

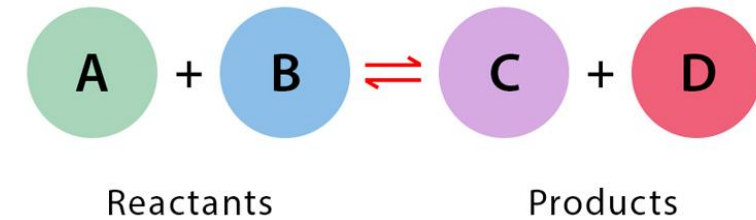
# AP CHEMISTRY -EQUILIBRIUM

Unit 9

# THINGS WE WANT TO KNOW

- What causes reactions to reach equilibrium
- How can we produce more products
- What stress can cause a shift in Equilibrium

## CHEMICAL EQUILIBRIUM - TERMS



**Reversible Reactions:** A chemical reaction in which the products can react to re-form the reactants

**Dynamic Equilibrium:** When the rate of the forward reaction equals the rate of the reverse reaction and the concentration of products and reactants remains unchanged



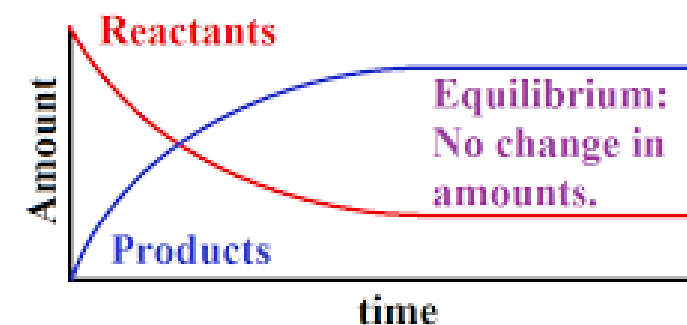
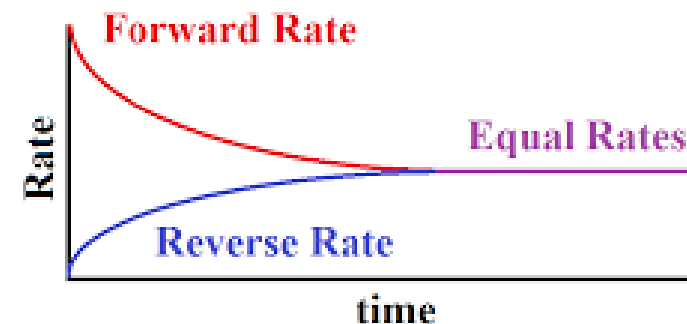
Arrows going both directions (  $\rightleftharpoons$  ) indicates equilibrium in a chemical equation

All reactions in a closed container will reach equilibrium

- \* If there is **a lot of reactant** at equilibrium – **equilibrium lies far to left**
- \* If there is **a lot of product** at equilibrium – **equilibrium lies far to right**

# CHEMICAL EQUILIBRIUM - TERMS

- **Equilibrium** is the state where the **RATE** of the forward and reverse reactions are **equal**.
  - It does **NOT** mean that there is the “same amount” of reactants and products!
- **Dynamic Equilibrium**: Indicates that the reaction is proceeding in the forward and reverse directions. Once equilibrium is established the **rate** of each direction is equal.
  - In the beginning only reactants, thus it pushes forward
  - In the middle product concentration increases and collisions may take place that lead to a reverse reaction.
  - Equilibrium – rates of both are equal.



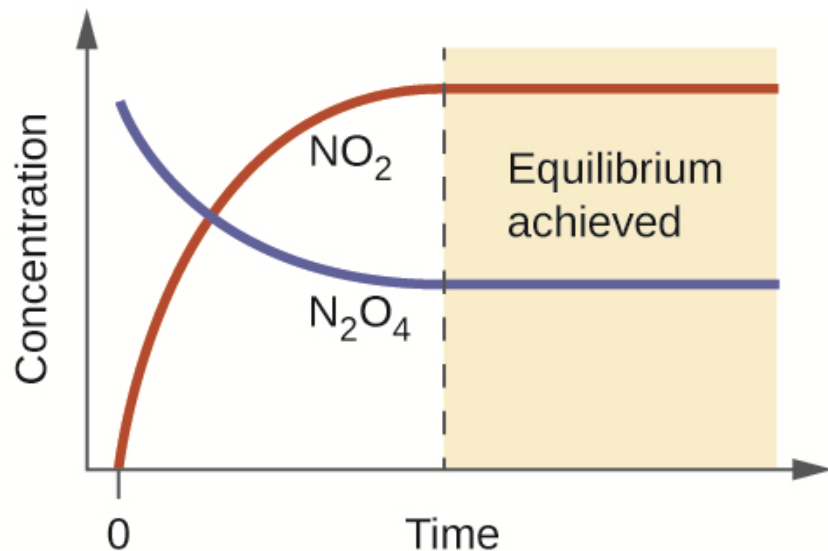
# CHEMICAL EQUILIBRIUM

Consider the equilibrium reaction of:

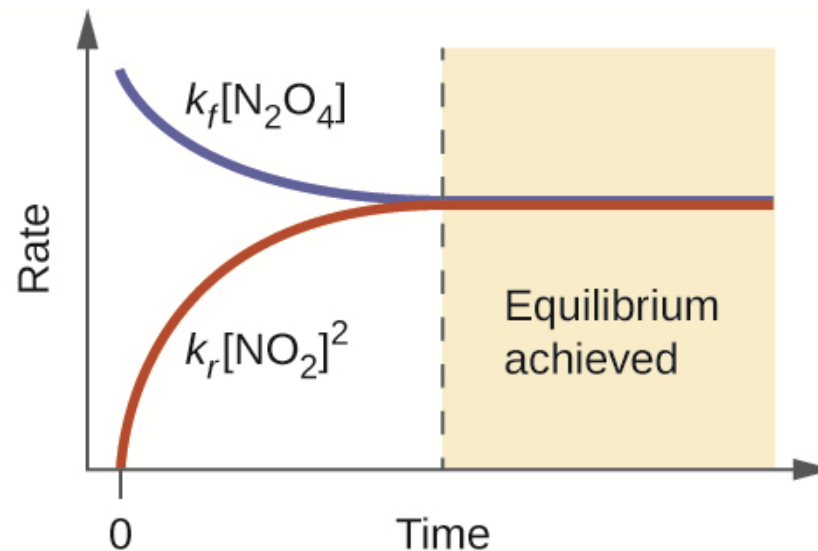


Chemical Equilibrium DOES NOT imply that the concentrations are equal!

Rather only the amounts remain constant



When equilibrium is established (no matter the starting amounts!), the forward and reverse rates are equal.



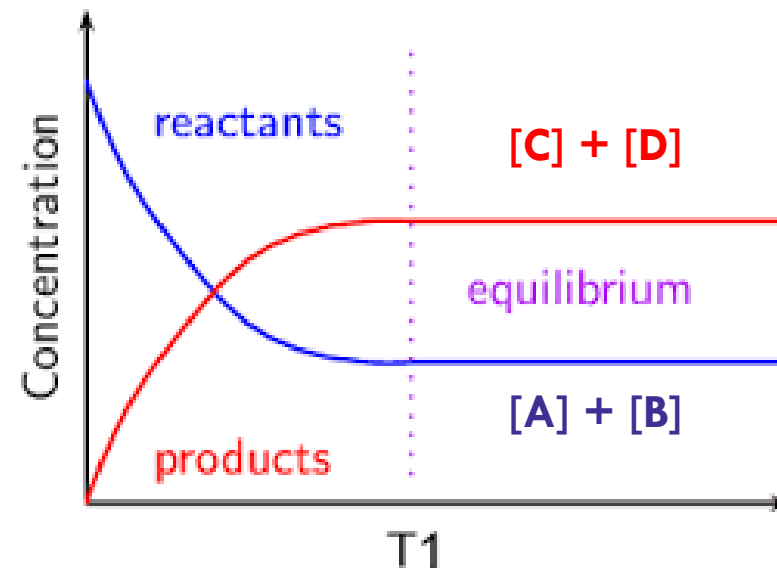
# EQUILIBRIUM CONSTANT - K

- The **equilibrium expression (K)** is a general description of the equilibrium condition known as the **Law of Mass Action**:
  - Equilibrium constant **is temperature dependent**
  - It does NOT change with concentration or pressure (just position of equilibrium changes)
  - The value of the equilibrium constant for any reaction is only determined by experiment.

$K = \frac{\text{concentration of the products (raised to their coefficients)}}{\text{concentration of the reactants (raised to their coefficients)}}$  ( P/R )

**Pure Solids and Liquids – do not appear in expressions**

- Includes water



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

# EQUILIBRIUM CONSTANT - K

■ What does K mean?

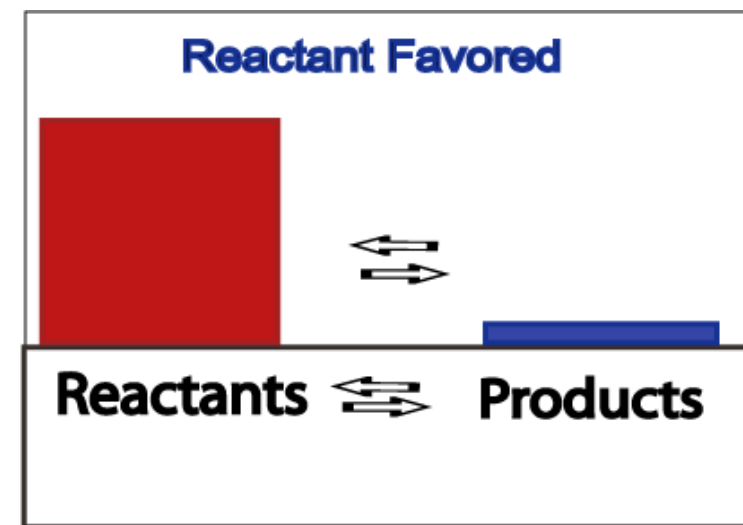
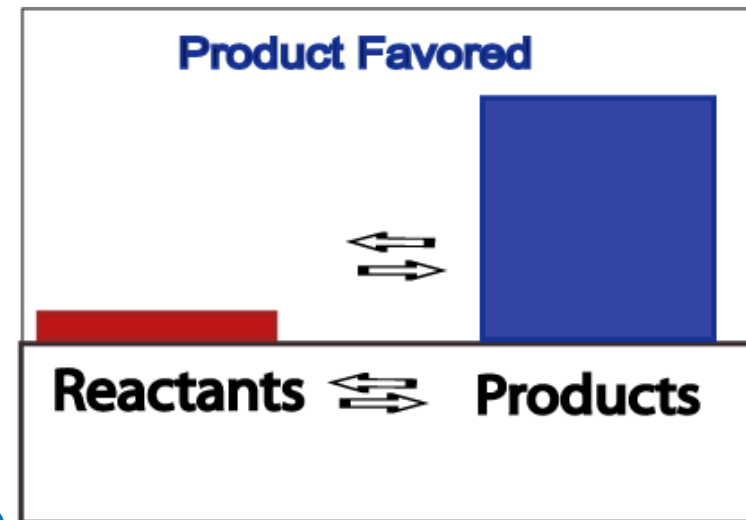
- If  $K > 1$  = means the reaction favors the products at equilibrium.
  - When equilibrium is achieved, most reactant has been converted to

product

- If  $K < 1$  = means that the reaction favors the reactants at equilibrium.

- When equilibrium is achieved, Large amount reactant hasn't been converted to product

- If  $K = 1$  = at equilibrium
- If The reverse is favored the Mass action equation is a reciprocal or  $1/K$
- If the balanced equation is multiplied by a factor of  $n$ , then the equilibrium expression for the new reaction is raised to the  $n$ th power.



REMEMEBER: **P/R**

# EQUILIBRIUM CONSTANT - K

K has multiple subscripts:

- $K_c$  = concentration (aqueous)
- $K_p$  = partial pressure (gas)  $\rightarrow K_p = K(RT)^n$   
n = total moles gas produced – total moles of gas reactants  
R = .0821 L atm/Mol K    T = temp (K)
- $K_a$  = acid
- $K_b$  = base
- $K_{sp}$  = solubility product



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

Products

**Reactants**



# EQUILIBRIUM CONSTANT — K EXAMPLES

- Write the equilibrium expressions for the following:

**The decomposition of solid phosphorus pentachloride to liquid phosphorus trichloride and chlorine gas.**



$K = [\text{Cl}_2]$       **Remember** – solids and liquids do not appear in equilibrium constant

**Deep blue solid copper(II) sulfate pentahydrate is heated to drive off water vapor to form white solid copper(II) sulfate.**



$K = [\text{H}_2\text{O}]^5$

# THE REACTION QUOTIENT – Q

## USED WHEN SYSTEM IS NOT AT EQUILIBRIUM

- Used in finding equilibrium shift from initial conditions – **Forecast of future**
- Q measures the relative amounts of products and reactants present during a reaction at a particular point in time. The reaction quotient aids in figuring out which direction a reaction is likely to proceed (written as  $[x]_o$ )

For the reaction  $aA + bB \rightleftharpoons cC + dD$

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

Q Looks the same as K BUT the concentrations are not at equilibrium

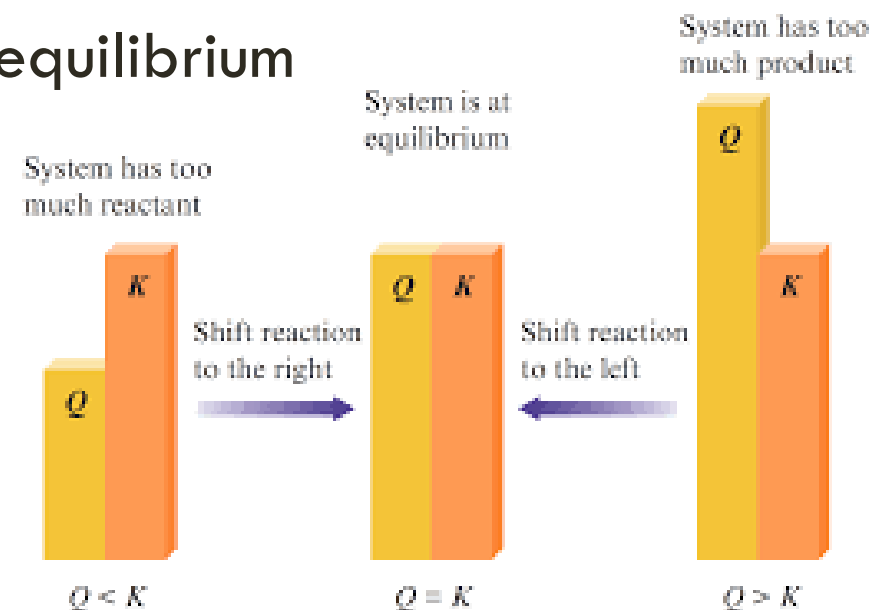
If  $Q < K$  **System has too much Reactant**

Therefore reaction is shifting right

If  $Q = K$  the system is at equilibrium

If  $Q > K$  **System has too much Products**

Therefore reaction is shifting left



# THE REACTION QUOTIENT

## Exercise 7

### Using the Reaction Quotient

For the synthesis of ammonia at 500°C, the equilibrium constant is  $6.0 \times 10^{-2}$ . Predict the direction in which the system will shift to reach equilibrium in each of the following cases:

a.  $[\text{NH}_3]_0 = 1.0 \times 10^{-3} M$ ;  $[\text{N}_2]_0 = 1.0 \times 10^{-5} M$ ;  $[\text{H}_2]_0 = 2.0 \times 10^{-3} M$

Shifts Left

b.  $[\text{NH}_3]_0 = 2.00 \times 10^{-4} M$ ;  $[\text{N}_2]_0 = 1.50 \times 10^{-5} M$ ;  $[\text{H}_2]_0 = 3.54 \times 10^{-1} M$

No Shifts

c.  $[\text{NH}_3]_0 = 1.0 \times 10^{-4} M$ ;  $[\text{N}_2]_0 = 5.0 M$ ;  $[\text{H}_2]_0 = 1.0 \times 10^{-2} M$

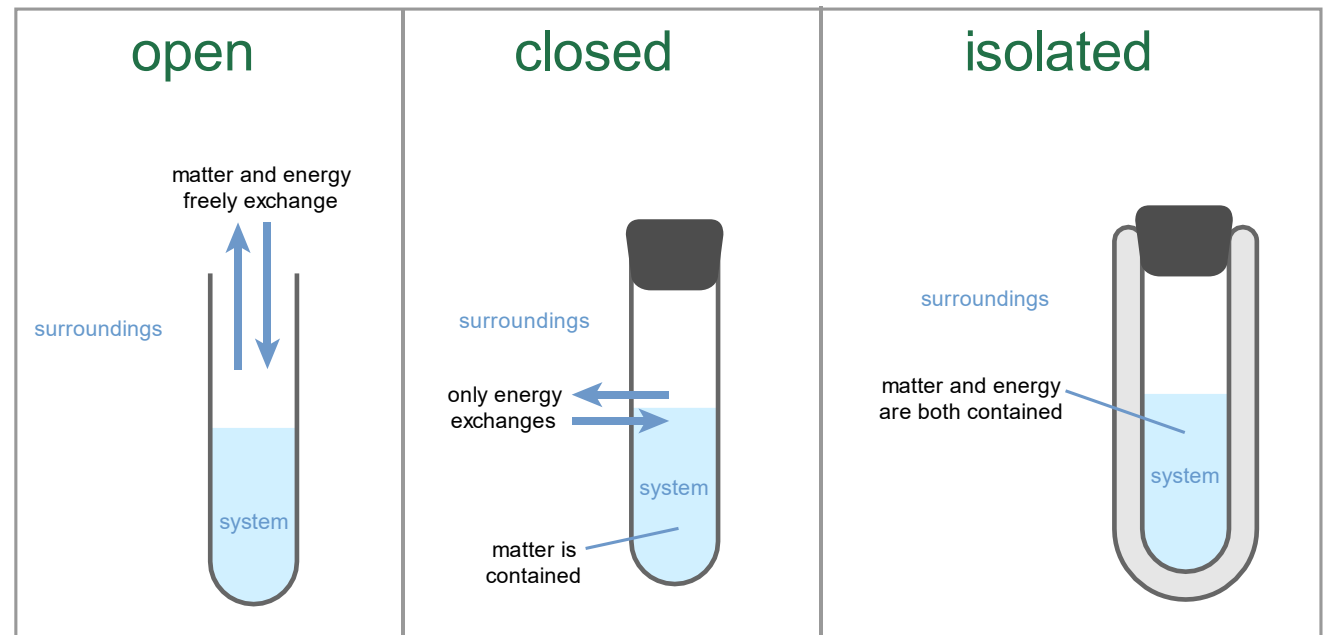
Shifts Right

# SOLVING EQUILIBRIUM PROBLEMS

1. This will require a RICE table!!
2. Set up the expression and set it equal to its value, if given
3. If you are given equilibrium concentrations skip down to E and fill them in. You may be asked to work backward to determine the change in equilibrium.
4. If you are given a K value, then use it to solve for “x” and use “x” to determine the equilibrium concentrations.
5. You may get “lucky” if the problem is a perfect square, if not then you will need to use the quadratic (might want to program it into your calculator?)
  - a. With the quadratic, you get two values, however when you plug one of them in for “x” a negative molarity will result, which cannot happen. Thus that value is removed and the other value is correct.
6. If none of the initial concentrations are 0, then Q must be calculated first to determine the direction of shift BEFORE following the basic steps above.

# LE CHATELIER'S PRINCIPLE

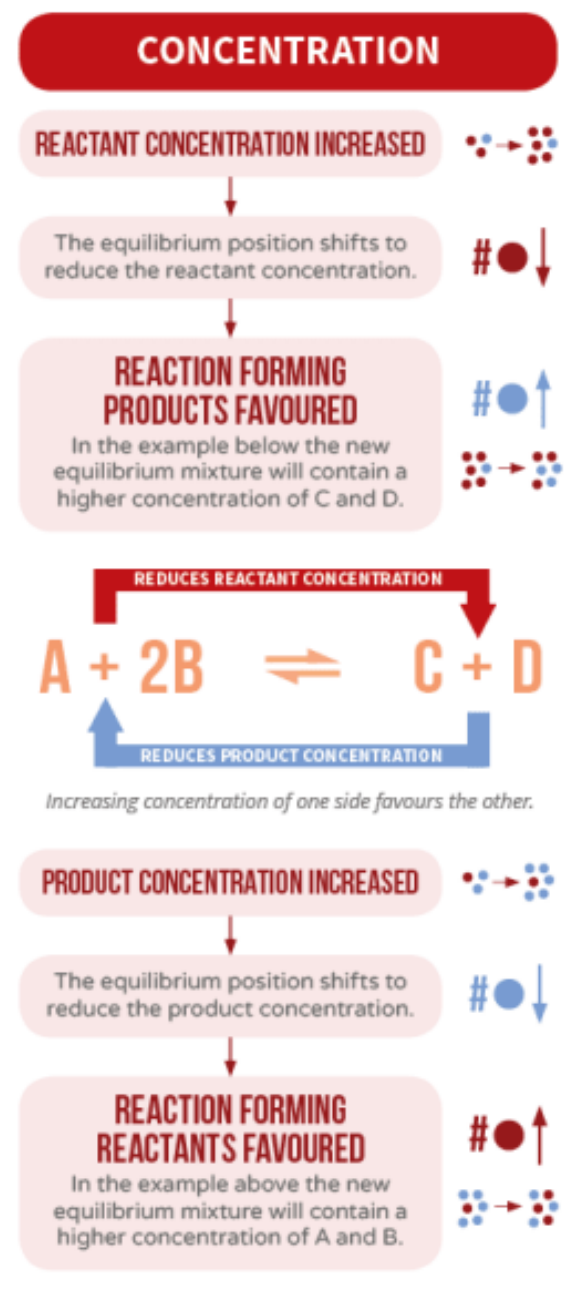
- If a stress is applied to a **system** at equilibrium, the position of the equilibrium will shift in the direction which reduces the stress.
  - In other words the reaction “pushes” toward the non-stressed part of the reaction.
- Stresses applied to a system:
  1. **Concentration** - [ ] Molarity (mol/L)
  2. **Pressure**
  3. **Temperature**



# LE CHATELIER'S PRINCIPLE - CONCENTRATION

## 1. Concentration:

- If a **reactants** are added, shifts right  $\Rightarrow$
- If **products** are added, shifts left  $\Leftarrow$
- Works in reverse if we remove each!



# LE CHATELIER'S PRINCIPLE - PRESSURE

## 2. Pressure:

- If pressure is  $\uparrow$ , the reaction shifts toward the side with the least gas molecules
- If Volume is  $\downarrow$ , the reaction shifts to the side with the least gas molecules (because it is an increase in pressure!)
- If pressure is  $\downarrow$ , the opposite will occur.

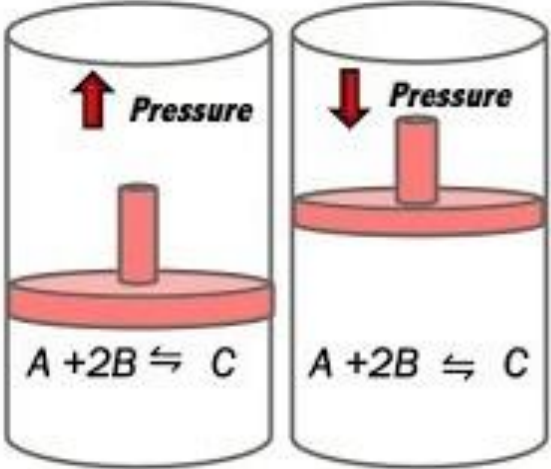
***Effect of the change in Pressure on Equilibrium state:***

$$A(g) + 2B(g) \rightleftharpoons C(g)$$

OR: 1 mole      2 mole      1 mole  
1 volume    2 volume    1 volume

**$\uparrow$  Pressure** equilibrium shift from **more** number of moles or volume towards **less** number of moles or volume

**$\downarrow$  Pressure** equilibrium shift from **lesser** number of moles or volume towards **more** number of moles or volume

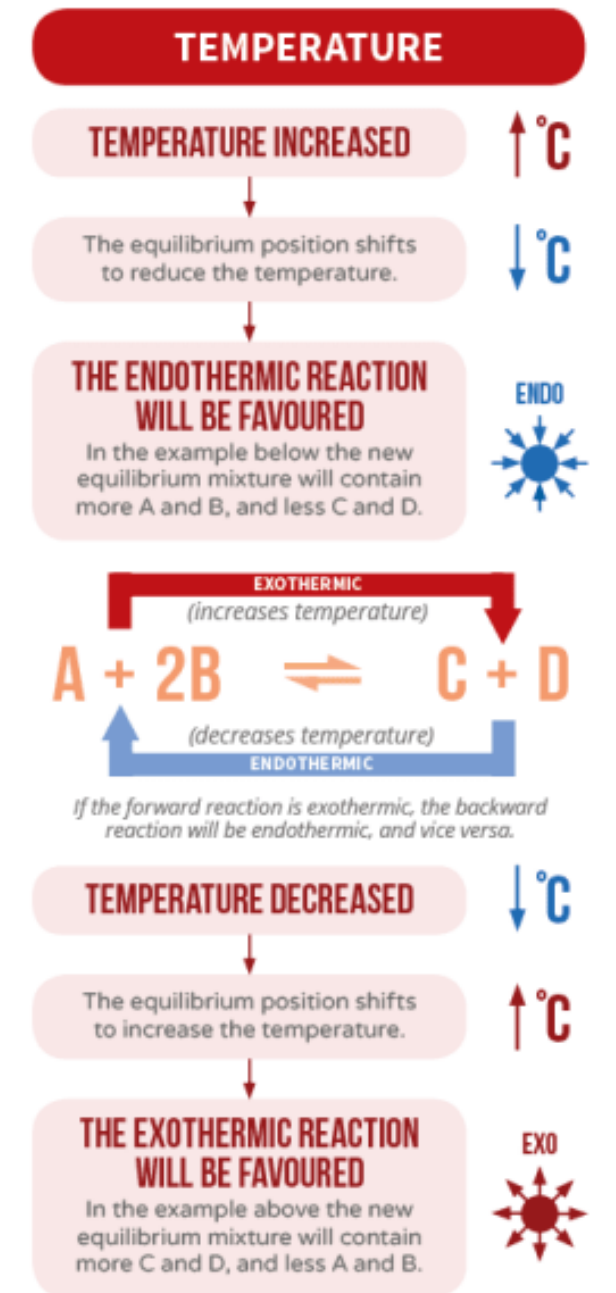


The diagram illustrates the effect of pressure changes on the equilibrium of the reaction  $A + 2B \rightleftharpoons C$ . It shows two cylinders with pistons. In the left cylinder, the piston is being pushed upwards, labeled 'Pressure' with an upward arrow, representing an increase in pressure. In the right cylinder, the piston is being pulled downwards, labeled 'Pressure' with a downward arrow, representing a decrease in pressure. Both cylinders contain the reaction mixture  $A + 2B \rightleftharpoons C$ .

# LE CHATELIER'S PRINCIPLE - TEMPERATURE

## 3. Temperature:

- α. Think of heat energy as a reactant or product.
  - If we add heat to a reaction(+H), it would be in the reactants thus it would shift right (just like if we increased the reactant concentration)
  - If we remove heat from the reaction (-H), it would in the products and it would shift left (just like if we increased product concentration)





# EQUILIBRIUM CONSTANT - K

$K_c$  - equilibrium constant (for non-gas phase reactions, sometimes we just write  $K$ , or we might write  $K_{eq}$ )

$K_p$  - equilibrium constant for gas phase reactions; using pressure

**$K_{sp}$  - equilibrium constant for solubility**

$K_a$  - equilibrium constant for acids (dissociation)

$K_b$  - equilibrium constant for bases (dissociation )

$K_w$  - equilibrium constant for water (dissociation for  $H_2O$  - really specific)

All of those specific  $K$ 's are slightly different snapshots of the same thing. If you get a handle on the general concept of equilibrium, understand the ratio, then you can use your status quo to predict which way you should be going, no matter if you're talking about dissolving something, gases reacting, or a triprotic acid producing  $H^+$  ions.

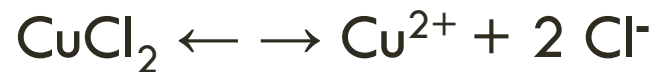
# EQUILIBRIUM CONSTANT — $K_{sp}$



This is equilibrium that deals only with the solubility of salts (ionic solids)

- **Insoluble** is defined as anything that dissolves 3g per 100 g of water.
- If something is “supposed to dissolve” it may not, if enough is not added to the solution.
- Insoluble substances **MAY** dissolve, it is just such a small amount,  $K_{sp}$  tells how much!!
- In other word, soluble and insoluble are not absolute terms.

Example: copper (II) chloride dissolves as follows:



$K_{sp} = [\text{Cu}^{2+}][\text{Cl}^-]^2$  Your solid salt **does not** factor in the equilibrium expression

**If a substance has a low  $K_{sp}$  value = less soluble**

# SOLUBILITY

**The solubility rules are not always correct...**

Slightly soluble salts establish a dynamic equilibrium.

- Initially when a solid is added to water, **no ions are present**
- As dissolution occurs, the concentration of ions increase until equilibrium is reached.

- All group 1 salts, all nitrates, all acetates are all soluble
  - the rest below, in theory, should have Ksp values given to determine the solubility.
- All of the halides (group 17) are soluble, except PMS which will precipitate
- Sulfates generally soluble – except PMS and Castro Bear, which form precipitates
- hydroxides - most form precipitates, except Group 1 and Castro Bear dissolve
- Carbonates – Almost all form precipitates, except group 1 and Ammonium will dissolve

## Solubility Rules

Mnemonic Tricks

Always Soluble  
NAG SAG

**N**itrates ( $\text{NO}_3^-$ )

**A**cetates ( $\text{C}_2\text{H}_3\text{O}_2^-$ )

**G**roup 1 ( $\text{Li}^+$ ,  $\text{Na}^+$ , etc.)

**S**ulfates ( $\text{SO}_4^{2-}$ )

**A**mmonium ( $\text{NH}_4^+$ )

**G**roup 17 ( $\text{F}^-$ ,  $\text{Cl}^-$ , etc.)

Exceptions  
PMS and Castro Bear

**P** ( $\text{Pb}^{2+}$ , lead)

**M** (mercury,  $\text{Hg}^{2+}$ )

**S** (silver,  $\text{Ag}^+$ )

**Ca**  $^{2+}$

**Sr**  $^{2+}$

**Ba**  $^{2+}$

# RELATIVE SOLUBILITIES – EFFECT $K_{sp}$

Make sure you can translate names of compounds into a formula

This affects how your proposed salt will dissolve → which in turn affects your **stoichiometry** → which in turn affects your **equilibrium expression**

**If the salts being compared produce the same number of ions in solution**

$K_{sp}$  can be used to directly compare solubility

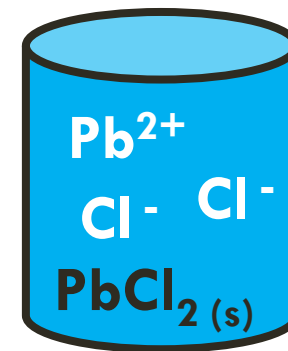


**If the salts being compared produce different numbers of ions**

$K_{sp}$  cannot be directly compared



# DETERMINING $K_{sp}$



If the ion concentration is found in a lab setting, that can be used to determine the  $K_{sp}$  of a compound.

## Example:

**Calculate the  $K_{sp}$ , if the  $Pb^{+2}$  concentration in the equation below is  $1.62 \times 10^{-2} M$**



Since there are 2 moles of  $Cl^-$  then simply multiply the Lead concentration by 2 (think stoich)

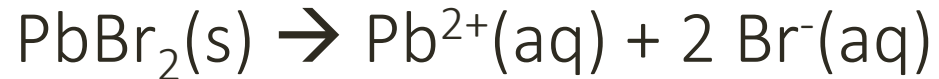
$$\text{Thus } Cl^- = 2(1.62 \times 10^{-2} M) = 3.24 \times 10^{-2} M$$

Then use the  $K_{sp}$  expression...  $K_{sp} = [Pb^{+2}][Cl^-]^2$  (raised by 2 because of the mole ratio)

$$K_{sp} = (1.62 \times 10^{-2})(3.24 \times 10^{-2})^2 = 1.70 \times 10^{-5} M$$

The concentration of  $\text{Br}^-$  in a solution saturated with  $\text{PbBr}_2(\text{s})$  is  $4.28 \times 10^{-2} \text{ M}$ .  
Calculate  $K_{\text{sp}}$  for  $\text{PbBr}_2$

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Br}^-]^2$$



I	O	O
C	+x	+2x
E	x	2x

$$K_{\text{sp}} = (x)(2x)^2 \quad x = 2.14 \times 10^{-2} \text{ M}$$

$$2x = 4.28 \times 10^{-2} \text{ M}$$

$$K_{\text{sp}} = (2.14 \times 10^{-2}) (4.28 \times 10^{-2})^2$$

$$K_{\text{sp}} = 3.92 \times 10^{-5}$$

# QUALITATIVE ANALYSIS

## Example:

You have silver nitrate (soluble), calcium nitrate (soluble), and potassium nitrate are in solution together. You want the silver to drop out first and the calcium to drop out second. You don't want to lose the potassium at all.

Suggest an approach to accomplish your goal?

Answer (one way) –

1. Add any sort of chloride (KCl would work) - the silver will precipitate out as AgCl. You can decant your solution.
2. Now you are left with potassium ions, calcium ions, nitrate ions, and chloride ions. Calcium will form a lot of insoluble salts. Take your pick of reagents, NaOH is easy. Calcium hydroxide is very insoluble.
3. Now you only have potassium ions in solution. You have accomplished your goal.

There are many ways, this is just one approach



# COMMON ION EFFECT

If you add a solid to water (or any solvent) -- Like calcium carbonate ( $\text{CaCO}_3$ ). It is not very soluble on its own, but a little will dissolve.

You'll have (in your beaker), mostly water, solid calcium carbonate, and a little ionic calcium ( $2+$ ) and ionic carbonate ( $2-$ ).

To see the equation:  $\text{CaCO}_3 \leftarrow \rightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$

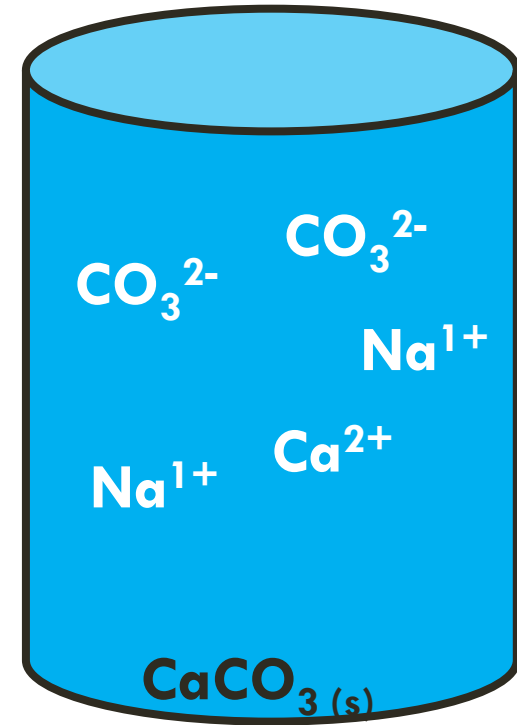
Next let's dissolve some  $\text{Na}_2\text{CO}_3$  in solution (which is soluble).

Now we have plenty  $\text{CO}_3^{2-}$  in solution. How much  $\text{CaCO}_3$  dissolves now? (more or less?)

Answer?

**Even less.** Remember, this is equilibrium. We don't care how extra carbonate got there. It just got there. Calcium carbonate has a small  $K_{sp}$ . One of the two product is already in solution. That makes it harder for calcium carbonate to dissolve.

Don't let the specialized name confuse you. It's an equilibrium effect, plain and simple.





Calculate the solubility of  $\text{Ce}(\text{IO}_3)_3$  in a 0.20 M  $\text{KIO}_3$  solution.

$\text{Ce}(\text{IO}_3)_3$   $K_{\text{sp}}$  is  $3.5 \times 10^{-10}$

$$K_{\text{sp}} = [\text{Ce}^{3+}][\text{IO}_3^-]^3$$



I	O	0.20 M
C	+x	+3x
E	x	0.20M + 3x

$$3.5 \times 10^{-10} = (x)(0.20 \text{ M} + 3x)^3$$

Assume: 3x is negligible since  $K_{\text{sp}}$  is so small compared to 0.20 M

$$3.5 \times 10^{-10} \approx (x)(0.20 \text{ M})^3$$

$$x = 4.38 \times 10^{-8} \text{ M}$$

# REACTION QUOTIENT (Q) AND KSP

Determined the same way as before but new “meanings”

- If  $Q > K_{sp}$  – precipitate forms (supersaturated solution)
- If  $Q < K_{sp}$  – no precipitate forms (unsaturated solution)
- If  $Q = K_{sp}$  – it's at equilibrium (no precipitate) (saturated solution)

This is used to determine if a precipitate will be formed in a solution

## Steps:

1. Calculate the Cation and Anion concentrations after the solutions have mixed.
  - Use  $M_1V_1 = M_2V_2$  for each ion.
2. Place into the Q expression and solve
3. Use the above conditions compared to K to see if a precip is formed.

Will a precipitate form when :

50.0 mL of 0.20 M  $\text{Ca}(\text{NO}_3)_2$  is added to 50.0 mL of 0.30 M  $\text{Na}_3\text{PO}_4$   
( $K_{sp}$  for  $\text{Ca}_3(\text{PO}_4)_2 = 1.3 \times 10^{-32}$ )



$$M_1 V_1 = M_2 V_2$$

$$\text{Ca}^{2+} \rightarrow (0.20 \text{ M})(50.0 \text{ mL}) = x(100.0 \text{ mL})$$

$$\text{Ca}^{2+} \rightarrow x = 0.10 \text{ M}$$

$$M_1 V_1 = M_2 V_2$$

$$\text{PO}_4^{3-} \rightarrow (0.30 \text{ M})(50.0 \text{ mL}) = x(100.0 \text{ mL})$$

$$\text{PO}_4^{3-} \rightarrow x = 0.15 \text{ M}$$

$$Q = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2$$

$$Q = [0.10 \text{ M}]^3 [0.15 \text{ M}]^2$$

$$Q = 2.3 \times 10^{-5}$$

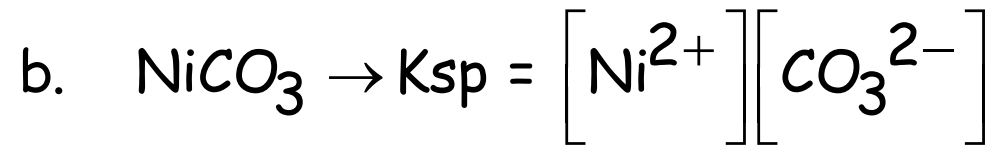
$$Q > K_{sp}$$

ppt will form

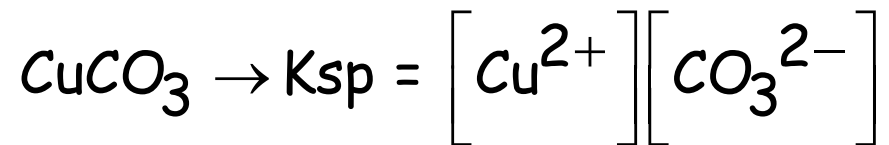
A solution contains 0.25 M  $\text{Ni}(\text{NO}_3)_2$  and 0.25 M  $\text{Cu}(\text{NO}_3)_2$ . A solution of  $\text{Na}_2\text{CO}_3$  is slowly added to this solution.

- Will  $\text{NiCO}_3$  ( $K_{\text{sp}} = 1.4 \times 10^{-3}$ ) or  $\text{CuCO}_3$  ( $K_{\text{sp}} = 2.5 \times 10^{-10}$ ) precipitate first?
- Calculate the concentration of  $\text{CO}_3^{2-}$  necessary to begin the precipitation of each salt.

a.  $\text{CuCO}_3$



$$1.4 \times 10^{-3} = (0.25 \text{ M})x \quad x = 5.6 \times 10^{-3} \text{ M}$$



$$2.5 \times 10^{-10} = (0.25 \text{ M})x \quad x = 1.0 \times 10^{-9} \text{ M}$$



## EXTRA INFORMATION

# LeChatelier's Principle



Raising the temperature...

...favors the endothermic reaction (the reverse reaction) in which the rise in temperature is counteracted by the absorption of heat.

Increasing the pressure...

...favors the forward reaction in which 4 mol of gas molecules is converted to 2 mol.

Decreasing the concentration of  $\text{NH}_3$ ...

...favors the forward reaction in order to replace the  $\text{NH}_3$  that has been removed.

## Chemical Equilibrium

1. Reaction begins.  
• No products yet formed.  
• High rate of collisions between A & B.  
• Rate of forward reaction HIGH.

2 & 3 Products formed  
• Collisions between reactants decrease.  
• Rate of forward reaction DECREASES  
• Reverse reaction begins.

4. Rate of forward reaction EQUAL to rate of reverse reaction.  
• Dynamic equilibrium established.  
• Concentrations constant.

# LE CHATELIER'S PRINCIPLE

<b>STRESS</b>	<b>SHIFT</b>	<b>WHY?</b>
increase concentration of a substance	<i>away</i> from substance	extra concentration needs to be used up
decrease concentration of a substance	<i>towards</i> substance	need to produce more of substance to make up for what was removed
increase pressure of system	towards <i>fewer</i> moles of gas	<u>for gas</u> : pressure increase = volume decrease
decrease pressure of system	towards <i>more</i> moles of gas	<u>for gas</u> : pressure decrease = volume increase
increase temperature of system	<i>away</i> from heat/ energy <i>exothermic</i> reaction is favored	extra heat/ energy must be used up
decrease temperature of system	<i>towards</i> heat/ energy <i>exothermic</i> reaction is favored	more heat/ energy needs to be produced to make up for the loss
add a catalyst	NO SHIFT	The rates of both the forward and reverse reactions are increased by the same amount.



# Le Châtelier's Principle Summary

Variable	Type of Change	Response of System
concentration	increase	shifts to consume some of the added reactant or product
	decrease	shifts to replace some of the removed reactant or product
temperature	increase	shifts to consume some of the added thermal energy
	decrease	shifts to replace some of the removed thermal energy
volume	increase (decrease in pressure)	shifts toward the side with the larger total amount of gaseous entities
	decrease (increase in pressure)	shifts toward the side with the smaller total amount of gaseous entities
<b>Variables That Do Not Affect Chemical Equilibria</b>		
catalysts	—	no effect
inert gases	—	no effect

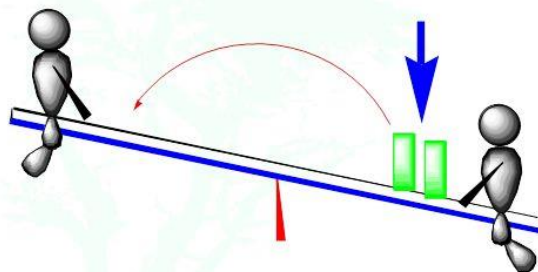


## LeChatelier Principle: A Review

Teeter•Totter  
At Equilibrium

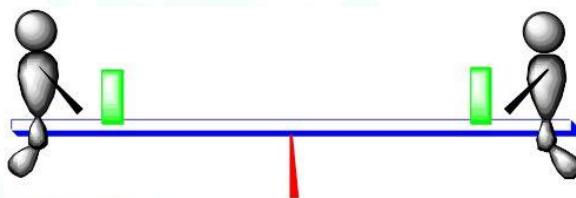


Stress applied



Self Adjust

Re-establish Equilibrium



# HABER PROCESS

**The Haber Process** is used in the manufacturing of ammonia from nitrogen and hydrogen

The process combines nitrogen from the air with hydrogen derived mainly from natural gas (methane) into ammonia.

## Making ammonia The Haber process

