Chemical Equilibrium

Chapter 15

Dueling graduated cylinders

- Follow instructions from my website
- Draw a sketch of your graph on the front board
- What do all the graphs have in common?

Chemical Equilibrium

- Occurs when opposing reactions are proceeding at equal rates
- In other words, the rate of the forward reaction is equal to the rate of the reverse reaction

Reversible Reactions

- Most reactions are reversible

$$A + B \rightarrow C + D \text{ (forward)}$$
$$C + D \rightarrow A + B \text{ (reverse)}$$

- Initially only have A and B - only forward reaction is possible
- As C and D are produced, the reverse reaction begins and its rate increases with increasing C and D
  - What happens to forward rate?

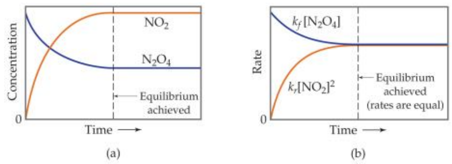
Reversible Reactions

- What are some reversible reactions you see in everyday life?

Equilibrium

- Equilibrium is reached when the rates of the forward and reverse reactions are **equal** and the concentrations of the reactants and products are constant
  - The concentration of the reactants and products **DO NOT** have to be equal but they have to remain constant
- The equilibrium state is dynamic (always changing)

Visual of Equilibrium



Types of Equilibrium

- **<u>Chemical Equilibrium:</u>** balance between reactants and new products
- **<u>Physical Equilibrium:</u>** involves changes in physical processes
  - Vaporization is a physical equilibrium
    - $H_2O_{(l)} \leftrightarrow H_2O_{(g)}$
  - Color change can be a physical equilibrium

2 Main Types of Equilibrium

- **Homogenous Equilibrium**
  - All reactant species are in the same phase
  - K is usually either K_p or K_c depending on phase
- **Heterogeneous Equilibrium**
  - Reactants and products are in different phases
  - **Pure solids or liquids are omitted from the equilibrium expression**

Direction of reversible reactions

- What does it mean when the rate of the forward reaction is greater than the rate of the reverse reaction?
- What does it mean when the rate of the reverse reaction is greater than the rate of the forward reaction?
- What does it mean when the rate of the forward reaction is equal to the rate of the reverse reaction?

Generic Reversible Reaction

aA + bB ↔ cC + dD

(Assume rate laws are based on stoichiometry)

- Person 1: Write rate law for forward reaction
- Person 2: Write rate law for reverse reaction
- Person 3: Compare rates at equilibrium
- Person 4: Substitute rate law for rates
- Person 5: Solve for $\frac{k_f}{k_r}$

Generic Reversible Reaction

aA + bB ↔ cC + dD

(a, b, c and d are coefficients)

- Write the rate law for the forward reaction
- Write the rate law for the reverse reaction
- At equilibrium, what do you know about the rates?

Assume these are elementary reactions

Generic Reversible Reaction

aA + bB ↔ cC + dD

(a, b, c and d are coefficients)

- **Law of Mass Action:** expresses the relationship between the concentrations of reactants and products present at equilibrium
- **K_c and K_p depend only on stoich**, not on reaction mechanism

Generic Reversible Reaction

aA + bB ↔ cC + dD

(a, b, c and d are coefficients)

- **Law of Mass Action:** expresses the relationship between the concentrations of reactants and products present at equilibrium
- **K_c and K_p depend only on stoich**, not on reaction mechanism

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

5 Types of Equilibrium Constants

- K_c For Molarity
- K_p For Pressure
- K_{sp} For Solubility
- K_a For Acids
- K_b For Bases

You can convert between K_c and K_p (but we won't)

Equilibrium Constant

- The equilibrium constant expression depends only on the stoichiometry of the reaction, not its mechanism
  - Ignore (s) and (l)
- The value of the equilibrium constant depends only on the particular reaction and on the temperature
  - As long as the reaction is at equilibrium and a constant temperature, it will always equal K
  - What happens when T changes?

Sample problem – Equilibrium expression

- Write the equilibrium expression, K_c, for the following reaction:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

- Write the equilibrium expression, K_p, for the same reaction:

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} \qquad K_p = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}$$

Practice 1

1. Write the equilibrium-constant expression K_c for $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$
2. Use the following chart to calculate the value of K_c

Experiment	Initial $[N_2O_4]$ (M)	Initial $[NO_2]$ (M)	Equilibrium $[N_2O_4]$ (M)	Equilibrium $[NO_2]$ (M)
1	0.0	0.0200	0.00140	0.0172
2	0.0	0.0300	0.00280	0.0243
3	0.0	0.0400	0.00452	0.0310
4	0.0200	0.0	0.00452	0.0310

Practice 1

1. Write the equilibrium-constant expression K_c for $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$
2. Use the following chart to calculate the value of K_c

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$K_c = 0.211$$

Practice 1

3. Write the equilibrium-constant expression K_p for

$$2N_2O_5(g) \rightleftharpoons O_2(g) + 4NO_2(g)$$

4. Use the following data to calculate the value of K_p

$$P_{N_2O_5} = 2.00\,\text{atm}$$

$$P_{O_2} = 0.296\,\text{atm}$$

$$P_{NO_2} = 1.70\,\text{atm}$$

Practice 1

3. Write the equilibrium-constant expression K_p for

$$2N_2O_5(g) \rightleftharpoons O_2(g) + 4NO_2(g)$$

4. Use the following data to calculate the value of K_p

$$K_p = \frac{(P_{O_2})(P_{NO_2})^4}{(P_{N_2O_5})^2}$$

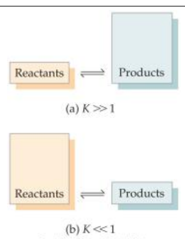
$K_p = 0.618$

Interpreting Equilibrium Constants

- The magnitude of the constant indicates if the reaction favors the products or reactants
- Use an equation for K_c or K_p to examine the relationship between equilibrium and K

If K > 1	Equilibrium lies to right	Product favored
If K < 1	Equilibrium lies to left	Reactants Favored

Interpreting the Magnitude of K_C



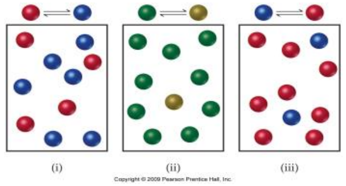
- When K >> 1, there are more products than reactants at equilibrium, and the equilibrium is said to lie to the right
- When K << 1, there are more reactants than products at equilibrium, and the equilibrium is said to lie to the left

Interpreting Equilibrium Constants

- What would happen to a reversible reaction if K>>>>>1?
- What would happen to a reversible reaction if K<<<<<1?

Sample K_c evaluation

Without doing any calculations, rank the three systems in order of increasing equilibrium constant, K_c



Practice 2

1. Write the equilibrium-constant expression K_c. What does the value of K_c indicate for this reaction?

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

$$K_c = 4.56 \times 10^9$$

Predicting the Direction of Reaction

- Q, the reaction quotient for aA + bB ↔ cC + dD

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

- Q at any time during reaction
- K **only** at equilibrium.

Predicting the Direction of Reaction

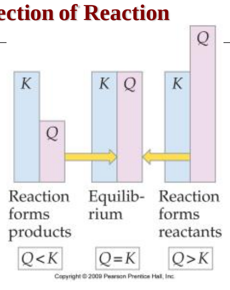
- What does it mean if Q > K?
- What does it mean if Q < K?
- What does it mean if Q = K?

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

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

Predicting the Direction of Reaction

- If **Q < K** , then the reaction will proceed in the forward direction to reach equilibrium
- If **Q > K**, then the reaction will proceed in the reverse direction to reach equilibrium



Sample problem

- For the reaction $N_2O_4(g)$ <==> $2NO_2(g)$, $K_c = 0.2$. At a particular time, the following concentrations are measured: $[N_2O_4] = 2.0$ M, $[NO_2] = 0.2$ M. Is this reaction at equilibrium? If not which direction will the reaction proceed?

Practice 3

1. 2.00 M hydrogen, 1.00 M nitrogen, and 2.00 M ammonia is placed in a flask and allowed to react. How will the mixture react to reach equilibrium? $K_c = 0.105$

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

The Reverse Reaction
(the reverse of a reversible reaction…)

What if instead of **aA + bB ↔ cC + dD**

we had **cC + dD ↔ aA + bB**

- What is the new equilibrium expression, K_r?
- How is this related to the old K_c?

The Reverse Reaction
(the reverse of a reversible reaction…)

cC + dD ↔ aA + bB

- This means that the new equilibrium expression is

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

- Or the value is $K_r = 1/K_{forward}$ (the reciprocal of K)

The Multiple Reaction

What if instead of **aA + bB ↔ cC + dD**

we had **2aA + 2bB ↔ 2cC + 2dD**

- What is the new equilibrium expression, K_2?
- How is this related to the old K_c?

The Multiple Reaction

naA + nbB ↔ ncC + ndD

- Where n is a multiple of the original equation
- This means that the new equilibrium expression is

$$\boxed{K'' = \frac{[C]^{nc}[D]^{nd}}{[A]^{na}[B]^{nb}}}$$

- Or the value is $K_n = (K_{forward})^n$

(multiplier becomes exponent)

Equilibrium and Hess's law

$2\,NOBr(g) \leftrightarrow 2\,NO(g) + Br_2(g)$	$K_{c1} = 0.014$
$Br_2(g) + Cl_2(g) \leftrightarrow 2\,BrCl(g)$	$K_{c2} = 7.2$
$2\,NOBr(g) + Cl_2(g) \leftrightarrow 2\,NO(g) + 2\,BrCl(g)$	$K_{c3} = ?$

Group 1: K_{c1} for 1st eqn

Group 2: K_{c2} for 2nd eqn

Group 3: K_{c3} for total eqn

Not in notes packet…sorry!

Equilibrium and Hess's law

$2\ NOBr(g) \leftrightarrow 2\ NO(g) + Br_2(g)$ $K_{c1} = 0.014$

$Br_2(g) + Cl_2(g) \leftrightarrow 2\ BrCl(g)$ $K_{c2} = 7.2$

$2\ NOBr(g) + Cl_2(g) \leftrightarrow 2\ NO(g) + 2\ BrCl(g)$ $K_{c3} = ?$

$$K_{c1} = \frac{[NO]^2[Br_2]}{[NOBr]^2} \qquad K_{c2} = \frac{[BrCl]^2}{[Br_2][Cl_2]} \qquad K_{c3} = \frac{[NO]^2[BrCl]^2}{[NOBr]^2[Cl_2]}$$

$$K_{c1} * K_{C2} = \frac{[NO]^2[Br_2]}{[NOBr]^2} * \frac{[BrCl]^2}{[NOBr]^2[Br_2]} \qquad \boxed{K_{c1} * K_{c2} = K_{c3}}$$

Not in notes packet…sorry!

Summary

- The equilibrium constant of a reaction …
  - in the reverse direction is the inverse of the equilibrium constant of the reaction in the forward direction
  - that has been multiplied by a number is the equilibrium constant raised to a power equal to that number
  - **that is made up of two or more steps is the product of the equilibrium constants for the individual steps**

Solving Equilibrium Problems

- If only initial values are given (not equilibrium values), then the problem is more difficult than before
- We are going to solve for equilibrium concentrations using an **ICE** table (**ICE** stands for **I**nitial, **C**hange, **E**quilibrium)
- There is a three step process for solving for the equilibrium values

Step 1: Ice, ice, baby

1. Make an ICE Table

- Initial amounts can be M, P, or moles **NOT** grams
- Change in concentration are given a variable, x, and determined using stoichiometric proportions
- Equilibrium is found by subtracting change from reactants but adding for products

Step 2: Stop, collaborate and listen

2. Write the equilibrium constant expression in terms of equilibrium concentrations

- Substitute the given K_C and then solve for x
- For small K, - x or + x *may be* negligible in calculation, simplifying math ("small x approximation")
- Quadratic formula *may be* needed

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Step 3:

- Using the value of "x" found in step 2, calculate the equilibrium concentrations of all species

Sample problem – ICE

$M^{2+} + 2L \leftrightarrows ML_2^{+}$

	$[M^{2+}]$	[L]	$[ML_4^{+}]$
I	0.20 *M*	0.40 *M*	0 *M*
C	____	____	____
E	____	____	____

Sample problem – ICE and K

- A mixture of 9.22 moles of **A**, 10.11 moles **B**, and 27.83 moles **C** is placed in a 1L container. The reaction is allowed to reach equilibrium. At equilibrium the number of moles of B is 18.32. Calculate the equilibrium constant for the reaction:

$$\mathbf{A}\ (g) + 2\ \mathbf{B}\ (g) \rightleftharpoons 3\ \mathbf{C}\ (g$$

Practice 4

1. When 4.00 mol of A and 4.00 mole of B are placed in a container and allowed to come to equilibrium, the mixture is found to contain 0.80 mol of D. What are the amounts of A, B, and C at equilibrium?

$$A(g) + 3B\ (g) \rightleftharpoons C\ (g) + D(g)$$

Sample problem

- What are the equilibrium concentrations of A and A_2 if the initial $[A_2]$ is 0.60 M? (Small x approximation)

$$A_2\ (g) \rightleftharpoons 2A(g) \qquad K = 4.2 \times 10^{-8}$$

Sample problem

- The reaction of bromine gas with chlorine gas, shown here, has a Kc value of 7.20 at 200ºC. If a closed vessel was charged with the two reactants, each at an initial concentration of 0.200 M, but with no initial concentration of BrCl, what would be the equilibrium concentration of BrCl(g)? (Use quadratic)

$$Br_2(g) + Cl_2(g) \leftrightarrows 2BrCl(g) \qquad K = 7.20$$

Practice 5

1. Given the initial concentrations shown below, find the equilibrium concentrations for A, B, and C. (Use small x approximation)

$$A(g) + B(g) \leftrightarrows 2C(g) \qquad K = 9.0 \times 10^{-8}$$

0.500M 0.500M 0.000M

Practice 5

2. A flask contains 1.000 M hydrogen and 2.000 M iodine. Kc = 50.5. What are the equilibrium concentrations of hydrogen, iodine, and hydrogen iodide in moles/L? (Use quadratic)

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

Practice 5

3. If 0.820 mole of NO and 0.223 mole each of N_2 and O_2 are mixed in a 1.00 L container at 1100 C, what are the concentrations of NO, N_2, and O_2 at equilibrium?

$$2\ NO\ (g) \rightleftharpoons N_2\ (g) + O_2\ (g)$$

$K_c = 2.60 \times 10^{-3}$

Practice 5 #4

FOLLOW-UP PROBLEM 17.9 In a study of halogen bond strengths, 0.50 mol of I_2 was heated in a 2.5-L vessel, and the following reaction occurred: $I_2(g) \rightleftharpoons 2I(g)$.
(a) Calculate $[I_2]$ and [I] at equilibrium at 600 K; $K_c = 2.94\times10^{-10}$.
(b) Calculate $[I_2]$ and [I] at equilibrium at 2000 K; $K_c = 0.209$.

Le Châtelier's Principle:

Factors that Affect Equilibrium

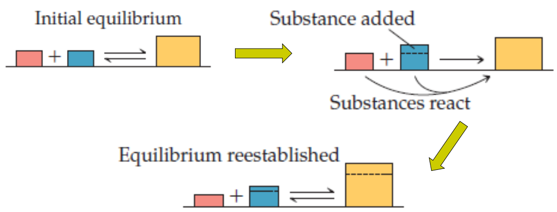
Chemical Equilibrium

- Chemical equilibrium is a balance between forward and reverse reactions
- This balance can be shifted by changing reaction variables such as
  - Concentrations
  - Pressure
  - Volume
  - Temperature

Le Châtelier's Principle

- A general rule for predicting how a rxn at equilibrium will respond (direction of shift) when a variable is changed
- **Le Châtelier's Principle**
  - If stress is applied to a system at equilibrium, the system will shift in a direction that tends to reduce that change

Le Châtelier's Principle



Effect of Concentration Change

- In general, if a component is added to a reaction system at equilibrium, the equilibrium position will shift in the direction that lowers the concentration of that component.
- If a component is removed from a reaction at equilibrium, the equilibrium position will shift in the direction that increases the concentration of that component

Effect of Concentration Change

$$\underset{\text{Red}}{FeSCN^{2+}_{(aq)}} \leftrightarrows \underset{\text{Pale Yellow}}{Fe^{3+}_{(aq)}} + \underset{\text{Colorless}}{SCN^{-}_{(aq)}}$$

- What happens if some NaSCN is added?
- What happens if we add $C_2O_4^{2-}$ which can bind to the Fe^{3+}?
- Did k_f or k_r change? Did Q? Did K_c?

Effect of a Pressure Change

- Typically does not affect solids, liquids or aqueous systems
- Gases are greatly affected by changes in pressure
- Three ways to change pressure:
  1. Add or remove a gaseous reactant or product
  2. Add an inert gas (one not involved in the reaction)
  3. Change the volume of the container

Effect of a Pressure Change

1. Adding or removing a gas will change the concentration so the result is the same as changes in concentration
2. Adding an inert gas increases the pressure **BUT** has no effect on concentrations or partial pressures, **therefore the equilibrium does NOT change**

Effect of a Pressure Change

3. When the volume of the container holding a gaseous system is reduced, the system responds by reducing its own volume. This is done by decreasing the total number of gaseous molecules

- Decrease volume → shift to side with less moles of gas
- Increase volume → shift to side with more moles of gas

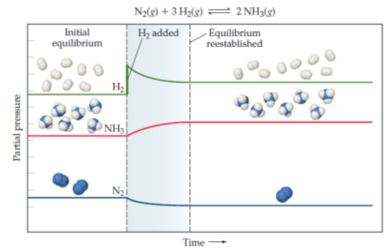
- Did k_f or k_r change? Did Q? Did K_c?

Sample problems

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

- The system is at equilibrium. What happens to the concentrations of nitrogen and ammonia after additional hydrogen is added?

Sample problems



Sample problems

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

- The system is at equilibrium. What happens to the concentrations of nitrogen and hydrogen after ammonia is removed from the system?

Sample problems

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

- The system is at equilibrium. What happens to the position of equilibrium when the partial pressure of nitrogen is increased?
- What happens to the system when the volume of the container is decreased?
- What happens when the pressure inside the container is increased by the addition of helium gas?

Le Châtlier's Principle

IMPORTANT NOTE

- Changes in concentration and pressure will change the **position** of equilibrium but will **NOT** change the **equilibrium constant (K)**
- For instance, the position may be shifted to the left but will maintain the value of the original equilibrium constant

Temperature

- Temperature is different: changing temperature will also change the value of K
- Why…
  - Since equilibrium and kinetics are inter-related, changing the temperature will change the rates of the forward and reverse reactions, therefore changing the equilibrium position

Temperature

- The effect of temperature depends on if the reaction is endothermic or exothermic
- If the reaction is **endothermic**….
  - An increase in temperature will cause the equilibrium to shift to the right and the value of K to increase

$$\mathbf{556\ kJ} + CaCO_{3(s)} \leftrightarrows CaO_{(s)} + CO_{2(g)}$$

- If the reaction is **exothermic**…
  - An increase in temperature will cause the equilibrium to shift to the left and the value of K to decrease

$$N_{2(g)} + 3H_{2(g)} \leftrightarrows 2NH_{3(g)} + \mathbf{92kJ}$$

Sample problem

$$2\ POCl_2(g) \rightleftharpoons 2\ PCl_3(g) + O_2(g) \qquad \Delta H = 508.3\ kJ$$

- Rewrite the equation with heat as a reactant or product.
- If heat is added to the equilibrium system, in which direction would the equilibrium shift?
- How would equilibrium shift if the system is cooled?

Temperature

- In summary:
  - to describe the effect of a temperature change on a system at equilibrium, treat energy as a reactant (in an endothermic reaction) or a product (in an exothermic reaction), and predict the direction of the shift in the same way as when an actual reactant or product is added or removed

Catalysts

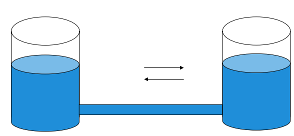
- Adding catalysts will speed up reactions so the equilibrium will be reached FASTER, but it will <u>not</u> change the value or position of the equilibrium

Practice 6

$$H_2(g) + Br_2(g) \leftrightarrows 2HBr(g) \qquad \Delta H° = -103.7kJ$$

Change	$[H_2]$	$[Br_2]$	[HBr]	K value
1. Some H_2 added				
2. Some HBr added				
3. Some H_2 removed				
4. Some HBr removed				
5. The temperature is increased				
6. The temperature is decreased				
7. Pressure is increased and the container volume decreased				

Analogy of Le Chatelier's Principle



Same side does opposite, opposite side does the same

Solubility Equilibria

Will it all dissolve, and if not, how much?

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Solubility

- Dissolving/precipitating is an equilibrium process
- If there is not much solid it will all dissolve
- As more solid is added the solution will become saturated
- Solid $\rightleftharpoons$ dissolved
- The solid will precipitate as fast as it dissolves at its equilibrium

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General equation for solubility product

$$M_aNm_{b\,(s)} \rightleftharpoons a\,M^+_{(aq)} + b\,Nm^-_{(aq)}$$

$$K_{sp} = [M^+]^a\,[Nm^-]^b$$

- M^+ stands for the cation (usually a metal)
- Nm^- stands for the anion (a nonmetal)

- Called the solubility product for each compound

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Sample problem

- Write the solubility-product expression (K_{sp}) for barium sulfate, which is only slightly soluble in water.

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Solubility vs Solubility Product

- Solubility is not the same as solubility product
- Solubility product is an equilibrium constant
  - doesn't change except with temperature
- Solubility is an equilibrium position for how much can dissolve
  - Often g/L or mol/L
- Addition of a common ion can shift this

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Sample problems: K_{sp} and solubility

- Write the solubility-product expression for K_{sp} for calcium fluoride. Calculate the solubility of calcium fluoride in mol/L and g/L. $K_{sp} = 3.9 \times 10^{-11}$
- Silver chromate is added to water. At equilibrium some solid is left undissolved. 0.022 g/L of silver chromate is dissolved. Calculate the K_{sp} and write the solubility-product expression.

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Practice 7

1. The K_{sp} for LaF_3 is $2x10^{-19}$. Write the expression for K_{sp}.What is the solubility of LaF_3 in mol/L and g/L?

2. Calculate the K_{sp} for magnesium hydroxide. Write the expression for K_{sp}. The concentration of hydroxide in solution is $1.5x10^{-4}$ M.

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Relative Solubilities

- K_{sp} will only allow us to compare the solubility of solids that separate into the **same number of ions**
- Large K_{sp} = more soluble

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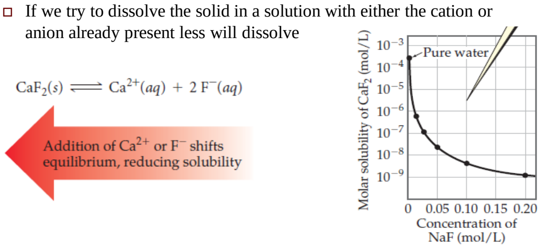
Common Ion Effect

- If we try to dissolve the solid in a solution with either the cation or anion already present less will dissolve



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Common Ion Effect

- If we try to dissolve the solid in a solution with either the cation or anion already present less will dissolve
- Examples:
  - $Mn(OH)_2$ has a Ksp of $1.6x10^{-13}$. The molar solubility of $Mn(OH)_2$ in water is $3.4x10^{-5}$ M. The molar solubility of $Mn(OH)_2$ in a solution that contains 0.020 M NaOH is $4.0x10^{-10}$ M.

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Sample Problem

- Calculate the **molar** solubility of calcium fluoride in a solution that is 0.0010 M in calcium nitrate.

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Practice 8

1. Calculate the solubility of $SrSO_4$, (K_{sp} of 3.2 x 10^{-7}) in M and g/L in a solution of 0.010 M Na_2SO_4.

2. Calculate the solubility of $SrSO_4$, (K_{sp} of 3.2 x 10^{-7}) in M and g/L in a solution of 0.010 M $SrNO_3$.

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pH and Solubility

- pH affects solubility of basic salts.
- If H^+ is present when $Mg(OH)_2$ is dissolved, the H_+ reacts with OH^-, decreasing the concentration of OH- in the solution.
  $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\ OH^-(aq)$
- Solubility of $Mg(OH)_2$ increases from $1.7\text{x}10^{-4}$ M in distilled water to 0.18 M in a solution with H^+ (pH = 5.0)

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Precipitation

- Ion Product:
  $Q = [M^+]^a[Nm^-]^b$
  - If $Q = K_{sp}$ equilibrium
  - If $Q > K_{sp}$ a precipitate forms
  - If $Q < K_{sp}$ No precipitate

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Sample Problem

A solution of 750.0 mL of 4.00 x 10^{-3} M $Ce(NO_3)_3$ is added to 300.0 mL of 2.00 x 10^{-2}M KIO_3. Will $Ce(IO_3)_3$ (K_{sp} = 1.9 x 10^{-10}M) precipitate and if so, what is the concentration of the ions?

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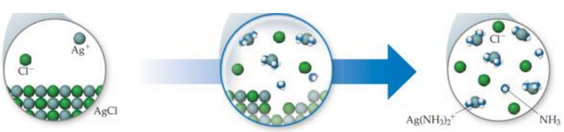
Complex Ion Equilibria

- A charged ion surrounded by ligands
  - Ligands are Lewis bases using their lone pair to stabilize the charged metal ions
- Common ligands are NH_3, H_2O, Cl^-,CN^-
- $[Cu(NH_3)_4]^{+2}$, $[Ag(CN)_2]^-$, $[Cu(H_2O)_4]^{2+}$

$$AgCl(s) + 2\ NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq)$$



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Ligand equilibrium

- Usually the ligand is in large excess
- And the individual K's will be large so we can treat them as if they go to equilibrium
- The complex ion will be the biggest ion in solution

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- Example:

  Calculate the concentrations of Ag^+, $Ag(S_2O_3)^-$, and $Ag(S_2O_3)^{-3}$ in a solution made by mixing 150.0 mL of $AgNO_3$ with 200.0 mL of 5.00 M $Na_2S_2O_3$

  $$Ag^+ + S_2O_3^{-2} \rightleftharpoons Ag(S_2O_3)^-$$
  $K_1=7.4 \times 10^8$

  $$Ag(S_2O_3)^- + S_2O_3^{-2} \rightleftharpoons Ag(S_2O_3)^{-3}$$
  $K_2=3.9 \times 10^4$

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Selective Precipitations

- Used to separate mixtures of metal ions in solutions
- Add anions that will only precipitate certain metals at a time
- Used to purify mixtures
- Often use H_2S because in acidic solution Hg^{+2}, Cd^{+2}, Bi^{+3}, Cu^{+2}, Sn^{+4} will precipitate.

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Selective Precipitation

- In basic solutions, adding OH^- solution S^{-2} will increase so more soluble sulfides will precipitate
- Co^{+2}, Zn^{+2}, Mn^{+2}, Ni^{+2}, Fe^{+2}, $Cr(OH)_3$, $Al(OH)_3$

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Selective Precipitation

- Follow the steps first with insoluble chlorides (Ag, Pb, Ba)
- Then sulfides in acid
- Then sulfides in base
- Then insoluble carbonate (Ca, Ba, Mg)
- Alkali metals and NH_4^+ remain in solution