**EQUILIBRIUM**

Dynamic state of balance between the rates of the forward and reverse reactions

- Not a static state, but **DYNAMIC**… things are changing but they are in a balanced state!
- Opposing processes (forward and reverse) are occurring at the **SAME RATE**
- Concentrations of the reactants and products do not change

**IDEA THAT ALL REACTIONS GO TO COMPLETION IS FALSE!!**

---

**Equilibrium**

**STATIC EQUILIBRIUM**
- No reaction taking place
- All product molecules remain product and all unused reactant stay unreacted

**DYNAMIC EQUILIBRIUM**
- Reaction continues to occur
- Forward and reverse reactions take place at same rate

---

**Equilibrium**

- Whether a reaction lies far to the right (**FAVORS PRODUCTS**) or to the left (**FAVORS REACTANTS**) depends on:
  1) Initial concentrations… more collisions = faster
  2) Energies of the reactants and products… nature goes to minimum energy
  3) Degree of organization of reactants and products… nature goes to maximum disorder
**Equilibrium Constant**

- **LAW OF MASS ACTION**: relationship between the [ ] of the reactants and the products in a reaction at equilibrium remains **CONSTANT**

\[ aA + bB \rightleftharpoons cC + dD \]

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

**Equilibrium Constant Expression**

- \(K_c\) = molar concentrations
- \(K_a\) = acid dissociation (weak acids)
- \(K_p\) = partial pressures
- \(K_b\) = base dissociation (weak bases)
- \(K_{sp}\) = solubility product
- \(K_w\) = ionization of water

**General Rules:**

1) [ ] are molar concentrations or partial pressures
2) Products are in numerator (TOP) and reactants in the denominator (BOTTOM)
3) Coefficients in the balanced equations become exponents in the expression

**Example:**

Write the equilibrium constant expression for the following reaction.

\[ 2 \text{H}_2\text{S}(g) + 3 \text{O}_2(g) \rightleftharpoons 2 \text{H}_2\text{O}(g) + 2 \text{SO}_2(g) \]

\[ K_{eq} = K_c = \frac{[\text{H}_2\text{O}]^2[\text{SO}_2]^2}{[\text{H}_2\text{S}]^2[\text{O}_2]^3} \]

Take note of how this is different from the **RATE** expression!

**Example:**

Write the equilibrium constant expression for the following reaction in terms of pressure.

\[ \text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g) \]

No denominator because the reactant is a **SOLID**!
**Equilibrium Constant**

- **EXAMPLES:**
  1. Write the equilibrium constant expression for the following reaction.
     
     \[4 \text{ NH}_3(g) + 7 \text{ O}_2(g) \rightleftharpoons 4 \text{ NO}_2(g) + 6 \text{ H}_2\text{O}(g)\]

  Write the equilibrium constant expression for the following reaction.
  
  \[\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)\]

**Equilibrium Constant**

- \(K_{eq}\) can be determined for **EITHER** direction of the reaction... still favors the **SAME** substances regardless of whether you use the forward or reverse.

- [ ] of reactants and products at equilibrium vary depending on the initial [ ], but \(K_{eq}\) is always the **SAME** as long as the TEMPERATURE is the same!!

- \(K_{eq}\) does NOT depend on the reaction mechanism, only stoichiometry and temperature.

**Ideal Gas Law and \(K_{eq}\)**

- \(K_{eq}\) does not always equal \(K_p\)

\[
K_p = K(RT)^\Delta n
\]

- \(R = 0.082 \text{ L \cdot atm / mol \cdot K}\)
- \(T = \text{temperature in Kelvin}\)
- \(n = \text{mole gas products - mole gas reactants}\)

- Only if \(n = 0\) will \(K_{eq} = K_p\)

**Ideal Gas Law and \(K_{eq}\)**

- **EXAMPLE:**
  
  For the Haber process given below, \(K_c = 9.60\) at 300.0°C. Calculate \(K_p\) for this reaction at this temperature.
  
  \[\text{N}_2(g) + 3 \text{ H}_2(g) \rightleftharpoons 2 \text{ NH}_3(g)\]

  \(\Delta n = 2 - 4 = -2\)

  \[
  K_p = K(RT)^\Delta n = (9.60)(0.082 \times 573)^{-2} = 4.35 \times 10^{-3}
  \]

**Significance of \(K_{eq}\)**

- **Magnitude of \(K_{eq}\)** gives info about the relative [ ] of reactants and products in equilibrium:

  \(K > 1\) = **LARGE** \(K\) = Greater [ ] of products... reaction favors the **PRODUCTS** (equilibrium lies to the **RIGHT**)

  \(K < 1\) = **SMALL** \(K\) = Greater [ ] of reactants... reaction favors the **REACTANTS** (equilibrium lies to the **LEFT**)

Remember how you thought most reactions always went to completion? They just have **VERY LARGE \(K\) values**!
**Equilibrium and Changing Direction**

- Equilibrium can be approached from either side of the reaction.
- \( K_{eq} \) for the reaction written in one direction is the \textbf{RECIPROCAL} of \( K_{eq} \) in the reverse direction.

\[ K_{eq} = \frac{\left[\text{products}\right]^n}{\left[\text{reactants}\right]^m} \]

**Example:**

\[ N_2(g) + O_2(g) \rightleftharpoons 2 \text{NO(g)} \quad K_c = 1.0 \times 10^{-30} \text{ at } 25^\circ C \]

\[ K_c = \frac{[\text{NO}]^2}{[N_2][O_2]} \]

\[ \text{REVERSE?} \]

\[ \frac{[\text{N}_2][O_2]}{[\text{NO}]^2} = \frac{1}{1.0 \times 10^{-30}} = 1.0 \times 10^{30} \]

Still favors the \( \text{N}_2 \) and \( \text{O}_2 \) side!

**Equilibrium and Changing Coefficients**

- \( K_{eq} \) changes with temperature, it also changes when stoichiometric coefficients are multiplied by some factor.
- \( K_{eq} \) is raised to the \textbf{POWER} of the multiplication factor \( (K^n) \).

**Example:**

\[ N_2(g) + O_2(g) \rightleftharpoons 2 \text{NO(g)} \quad K_c = 1.0 \times 10^{-30} \text{ at } 25^\circ C \]

What is the \( K_c \) for 3 \( \text{N}_2(g) \) + 3 \( \text{O}_2(g) \) = 6 \( \text{NO(g)} \)?

\[ K^3 = (1.0 \times 10^{-30})^3 = 1.0 \times 10^{-90} \]

**Equilibrium and Multistep Reactions**

- Multistep reactions have many \( K_{eq} \) values… just as you combine reactions to give overall equation you must combine \( K_{eq} \) values too.
- \( K_{eq} \) for the reaction is obtained by \textbf{MULTIPLYING} all of the \( K_{eq} \) values together.

**Example:**

\[ 2 \text{NO(g)} \rightleftharpoons \text{N}_2(g) + \text{O}_2(g) \quad K_{11} = 1.0 \times 10^{30} \]

\[ \text{N}_2(g) + \text{Br}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NOBr(g)} \quad K_{12} = 2.0 \times 10^{-27} \]

\[ 2 \text{NO(g)} + \text{Br}_2(g) \rightleftharpoons 2 \text{NOBr(g)} \quad K = ??? \]

\[ (1.0 \times 10^{30}) (2.0 \times 10^{-27}) = 2.0 \times 10^{3} \]

**Summary**

1) \( K_{eq} \) of the reverse reaction is the \textbf{RECIPROCAL} of the \( K_{eq} \) in the forward direction.

2) \( K_{eq} \) of a reaction that has been multiplied by a number must the raised to the \textbf{POWER} equal to that number.

3) \( K_{eq} \) of a net reaction of 2 or more steps is the \textbf{PRODUCT} of the individual \( K_{eq} \) values.

**Calculating \( K_{eq} \)**

- If \textbf{ALL } [ ] or pressures at \textbf{EQUILIBRIUM} are known, just plug the values into the \( K_{eq} \) expression and solve.

**Example:**

The reaction below takes place in a sealed flask. Determine the value of the \textit{equilibrium constant} with the following concentrations at equilibrium: \([\text{CH}_4]\) = 0.0032 \text{ M}, \([\text{C}_2\text{H}_2]\) = 0.025 \text{ M}, and \([\text{H}_2]\) = 0.040 \text{ M}.

\[ 2 \text{CH}_4(g) \rightleftharpoons \text{C}_2\text{H}_2(g) + 3 \text{H}_2(g) \]

\[ K_{eq} = \frac{[\text{C}_2\text{H}_2][\text{H}_2]^3}{[\text{CH}_4]^2} = \frac{[0.025][0.04]^3}{[0.0032]^2} = 0.16 \]

**Practice**

- If ALL [ ] or pressures at \textit{EQUILIBRIUM} are known, just plug the values into the \( K_{eq} \) expression and solve.

**Example:**

\[ \text{HF(aq)} \rightleftharpoons \text{H}^+(aq) + \text{F}^-(aq) \quad K_c = 6.8 \times 10^{-4} \]

\[ \text{H}_2\text{C}_2\text{O}_4(aq) \rightleftharpoons 2 \text{H}^+(aq) + \text{C}_2\text{O}_4^{2-}(aq) \quad K_c = 3.8 \times 10^{-6} \]

Find \( K_c \) for the reaction:

\[ 2 \text{HF(aq)} + \text{C}_2\text{O}_4^{2-}(aq) \rightleftharpoons 2 \text{F}^-(aq) + \text{H}_2\text{C}_2\text{O}_4(aq) \]

What do you need to do to the \textbf{reactions} to make them add up to that equation? Then, what do you do to the \( K_c \) for those reactions?
**Reaction Quotient, Q**

* Tells you about the system when it is NOT at equilibrium

- Plug in [ ] or pressure values at ANY point during a reaction into the $K_{eq}$ expression to get Q
- Useful for predicting what will happen to the system at ANY time... TELLS YOU WHICH WAY THE RXN WILL GO TO ESTABLISH EQUILIBRIUM!!

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

**Calculating $K_{eq}$**

- What if the [ ] of the species at EQUILIBRIUM are not all known?
- If we know at least one [ ] and the balanced equation, we can use stoich and mole ratios to determine the equilibrium [ ] by making an ICE table...

**STEPS:**

1) Write down all givens and balanced equation
2) Determine the changes in [ ] using mole ratio
3) Set up the ICE table (Initial, Change, Equilibrium)... SIGN of the change does matter!
4) Plug in [Equilibrium] into $K_{eq}$ and solve

**Reactant Stoichiometry**

\[
\begin{align*}
\text{Reactants} & : aA + bB \\
\text{Products} & : cC + dD
\end{align*}
\]

**ICE Tables**

<table>
<thead>
<tr>
<th>Species</th>
<th>Initial</th>
<th>Change</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **INITIAL** = initial [ ] of each species
- **CHANGE** = change taking place in terms of x
- **EQUILIBRIUM** = [ ] at equilibrium in terms of x
Calculating $K_{eq}$

**EXAMPLE:**
A closed system containing 0.0010 M $H_2$ and 0.0020 M $I_2$ is allowed to reach equilibrium. The [HI] at equilibrium is 0.00187 M. Calculate $K_{eq}$ for the reaction below.

$$H_2(g) + I_2(g) \rightleftharpoons 2 \text{HI}(g)$$

<table>
<thead>
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<th>2 HI</th>
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<tr>
<td>Initial</td>
<td>0.0010 M</td>
<td>0.0020 M</td>
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<tr>
<td>Change</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fill in what we are given

Fill in the rest using logic and math

"+" sign because product is forming

"-" sign because reactants are consumed

Divided by 2 because there's TWICE as much HI according to mole ratio!
Calculating $K_{eq}$

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<td>0.0010 M</td>
<td>0.0020 M</td>
<td>0 M</td>
</tr>
<tr>
<td>Change</td>
<td>-0.000935 M</td>
<td>-0.000935 M</td>
<td>+0.00187 M</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.000065 M</td>
<td>0.001065 M</td>
<td>0.00187 M</td>
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Do the math (initial – change) to get [ ] of each at equilibrium!

Calculating $K_{eq}$

**EXAMPLE:**
A closed system containing 0.0010 M $H_2$ and 0.0020 M $I_2$ is allowed to reach equilibrium. The [HI] at equilibrium is 0.00187 M. Calculate $K_{eq}$ for the reaction below:

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Now we can set up and solve $K_{eq}$!

Calculating $K_{eq}$

**EXAMPLE:**
Initially, a vessel with $SO_3(g)$ has a partial pressure of 0.500 atm. At equilibrium, the partial pressure of $SO_3$ is 0.200 atm. Calculate $K_p$.

$$2 SO_3(g) \rightleftharpoons 2 SO_2(g) + O_2(g)$$

Calculating [Equilibrium]

**EXAMPLE:**
The value of $K_{eq}$ for the reaction below is 50.0. What is the [equilibrium] for all species if the [initial] are: $[H_2] = 1.00$ M and $[I_2] = 2.00$ M?

$$H_2(g) + I_2(g) \rightleftharpoons 2 \text{HI}(g)$$

Calculating [Equilibrium]

**EXAMPLE:**
The value of $K_{eq}$ for the reaction below is 50.0. What is the [equilibrium] for all species if the [initial] are: $[H_2] = 1.00$ M and $[I_2] = 2.00$ M?

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**EXAMPLE:**

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Calculating [Equilibrium]

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Fill in what we know

Calculating [Equilibrium]

**EXAMPLE:**
The value of $K_{eq}$ for the reaction below is 50.0. What is the [equilibrium] for all species if the [initial] are: $[H_2] = 1.00 \text{ M}$ and $[I_2] = 2.00 \text{ M}$?

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Use x since we don’t know the change, and “-” because it is consumed

Calculating [Equilibrium]

**EXAMPLE:**
The value of $K_{eq}$ for the reaction below is 50.0. What is the [equilibrium] for all species if the [initial] are: $[H_2] = 1.00 \text{ M}$ and $[I_2] = 2.00 \text{ M}$?

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Fill in the equilibrium values by adding or subtracting change from initial

Calculating [Equilibrium]

**EXAMPLE:**
The value of $K_{eq}$ for the reaction below is 50.0. What is the [equilibrium] for all species if the [initial] are: $[H_2] = 1.00 \text{ M}$ and $[I_2] = 2.00 \text{ M}$?

$$H_2(g) + I_2(g) \rightleftharpoons 2 \text{ HI(g)}$$

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Plug values into $K_{eq}$ for the reaction

Calculating [Equilibrium]

**EXAMPLE:**
The value of $K_{eq}$ for the reaction below is 50.0. What is the [equilibrium] for all species if the [initial] are: $[H_2] = 1.00 \text{ M}$ and $[I_2] = 2.00 \text{ M}$?

$$H_2(g) + I_2(g) \rightleftharpoons 2 \text{ HI(g)}$$

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Figure out the change for each
Calculating [Equilibrium]

**EXAMPLE:**

\[ \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2 \text{HI}(g) \]

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<td>(1.00 – x) M</td>
<td>(2.00 – x) M</td>
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\[
K_{eq} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} \quad 50.0 = \frac{[2x]^2}{[1.00-x][2.00-x]} =
\]

Simplify and then rearrange

\[
x = 2.33 \quad \text{OR} \quad x = 0.934
\]

One answer is always not chemically meaningful so it gets rejected. When \( x = 2.33 \) is plugged in for \( x \), we get “-” values which can’t happen!

**Calculating [Equilibrium]**

**EXAMPLE:**

\[ \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2 \text{HI}(g) \]

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\[
4x^2 = 50.0 \left( x^2 - 3.00x + 2 \right)
\]

\[
4x^2 = 50.0x^2 - 150.0x + 100
\]

\[
46x^2 - 150.0x + 100 = 0
\]

Plug into quadratic equation and solve for \( x \)!

**Calculating [Equilibrium]**

**EXAMPLE:**

\[ \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2 \text{HI}(g) \]

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\[
1.00 - 0.934 = 0.07 \text{ M} \quad [\text{H}_2]
\]

\[
2.00 - 0.934 = 1.06 \text{ M} \quad [\text{I}_2]
\]

\[
2(0.934) = 1.87 \text{ M} \quad [\text{HI}]
\]

Check these numbers by placing into \( K_{eq} \)!

**Summary**

• If **ALL** [EQU] known...
  Plug [ ] into \( K_{eq} \) and solve

• If **ONE** [EQU] known...
  Use ICE table with math / logic

• If **NO** [EQU] known...
  Use ICE table with “x”

• If **NO** [EQU] known and **NO** [Initial] are zero...
  \( Q \) must be found first to find which way the rxn shifts... Tells what sign to put for reactants / products for the “change” part of the table! Then ICE table with “x”
Watch Out!

- Always set up the ICE table with the BALANCED equation... pay attention to the sign of the change
- Write the equilibrium expression... NO SOLIDS!
- [Equilibrium] NEEDS to be in mol/L
- When solving for x: if problem is a perfect square you can take the square root... if not, you must use quadratic equation
- Check your work!

Practice

- EXAMPLE: For the reaction below, the $K_{eq}$ at 200°C is 4.2. What is the [equilibrium] for all species if initially there are 0.25 moles of $H_2$ and CO$_2$ in a 5.0 L closed container?
  $$H_2(g) + CO_2(g) = H_2O(g) + CO(g)$$

Calculating [Equilibrium]

- EXAMPLE: Determine the [equilibrium] for all species in the reaction below ($K_c = 1.60 \times 10^{-5}$) with an initial [NOCl] = 0.50 M.
  $$2 \text{ NOCl}(g) \rightleftharpoons 2 \text{ NO}(g) + \text{ Cl}_2(g)$$

- EXAMPLE: Determine the [equilibrium] for all species in the reaction below ($K_c = 1.60 \times 10^{-5}$) with an initial [NOCl] = 0.50 M.
  $$2 \text{ NOCl}(g) \rightleftharpoons 2 \text{ NO}(g) + \text{ Cl}_2(g)$$
**Calculating [Equilibrium]**

**EXAMPLE:**
Determine the equilibrium for all species in the reaction below \( K_c = 1.60 \times 10^{-5} \) with an initial 
\[ \text{[NOCI]} = 0.50 \text{ M} \]
\[ 2 \text{ NOCl}(g) \rightleftharpoons 2 \text{ NO}(g) + \text{Cl}_2(g) \]

<table>
<thead>
<tr>
<th></th>
<th>[2 \text{ NOCl}]</th>
<th>[2 \text{ NO}]</th>
<th>[\text{Cl}_2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.50 M</td>
<td>0 M</td>
<td>0 M</td>
</tr>
<tr>
<td>Change</td>
<td>-2x</td>
<td>+2x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>(0.50 – 2x) M</td>
<td>2x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[ K_{eq} = \frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCI}]^2} = 1.60 \times 10^{-5} = \frac{[2x]^2 [x]}{[0.50 – 2x]^2} \]

Since \( K_c \) is really small, we can assume that \( x \) is negligible and doesn’t contribute to the [ ] at equilibrium for NOCl!!

\[ 1.60 \times 10^{-5} = \frac{4x^3}{[0.50]^2} \]

\[ x = 1.0 \times 10^{-2} \]

Now, check the assumption!

\[ \frac{\Delta \%}{\text{Initial [ ]}} = \frac{2x}{0.50} \times 100 = \frac{2(1.0 \times 10^{-2})}{0.50} \times 100 = 4\% \]

\(< 5\% \) so it’s VALID!
Calculating [Equilibrium]

**EXAMPLE:**

<table>
<thead>
<tr>
<th></th>
<th>2 NOCl</th>
<th>2 NO</th>
<th>Cl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.50 M</td>
<td>0 M</td>
<td>0 M</td>
</tr>
<tr>
<td>Change</td>
<td>-2x</td>
<td>+2x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>(0.50 - 2x) M</td>
<td>2x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[ [\text{NOCl}] = 0.48 \text{ M} \]
\[ [\text{NO}] = 0.020 \text{ M} \]
\[ [\text{Cl}_2] = 0.010 \text{ M} \]

---

**K\text{sp}**

- Indicates how soluble a solid is in water
- Since solids do **NOT** change [ ], they do **NOT** participate in the equilibrium expression (no denominator)
- Example:
  \[ \text{Ca}_3(\text{PO}_4)_2(s) = 3 \text{ Ca}^{2+}(aq) + 2 \text{ PO}_4^{3-}(aq) \]
  \[ K_{\text{sp}} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2 \]

*We have done these problems without ICE tables, but they can be done with the tables!*

---

**Practice**

- **EXAMPLE:**
  
  The \( K_{\text{sp}} \) value for \( \text{Cu(IO}_3)_2 \) is \( 1.4 \times 10^{-7} \) at \( 25^\circ\text{C} \). Calculate its **solubility** at this temperature.

---

**K\text{sp}**

- **EXAMPLES:**
  
  Calculate the \( K_{\text{sp}} \) for \( \text{Mg}_3(\text{PO}_4)_2 \) given that its molar solubility is \( 3.57 \times 10^{-6} \) M.

  Calculate the **solubility** of \( \text{CaF}_2 \) and the **concentration** of each ion \( (K_{\text{sp}} = 4.9 \times 10^{-11}) \).

---

**WHAT DOES IT ALL MEAN?**

- According to \( K_{\text{sp}} \), everything is at least very, very, very **SLIGHTLY** soluble
- Looking at the \( K_{\text{sp}} \) can help you figure out which compounds are more soluble...
Ksp

- Salts that produce the SAME # of ions when dissolved can be compared to see which is more/less soluble (if different #, then must be calculated using Ksp expression)
- Example:

<table>
<thead>
<tr>
<th>Salt</th>
<th>Ksp</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgBr</td>
<td>5.0 x 10^{-13}</td>
</tr>
<tr>
<td>AgI</td>
<td>1.5 x 10^{-16}</td>
</tr>
<tr>
<td>AgCl</td>
<td>1.6 x 10^{-10}</td>
</tr>
</tbody>
</table>

**SMALLER** the Ksp = LESS soluble!

Will It PPT?... Q and Ksp

Steps to Follow for Problems:
1) Determine which ions form the PPT
2) Find the # of moles of each ION... ***pay attention to overall # in the compound
3) Calculate the TOTAL volume after mixing
4) Calculate the [ ] of each ion
5) SUBSTITUTE [ ] of ions into Ksp expression and solve for Q
6) Compare Q and Ksp

Practice

- EXAMPLE:
  Fe(OH)3 has a Ksp = 4.87 x 10^{-37}. If 500.0 mL of 4.0 x 10^{-4} M Fe(NO3)3 is mixed with 250.0 mL of 3.0 x 10^{-4} M NaOH, will a precipitate form? Show calculations to justify your answer.

Common Ion Effect

- REDUCTION in the solubility of an ionic precipitate when a soluble compound containing one of the SAME ions of the precipitate is added at equilibrium
  
- More of the ion means more of the solid will precipitate out (so compound is LESS soluble)
  
- Ignore the ion that is NOT common and focus on the common one
  
- Example: Adding 0.10 M NaCl to a solution of AgCl... No ions have no effect, but additional Cl- ions cause MORE solid AgCl to form
Common Ion Effect
REDUCTION in the solubility of an ionic precipitate when a soluble compound containing one of the SAME ions of the precipitate is added at equilibrium

• EXAMPLE:
A 0.100 mol sample of solid AgNO₃ is added to a 1.00 L saturated solution of Ag₂CrO₄. Assuming no volume change, does [CrO₄²⁻] increase, decrease, or remain the same? Justify your answer. No calculations are needed.

Common Ion Effect
REDUCTION in the solubility of an ionic precipitate when a soluble compound containing one of the SAME ions of the precipitate is added at equilibrium

• EXAMPLE:
Calculate the equilibrium concentration of Mg²⁺ in 1.000 liter of saturated MgF₂ (Ksp = 7.09 x 10⁻⁹) solution at 18°C to which 0.100 mole of solid KF has been added. The KF dissolves completely. Assume the volume change is negligible.

Use ICE table and x approximation to solve... ONE ion has an initial [ ] in these types of problems!

Which Precipitates First?
• Sometimes you might be asked to determine which compound will precipitate from a solution FIRST when a substance is added
• Write the Ksp expressions for BOTH possible PPT
• Substitute in all known values and [ ] and solve for the [ ] of the ion that is being added (unknown)
• LOWER [ ] reached first, so precipitates FIRST

In GENERAL (if no calculations required AND form same # of ions), when two salt solutions that share a common ion are mixed, the salt with the LOWER value for Ksp will precipitate FIRST!

Practice
• EXAMPLE:
A solution contains 1.0 x 10⁻⁴ M Cu⁺ and 0.0020 M Pb²⁺. If a source of I⁻ is added gradually to this solution, will PbI₂ (Ksp = 1.4 x 10⁻⁹) or CuI (Ksp = 5.3 x 10⁻¹⁵) precipitate first? Specify the concentration of I⁻ necessary to begin precipitation of each salt.

Summary
1) Find Ksp or Molar Solubility:
Write expression (no solids) and solve... x is the value of molar solubility!

2) Will It PPT?
Find moles of each, [ ] of each, plug into expression, and compare Q with Ksp. If Q is GREATER, then PPT forms!

3) Common Ion Impacts:
Use ICE table with "x" approx... One ion will have an initial value! Solubility always LOWER!

4) Which PPTs First?
Write Ksp for both, plug in known [ ], and solve for unknown [ ]... LOWER [ ] PPTs first!
More Practice

**EXAMPLE:**
The \( K_{sp} \) value for \( \text{Cu(OH)}_2 \) is \( 1.6 \times 10^{-9} \). Determine its molar solubility and the concentration of each ion.

More Practice

**EXAMPLE:**
What compound, if any, will precipitate when 80.0 mL of \( 1.0 \times 10^{-5} \) M \( \text{Ba(OH)}_2 \) is added to a solution of 20.0 mL of \( 1.0 \times 10^{-5} \) M \( \text{Fe}_2(\text{SO}_4)_3 \)? \((K_{sp} \ \text{BaSO}_4 = 1.1 \times 10^{-10}, \ K_{sp} \ \text{Fe(OH)}_3 = 2.6 \times 10^{-39})\)

More Practice

**EXAMPLE:**
Calculate the solubility of \( \text{CaCO}_3 \) \((K_{sp} = 3.4 \times 10^{-9})\) in... a) pure water and b) \( 0.45 \) M \( \text{CaCl}_2 \).

More Practice

**EXAMPLE:**
Which salt precipitates first and what is the minimum concentration of \( \text{Ag}^+ \) necessary to cause this precipitation in a solution containing 7.5 mL of \( 0.025 \) M \( \text{NaCl} \) and 7.5 mL of \( 0.035 \) M \( \text{Na}_3\text{PO}_4 \)? \((K_{sp} \ \text{AgCl} = 1.8 \times 10^{-10}, \ K_{sp} \ \text{Ag}_3\text{PO}_4 = 1.3 \times 10^{-20})\)

More Practice

**EXAMPLES:**
A solution contains \( 2.0 \times 10^{-4} \) M \( \text{Ca}^{2+} \). If 40.0 mL of this solution is added to 25.0 mL of \( 5.0 \times 10^{-3} \) M \( \text{Na}_3\text{PO}_4 \), will a precipitate form? \((K_{sp} \ \text{Ca}_3(\text{PO}_4)_2 = 2.0 \times 10^{-29})\)

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*

**THREE STRESSORS:**
1) Change the [ ] by adding or removing reactant or product
2) Change the PRESSURE by changing the volume
3) Change the TEMPERATURE of the system

RATE of the forward or reverse reaction changes in response!
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

**CONCENTRATION**
- Increasing the \[ \] of a reactant will shift the reaction to the RIGHT to use up the added reactants, while increasing the [ ] of a product will shift the reaction to the LEFT
- Decreasing the [ ] of a reactant or product will shift the reaction in the direction to create MORE of the substance removed

**NO CHANGE** when more solid or liquid added!!

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

**CONCENTRATION**
- Remember the **COMMON ION EFFECT**?...
  - Precipitate is LESS soluble when a soluble compound containing one of the SAME ions is added
  - WHY?... Reaction shifts **LEFT**
  - Example: Adding 0.10 M NaCl to a solution of AgCl

\[
\text{AgCl(s)} \rightleftharpoons \text{Ag}^{+}(aq) + \text{Cl}^{-}(aq)
\]

**PRESSURE**
- Decreasing the volume will increase the pressure and vice versa
- To decrease the pressure, need to decrease the total number of gas molecules in the system
- At constant temp, decreasing volume increases the pressure so equilibrium will shift to the side with FEWER molecules of gas

In GENERAL, when two salt solutions that share a common ion are mixed, the salt with the **LOWER** value for K\text{sp} will precipitate **FIRST**!

(assuming same \# of ions in each)
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

PRESSURE
\[ \text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g) \]
Reactants have 4 molecules of gas
Products have 2 molecules of gas

Increasing the pressure on this reaction shifts the equilibrium to the **RIGHT** which has **FEWER** gas molecules

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

TEMPERATURE
• Effects of temp change depend on whether the reaction is endothermic or exothermic
• Think of each reaction with heat energy as a reactant or product

**ENDO**: Reactants + HEAT \rightleftharpoons Products
**EXO**: Reactants \rightleftharpoons Products + HEAT

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

TEMPERATURE
• Increase Temp = shifts LEFT (removes heat)
• Decrease Temp = shifts RIGHT (adds heat)

**ENDO**: Reactants + HEAT \rightleftharpoons Products
Increase Temp = shifts \text{RIGHT} (removes heat)
Decrease Temp = shifts \text{LEFT} (adds heat)

**EXO**: Reactants \rightleftharpoons Products + HEAT
Increase Temp = shifts \text{LEFT} (removes heat)
Decrease Temp = shifts \text{RIGHT} (adds heat)

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

CATALYSTS
• Have NO effect on equilibrium
• Speed up the forward and reverse reaction the same
• Increase the rate at which the equilibrium is achieved but do NOT change the composition of the equilibrium mixture
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.

How is $K_{eq}$ affected by the stressors?

- Changes in [ ], pressure, or volume have NO effect on the value of $K_{eq}$
- Temperature changes WILL affect the value of $K_{eq}$
  - Shifts to the LEFT... Decrease $K_{eq}$
  - Shifts to the RIGHT... Increase $K_{eq}$
- Catalysts or other compounds not present in the reaction have NO effect on $K_{eq}$ or equilibrium

Practice

**EXAMPLE:**
Consider the equilibrium reaction below. In which direction will the equilibrium shift when (a) $N_2O_4$ is added, (b) $NO_2$ is removed, (c) the total pressure is increased by addition of $N_2(g)$, (d) the volume is increased, and (e) the temperature is decreased?

$$N_2O_4(g) \rightleftharpoons 2 NO_2(g) \quad \Delta H = 58.0 \text{ kJ}$$

Practice

**EXAMPLE:**
Consider the equilibrium reaction below. In which direction will the equilibrium shift when (a) $Cl_2(g)$ is removed, (b) the temperature is increased, (c) the volume of the reaction system is decreased, and (d) $PCl_3(g)$ is added?

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \quad \Delta H = 87.9 \text{ kJ}$$

Practice

**EXAMPLE:**
At temperatures near 800°C, steam passed over hot coke (form of carbon from coal) reacts to form CO and $H_2$ as seen below. (a) At 800°C, the $K_p$ for this reaction is 14.1. What are the equilibrium partial pressures of $H_2O$, CO, and $H_2$ if we start with solid carbon and 0.100 mol of $H_2O$ in a 1.00 L vessel? (b) What is the minimum amount of carbon required to achieve equilibrium? (c) What is the total pressure in the vessel at equilibrium? (d) At 25°C, the value of $K_p$ for this reaction is $1.7 \times 10^{-21}$. Is the reaction exothermic or endothermic? (e) To produce the maximum amount of CO and $H_2$ at equilibrium, should the pressure of the system be increased or decreased?

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$