

AP Chemistry  
Exam Review

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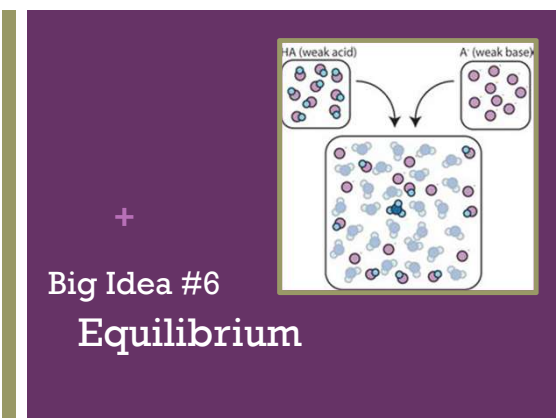
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Big Idea #6  
Equilibrium

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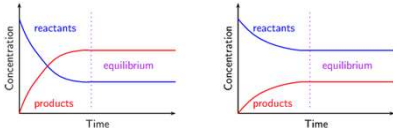
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**+ What is chemical equilibrium?**

- Systems that have reached the state where the rates of the forward reaction and the reverse reaction are constant and equal.
- It is a dynamic process where reactants continuously form products and vice versa, but the net amounts of reactants and products remain constant.
- The proportions of products and reactants formed in a system at a specific temperature that has achieved equilibrium is represented by  $K$ , the equilibrium constant.

[Source](#)  
[Video](#)



In the reaction:  
 $aA + bB \rightleftharpoons cC + dD$

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

[A] = concentration of A in  $\text{mol dm}^{-3}$   
a = number of moles of A

LO 6.1: Given a set of experimental observations regarding processes that are reversible, construct an explanation that connects the observations to the reversibility of the underlying chemical reactions or processes.

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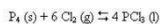
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## + Manipulating Q and K

■  $K$  (equilibrium constant) represents the relative amounts of products to reactants at equilibrium at a given temperature.

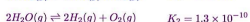
■  $Q$  (reaction progress) describes the relative amounts of products to reactants present at any point in the reaction at a given temperature.

■  $Q$  and  $K$  only include substances that are gases or in aqueous solutions. No solids or liquids are ever included in these expressions.



$$K = \frac{1}{[\text{Cl}_2]^6}$$

$$K_p = \frac{1}{P_{\text{Cl}_2}^6}$$



Click reveals answer.

■ Similar reactions will have related  $K$  values at the same temperature.

Reaction Run in Reverse	Inverse the value of $K$ (i.e. raise it to the -1 power)
Multiplying by a Constant	Raise the equilibrium constant to the power that was multiplied by
Adding Reactions	Multiply the equilibrium constant by one another

LO 6.2: The student can, given a manipulation of a chemical reaction or set of reactions (e.g., reversal of reaction or addition of two reactions), determine the effects of that manipulation on  $Q$  or  $K$ .

Source

Video

## + Kinetics and Equilibrium

■ Kinetics examines the rate at which reactions proceed. Rate laws are used to describe how reactant concentrations affect a reaction's rate. Rate constants ( $k$ ) in rate law expressions are determined experimentally at a given temperature.

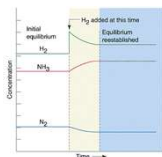
■ Equilibrium describes the state at which the rates of the forward reaction and the reverse reaction are constant and equal.

■ If the rates are initially unequal (the system is not at equilibrium), the faster direction depletes its reactants, which feeds back to slow down that direction.

■ At the same time, the slower direction accumulates its reactants, speeding up the slower direction.

■ These loops continue until the faster rate and the slower rate have become equal.

■ In the graph to the right, after equilibrium has been achieved, additional hydrogen gas is added to the system. The system then consumes both  $\text{H}_2$  and  $\text{N}_2$  to form additional  $\text{NH}_3$  molecules, eventually reestablishing equilibrium.



LO 6.3: The student can connect kinetics to equilibrium by using reasoning, such as LeChatelier's principle, to infer the relative rates of the forward and reverse reactions.

Source

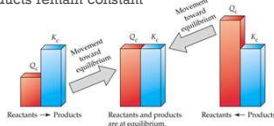
Video

## + Q vs. K

■ Equilibrium is reached when the rates of the forward reaction and the rates of the reverse reaction are equal, which is when  $Q$  is equal to  $K$ .

■ Comparing  $Q$  to  $K$  enables us to determine if a chemical system has achieved equilibrium or will need to move towards reactants or products to reach equilibrium.

- if  $Q < K$ , the reaction will proceed in the forward direction until  $Q = K$
- if  $Q > K$ , the reaction will proceed in the reverse direction until  $Q = K$
- if  $Q = K$ , the reaction is at equilibrium, and the concentrations of reactants and products remain constant



LO 6.4: Given a set of initial conditions and the equilibrium constant,  $K$ , use the tendency of  $Q$  to approach  $K$  to predict and justify the prediction as to whether the reaction will proceed toward products or reactants as equilibrium is approached.

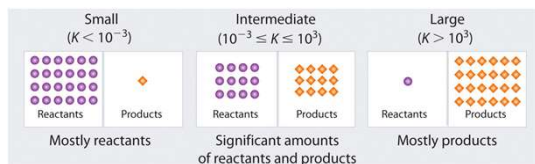
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## + Magnitude of $K$

- For many reactions involving aqueous solutions,  $K$  is either very large (favoring the forward reaction) or very small (favoring the reverse reaction)
- The size of  $K$  can be used to describe the relationship between the numbers of reactant and product particles present at equilibrium.



LO 6.7: The student is able, for a reversible reaction that has a large or small  $K$ , to determine which chemical species will have very large versus very small concentrations at equilibrium.

Source

Video

## + Le Chatelier's Principle

- This principle is used to describe changes that occur in a system that has achieved equilibrium. There are three factors that can cause shifts in a system at equilibrium: concentration, pressure, and temperature.

Change	Direction System Shifts to Reestablish Equilibrium
Adding a reactant	Shifts towards products
Adding a product	Shifts towards reactants
Removing a reactant	Shifts towards reactants
Removing a product	Shifts towards products
Increasing pressure (decreasing volume)	Shifts toward less gas molecules
Decreasing pressure (increasing volume)	Shifts towards more gas molecules
Adding an inert gas	No effect
Increasing the temperature	Endothermic: shifts towards products Exothermic: shifts towards reactants
Decreasing the temperature	Endothermic: shifts towards reactants Exothermic: shifts towards products

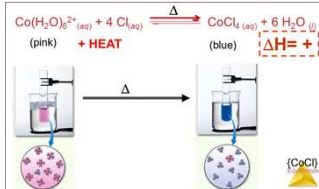
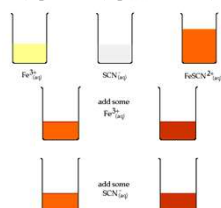
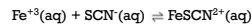
LO 6.8: The student is able to use LeChatelier's principle to predict the direction of the shift resulting from various possible stresses on a system at chemical equilibrium.

Animation Source

Video

## + Experimentally Examining Le Chatelier's Principle

- Systems at equilibrium can be examined using Le Chatelier's Principle by measuring its properties, including pH, temperature, solution color (absorbance)



LO 6.9: The student is able to use LeChatelier's principle to design a set of conditions that will optimize a desired outcome, such as product yield.

Animation Source

Video

## + Changes to $Q$ and $K$ for a System at Equilibrium

- Some changes that occur to a system at equilibrium will affect the reaction's current position ( $Q$ ). Others will affect the value of  $K$

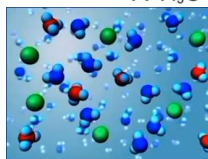
Change	Direction System Shifts to Reestablish Equilibrium	Effect on $Q$ or $K$
Adding a reactant	Shifts towards products	$Q$ decreases
Adding a product	Shifts towards reactants	$Q$ increases
Removing a reactant	Shifts towards reactants	$Q$ increases
Removing a product	Shifts towards products	$Q$ decreases
Increasing pressure (decreasing volume)	Shifts toward less gas molecules	$Q$ can increase, decrease, or remain constant depending on ratio of gas molecules between reactants and products
Decreasing pressure (increasing volume)	Shifts towards more gas molecules	
Adding an inert gas	No effect	$Q$ doesn't change
Increasing the temperature	Endothermic: shifts towards products Exothermic: shifts towards reactants	Endothermic: $K$ increases Exothermic: $K$ decreases
Decreasing the temperature	Endothermic: shifts towards reactants Exothermic: shifts towards products	Endothermic: $K$ decreases Exothermic: $K$ increases

LO 6.10: The student is able to connect LeChatelier's principle to the comparison of  $Q$  to  $K$  by explaining the effects of the stress on  $Q$  and  $K$ .

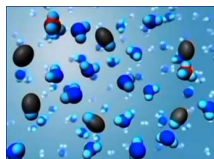
Animation

Video Source

## + Acid/Base Particulates



Strong: Since  $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$  is much greater than 1, at equilibrium strong acids are molecules that essentially ionize to *completion* in aqueous solution, disassociating into  $\text{H}_3\text{O}^+$  ions and the additional anion.



Weak: Since  $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$  is much less than 1, at equilibrium weak acids are molecules that only partially ionize in aqueous solution, disassociating into few  $\text{H}_3\text{O}^+$  ions and the additional anion.

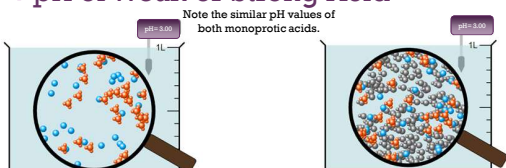
LO 6.11: The student can generate or use a particulate representation of an acid (strong or weak or polyprotic) and a strong base to explain the species that will have large versus small concentrations at equilibrium.

Source

Video Source

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## + pH of Weak or Strong Acid



- This is a particulate picture of a strong acid whose  $[\text{HA}] = 0.00100\text{M}$ .
- Note the 100% ionization of this acid.

- This is a particulate picture of a weak acid whose  $[\text{HA}] = 1.00\text{M}$  and  $K_a = 1.00 \times 10^{-6}$ .
- pH is a measure of the  $[\text{H}^+]$  in solution. More moles of a weak acid are needed to achieve equivalent  $[\text{H}^+]$  values of a strong acid of the same pH, since a weak acid only partially ionizes.

If similar volumes of both acids above were titrated with the same strong base, the weak acid would require a larger volume of base to reach its equivalence point.

LO 6.12: Reason about the distinction between strong and weak acid solutions with similar values of pH, including the percent ionization of the acids, the concentrations needed to achieve the same pH, and the amount of base needed to reach the equivalence point in a titration.

Source

Video



### + pH and Acid/Base Equilibria

1. Vinegar is 0.50M acetic acid,  $\text{HC}_2\text{H}_3\text{O}_2$ , with a  $K_a = 1.8 \times 10^{-5}$ . What would be the pH of this solution?

1<sup>st</sup> click reveals answer and explanation.

2. Identify and compare the relative strengths of the two acids and the two bases in this neutralization reaction:  $\text{OH}^-(aq) + \text{NH}_4^+(aq) \rightleftharpoons \text{H}_2\text{O}(l) + \text{NH}_3(aq)$ .

2<sup>nd</sup> click reveals answer and explanation.

LO 6.16: The student can identify a given solution as being the solution of a monoprotic weak acid or base (including salts in which one ion is a weak acid or base), calculate the pH and concentration of all species in the solution, and/or infer the relative strengths of the weak acids or bases from given equilibrium concentrations.

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### + Acid/Base reaction species

Ask yourself:  
Is it strong? Weak? A salt? A buffer? What will it do in water?  
See Source link for more details

Deal w/strong A/B first. These will react to completion with the available species.

LO 6.17: The student can, given an arbitrary mixture of weak and strong acids and bases (including polyprotic systems), determine which species will react strongly with one another (i.e., with  $K > 1$ ) and what species will be present in large concentrations at equilibrium.

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### + How to Build a Buffer:

**Getting the pH correct:**

- The pH of a buffer is primarily determined by the  $pK_a$  of the weak acid in the conjugate acid-base pair.
- When both species in the conjugate acid-base pair have equal concentrations, the pH of the buffer is equal to the  $pK_a$ .
- Choose a conjugate acid-base pair that has a  $pK_a$  closest to the pH you desire and then adjust concentrations to fine tune from there.

**Estimating Buffer Capacity:**

- A buffer is only effective as long as it has sufficient amounts of both members of the conjugate acid-base pair to allow equilibrium to shift during a stress.

LO 6.18: The student can design a buffer solution with a target pH and buffer capacity by selecting an appropriate conjugate acid-base pair and estimating the concentrations needed to achieve the desired capacity.

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## + Finding the Major Species

[Source](#)

- A 50.0 mL sample of 0.50 M  $\text{HC}_2\text{H}_3\text{O}_2$  is titrated to the half equivalence point with 25.0 mL of 0.50 M NaOH. Which of the following options shows the correct ranking of the molarities of the species in solution?

( $\text{pK}_a$  for  $\text{HC}_2\text{H}_3\text{O}_2$  is 4.7)

- $[\text{HC}_2\text{H}_3\text{O}_2] > [\text{C}_2\text{H}_3\text{O}_2^-] > [\text{H}^+] > [\text{OH}^-]$
- $[\text{HC}_2\text{H}_3\text{O}_2] = [\text{C}_2\text{H}_3\text{O}_2^-] > [\text{H}^+] > [\text{OH}^-]$
- $[\text{HC}_2\text{H}_3\text{O}_2] > [\text{C}_2\text{H}_3\text{O}_2^-] = [\text{H}^+] > [\text{OH}^-]$
- $[\text{C}_2\text{H}_3\text{O}_2^-] > [\text{HC}_2\text{H}_3\text{O}_2] > [\text{OH}^-] > [\text{H}^+]$

[Video](#)

Click reveals answer and explanation.

LO 6.19: The student can relate the predominant form of a chemical species involving a labile proton (i.e., protonated/deprotonated form of a weak acid) to the pH of a solution and the  $\text{pK}_a$  associated with the labile proton.

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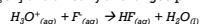
## + The Buffer Mechanism

[Source](#)

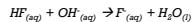
A buffer is able to resist pH change because the two components (conjugate acid and conjugate base) are both present in appreciable amounts at equilibrium and are able to neutralize small amounts of other acids and bases (in the form of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$ ) when they are added to the solution. Take, for example, a fluoride buffer made from hydrofluoric acid and NaF. A model fluoride buffer would contain equimolar concentrations of HF and NaF. Since they are a weak acid and a weak base, respectively, the amount of hydrolysis is minimal and both buffer species are present at, effectively, their initial supplied concentrations.

[Video](#)

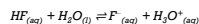
If a strong acid is added to the HF/ $\text{F}^-$  buffer, then the added acid will react completely with the available base,  $\text{F}^-$ . This results in a nearly unchanged  $[\text{H}_3\text{O}^+]$  and a nearly unchanged pH.



If a strong base is added to the HF/ $\text{F}^-$  buffer, then the added base will react completely with the available acid, HF. This results in a nearly unchanged  $[\text{H}_3\text{O}^+]$  and a nearly unchanged pH.



The slight shift in pH after challenge is governed by the hydrolysis equilibrium of HF, based on the new HF and  $\text{F}^-$  concentrations:



LO 6.20: The student can identify a solution as being a buffer solution and explain the buffer mechanism in terms of the reactions that would occur on addition of acid/base.

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## + $\text{K}_{\text{sp}}$ and Solubility Calculations

[Source](#)

### Question:

What is the maximum number of moles of AgBr that will fully dissolve in 1.0 L of water, if the  $\text{K}_{\text{sp}}$  value of silver bromide is  $4.0 \times 10^{-12}$ ?

- a.  $4.0 \times 10^{-12}$       b.  $2.0 \times 10^{-12}$       c.  $4.0 \times 10^{-6}$       d.  $2.0 \times 10^{-6}$

[Video](#)

Click reveals answer and explanation.

LO 6.21: The student can predict the solubility of a salt, or rank the solubility of salts, given the relevant  $\text{K}_{\text{sp}}$  values.

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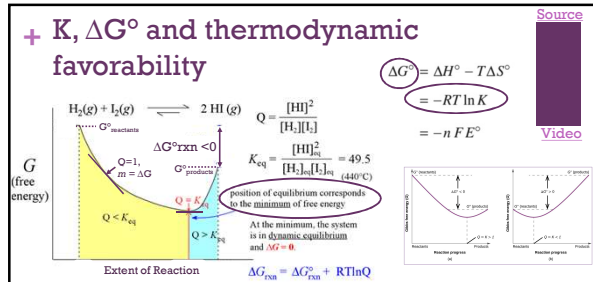
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## + K, $\Delta G^\circ$ and thermodynamic favorability



The key to understanding the relationship between  $\Delta G^\circ$  and K is recognizing that the magnitude of  $\Delta G^\circ$  tells us how far the standard-state is from equilibrium. The smaller the value of  $\Delta G^\circ$ , the closer the standard-state is to equilibrium. The larger the value of  $\Delta G^\circ$ , the further the reaction has to go to reach equilibrium.

LO 6.25: The student is able to express the equilibrium constant in terms of  $\Delta G^\circ$  and RT and use this relationship to estimate the magnitude of K and, consequently, the thermodynamic favorability of the process.

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