	-

# SUMMARY OF GIBBS

$\Delta H$	$\Delta S$	$\Delta G$
+	+	Reaction proceeds spontaneously at high temperatures. At low temperatures, reaction is spontaneous in the reverse direction.
+	-	$\Delta G$ is always positive. Reaction is spontaneous in the reverse direction at all temperatures.
-	+	$\Delta G$ is always negative. Reaction proceeds spontaneously at all temperatures.
-	-	Reaction proceeds spontaneously at low temperatures. At high temperatures, the reverse reaction becomes spontaneous.

# TOGETHER

Which solution would have greater entropy with all other factors remaining equal? Justify your answer

- A saturated solution of cobalt hydroxide ( $\text{Co}(\text{OH})_2$   $K_{\text{SP}}=5.92 \times 10^{-15}$ )
- A saturated solution of beryllium hydroxide ( $\text{Be}(\text{OH})_2$   $K_{\text{SP}}=6.92 \times 10^{-22}$ )

# YOU DO, WE REVIEW

The dissolution of calcium chloride,  $\text{CaCl}_2$ , is exothermic. Draw a model of the following:

- Water
- $\text{CaCl}_{2(s)}$
- $\text{CaCl}_{2(aq)}$

## 7.11 Introduction to Solubility Equilibria

### ENDURING UNDERSTANDING:

SPQ-5

The dissolution of a salt is a reversible process that can be influenced by environmental factors such as pH or other dissolved ions.

### LEARNING OBJECTIVE:

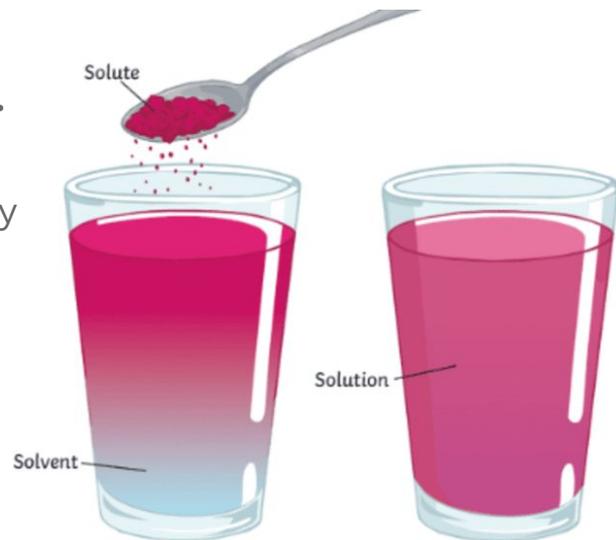
SPQ-5.A

Calculate the solubility of a salt based on the value of  $K_{sp}$  for the salt.



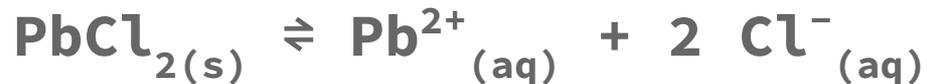
Another application of equilibrium is the solubility of solids.

- Not all substances are completely soluble or insoluble, some are partially soluble.
- The process of dissolution is reversible; the solid and aqueous ions are in dynamic equilibrium.
- We denote this type of equilibrium constant expression with  $K_{sp}$ , the “sp” stands for solubility product.
- The reaction is always written as a dissociation equation for a solid going to its aqueous ions.
- The  $K_{sp}$  represents the maximum amount of ions that can be present in the solution before a precipitate appears.



$K_{sp}$ 

Since solids are not included in a K expression,  $K_{sp}$  **never** have denominators.



The  $K_{sp}$  expression is:

$$K_{sp} = 1.7 \times 10^{-5} = [\text{Pb}^{2+}][\text{Cl}^{-}]^2$$

# MOLAR SOLUBILITY & SOLUBILITY

- Molar solubility (mol/L)- the number of moles of solute in 1 L of a saturated solution
- Solubility (g/L)- the number of grams of solute in 1 L of a saturated solution

But what does saturated mean?

# UNSATURATED, SATURATED, & SUPERSATURATED

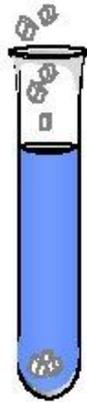
## UNSATURATED SOLUTION

more solute  
dissolves



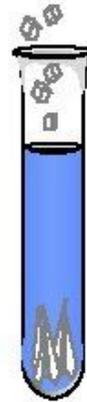
## SATURATED SOLUTION

no more solute  
dissolves



## SUPERSATURATED SOLUTION

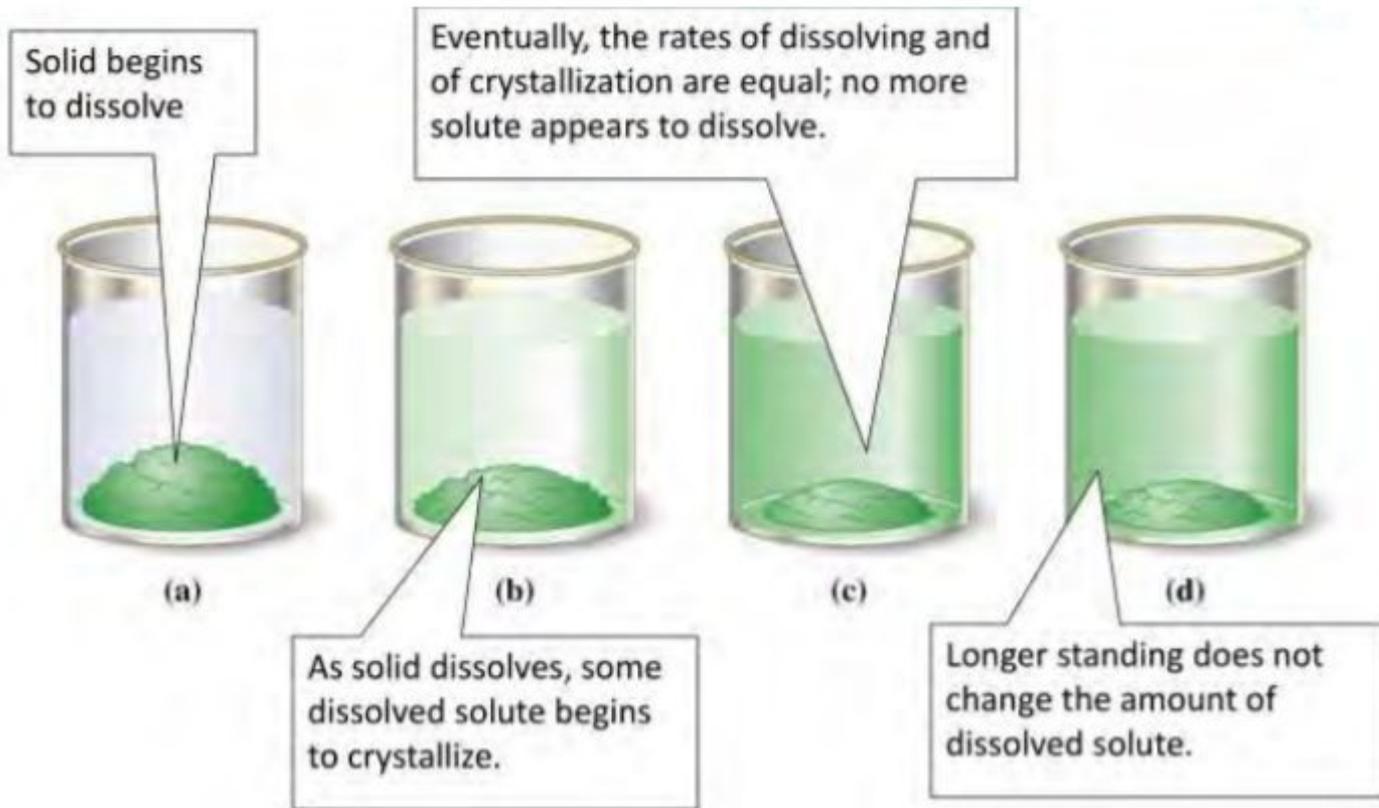
becomes unstable,  
crystals form



increasing concentration



# SATURATED = EQUILIBRIUM



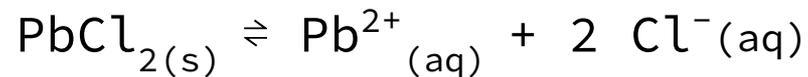
$$K_{sp} > 1 = \text{SOLUBLE}$$

So the closer the  $K_{sp}$  is to 1, the more soluble the solid is.

Compound	$K_{sp}$
Aluminum hydroxide $[\text{Al}(\text{OH})_3]$	$1.8 \times 10^{-33}$
Barium carbonate ( $\text{BaCO}_3$ )	$8.1 \times 10^{-9}$
Barium fluoride ( $\text{BaF}_2$ )	$1.7 \times 10^{-6}$
Barium sulfate ( $\text{BaSO}_4$ )	$1.1 \times 10^{-10}$
Bismuth sulfide ( $\text{Bi}_2\text{S}_3$ )	$1.6 \times 10^{-72}$
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Calcium carbonate ( $\text{CaCO}_3$ )	$8.7 \times 10^{-9}$
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Calcium hydroxide $[\text{Ca}(\text{OH})_2]$	$8.0 \times 10^{-6}$
Calcium phosphate $[\text{Ca}_3(\text{PO}_4)_2]$	$1.2 \times 10^{-26}$
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Cobalt(II) sulfide ( $\text{CoS}$ )	$4.0 \times 10^{-21}$
Copper(I) bromide ( $\text{CuBr}$ )	$4.2 \times 10^{-8}$
Copper(I) iodide ( $\text{CuI}$ )	$5.1 \times 10^{-12}$
Copper(II) hydroxide $[\text{Cu}(\text{OH})_2]$	$2.2 \times 10^{-20}$
Copper(II) sulfide ( $\text{CuS}$ )	$6.0 \times 10^{-37}$
Iron(II) hydroxide $[\text{Fe}(\text{OH})_2]$	$1.6 \times 10^{-14}$
Iron(III) hydroxide $[\text{Fe}(\text{OH})_3]$	$1.1 \times 10^{-36}$
Iron(II) sulfide ( $\text{FeS}$ )	$6.0 \times 10^{-19}$
Lead(II) carbonate ( $\text{PbCO}_3$ )	$3.3 \times 10^{-14}$
Lead(II) chloride ( $\text{PbCl}_2$ )	$2.4 \times 10^{-4}$

## EXAMPLE 1

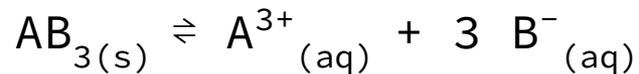
$$K_{\text{SP}} = 1.7 \times 10^{-5} = [\text{Pb}^{2+}][\text{Cl}^{-}]^2$$



What are the concentrations of  $\text{Pb}^{2+}$  and  $\text{Cl}^{-}$  in a saturated solution?

## EXAMPLE 2

The compound  $AB_3$  was dissolved in water. The molarity of ion  $A^{3+}$  is found to be 0.00213M, what is the value for the  $K_{SP}$  of  $AB_3$ ?



$$K_{SP} = [A^{3+}][B^{-}]^3$$

## YOU DO, WE REVIEW

The compound  $XBr_3$  has a  $K_{sp}$  value of  $4.52 \times 10^{-8}$ , when  $XBr_3$  is added to water, what is the concentration of the  $X^{3+}$  and  $Br^-$  ions?