AP Chemistry
Exam Review

HA (weak acid)

A⁻ (weak base)
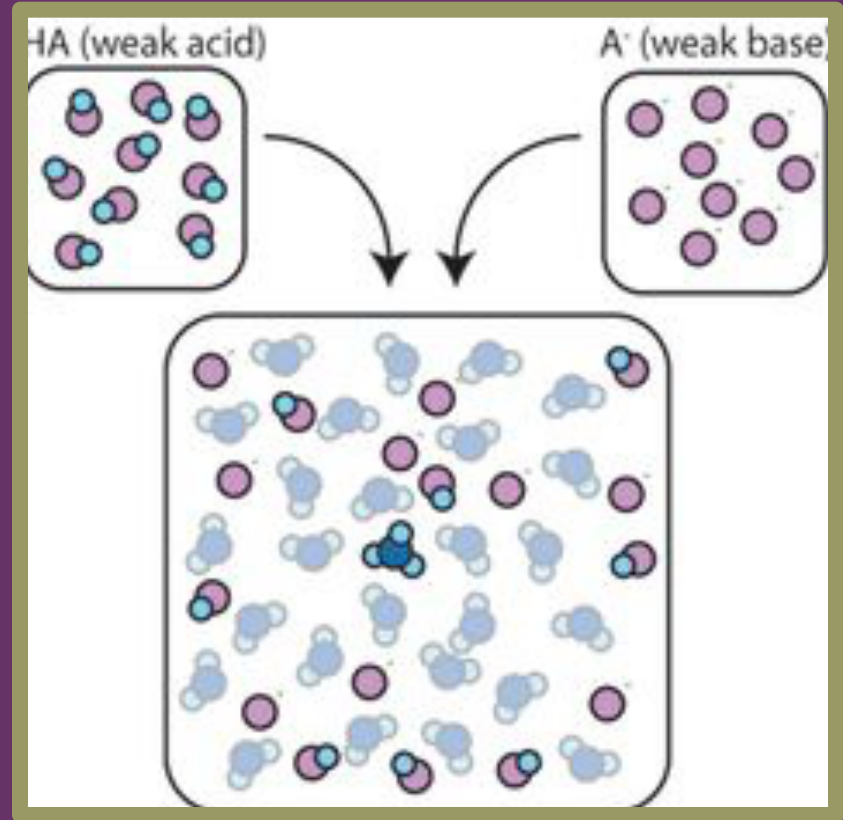
+

Big Idea #6
Equilibrium

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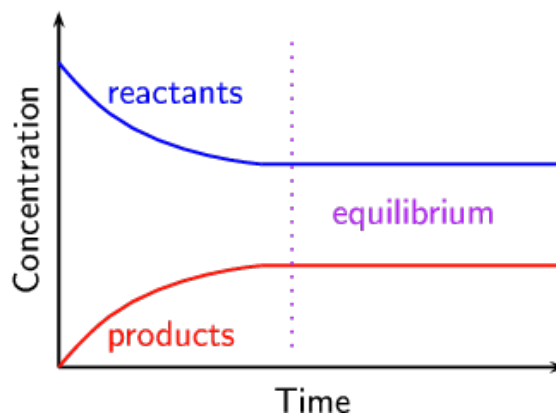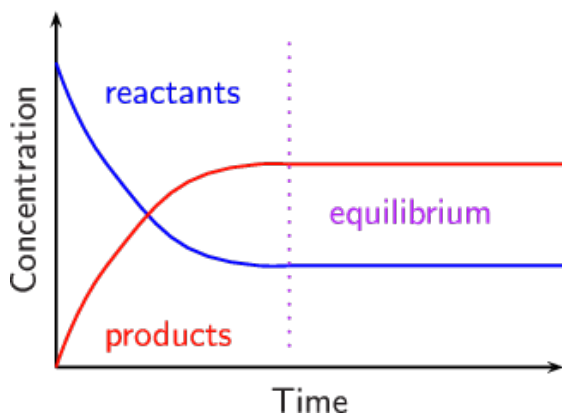
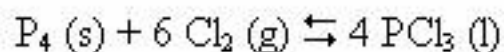In the reaction:
$$aA + bB \rightleftharpoons cC + dD$$

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

[A] = concentration of A in moldm^{-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.
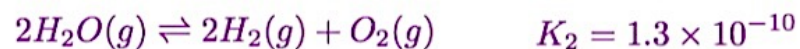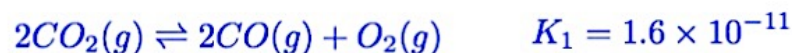
+ Manipulating Q and K

- 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.

$$P_4\ (s) + 6\ Cl_2\ (g) \rightleftharpoons 4\ PCl_3\ (l)$$

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

$$K = \frac{1}{[Cl_2]^6}$$

$$K_p = \frac{1}{P_{Cl2}^6}$$

$$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g) \qquad K_1 = 1.6 \times 10^{-11}$$

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g) \qquad K_2 = 1.3 \times 10^{-10}$$

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g) \qquad K_3 = ?$$
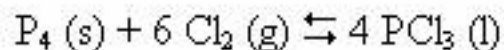
Click reveals answer.

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.
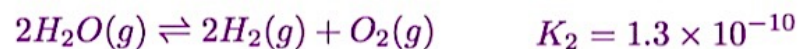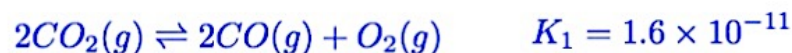
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$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g) \qquad K_3 = ?$

2.9

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.

+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 H_2 and N_2 to form additional NH_3 molecules, eventually reestablishing equilibrium.
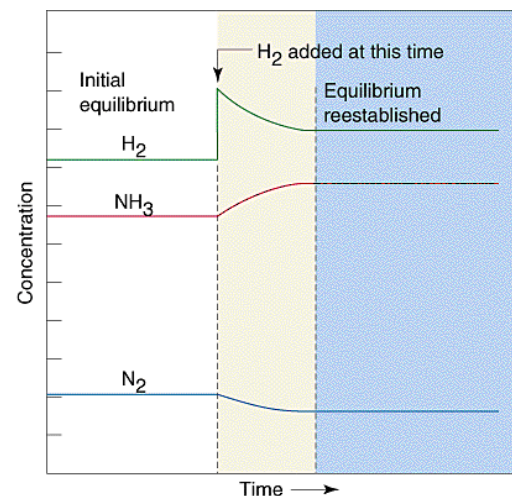
LO 6.3: The student can connect kinetics to equilibrium by using reasoning, such as LeChatelier's principle, to infer the relative rates of the forward and reverse reactions.

$+Q$ vs. K

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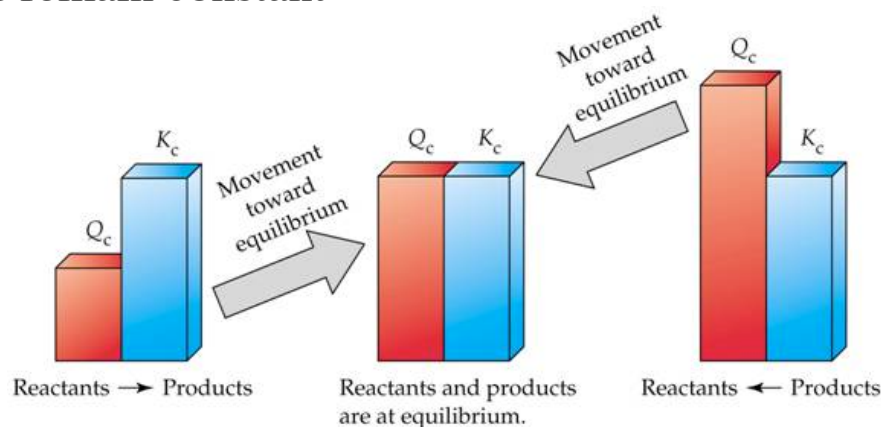
LO 6.4: Given a set of initial conditions and the equilibrium constant, K, use the tendency of Q to approach K to predict and justify the prediction as to whether the reaction will proceed toward products or reactants as equilibrium is approached.

+Calculating *K*

- Equilibrium constants can be determined using experimental concentrations of reactants and products at equilibrium.

- Steps:
  1) Write an equilibrium expression
  2) Determine equilibrium molar concentrations or partial pressures for all substances in expression
  3) Substitute quantities into equilibrium expression and solve.

- Example: Calculate *K* for the following system if 0.1908 mol CO_2, 0.0908 mol H_2, 0.0092 CO, and 0.0092 mol H_2O vapor are present in a 2.00 L vessel at equilibrium:
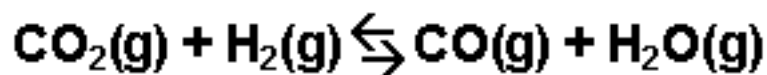
$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

> Click reveals answer and explanation.

LO 6.5: The student can, given data (tabular, graphical, etc.) from which the state of a system at equilibrium can be obtained, calculate the equilibrium constant, K.

+Calculating K

- Equilibrium constants can be determined using experimental concentrations of reactants and products at equilibrium.

Write the equilibrium expression for the reaction system.

$$K_c = \frac{[CO][H_2O]}{[CO_2][H_2]}$$

Since K_c is being determined, check to see if the given equilibrium amounts are expressed in moles per liter (molarity). In this example they are not; conversion of each is requried.

$$[CO_2] = 0.1908 \text{ mol } CO_2/2.00 \text{ L} = 0.0954 \text{ M}$$
$$[H_2] = 0.0454 \text{ M}$$
$$[CO] = 0.0046 \text{ M}$$
$$[H_2O] = 0.0046 \text{ M}$$

Substitute each concentration into the equilibrium expression and calculate the value of the equilibrium constan

$$K_c = \frac{[0.0046][0.0046]}{[0.0954][0.0454]} = 0.0049 \text{ or } 4.9 \times 10^{-3}$$

LO 6.5: The student can, given data (tabular, graphical, etc.) from which the state of a system at equilibrium can be obtained, calculate the equilibrium constant, K.

+Calculating K

- Equilibrium constants can also be determined from both initial and equilibrium concentrations using an ICE chart.

- Steps:
  1) Write an equilibrium expression
  2) Determine molar concentrations or partial pressures for all substances in expression
  3) Determine equilibrium concentrations or partial pressures using an ICE chart.
  4) Substitute quantities into equilibrium expression and solve.
- Example: Initially, a mixture of 0.100 M NO, 0.050 M H2, and 0.100 M H2O was allowed to reach equilibrium. No N2 was present initially. At equilibrium, NO had a concentration of 0.062 M. Determine the value of K for the reaction:
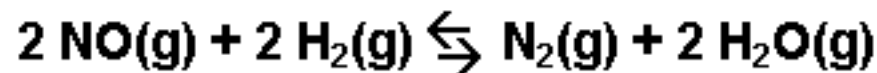
$$2\ NO(g) + 2\ H_2(g) \leftrightarrows N_2(g) + 2\ H_2O(g)$$

> Click reveals answer and explanation.

LO 6.5: Given data (tabular, graphical, etc.) from which the state of a system at equilibrium can be obtained, calculate the equilibrium constant, K.

+Calculating *K*

- Write the equilibrium expression for the reaction.

$$K_c = \frac{[N_2][H_2O]^2}{[NO]^2[H_2]^2}$$

- Check to see if the amounts are expressed in moles per liter (molarity) since K_c is being . In this example they are.

- Create an ICE chart that expresses the initial concentration, the change in concentration, and the equilibrium concentration for each species in the reaction. From the chart you can determine the changes in the concentrations of each species and the equilibrium concentrations. From the example, we start with the following information.

	NO	H_2	N_2	H_2O
Initial Concentration (M)	0.100	0.0500	0	0.100
Change in Concentration (M)	- 2 x	- 2 x	+ x	+ 2 x
Equilibrium Concentration (M)	0.062			

The change in concentration of the NO was (0.062 M - 0.100M) = - 0.038 M. Thus -2 x = - 0.038 and x = 0.019. Note: the negative sign indicates a decreasing concentration, not a negative concentration. The changes in the other species must agree with the stoichiometry dictated by the balance equation. The hydrogen will also change by - 0.038 M, while the nitrogen will increase by + 0.019 M and the water will increase by + 0.038 M. From these changes we can complete the chart to find the equilibrium concentrations for each species.

	NO	H_2	N_2	H_2O
Initial Concentration (M)	0.100	0.0500	0	0.100
Change in Concentration (M)	- 0.038	- 0.038	+ 0.019	+ 0.038
Equilibrium Concentration (M)	0.062	0.012	0.019	0.138

- Substitute the equilibrium concentrations into the equilibrium expression and solve for K_c.

$$K_c = \frac{[0.019][0.138]^2}{[0.062]^2[0.012]^2} = 650 \text{ or } 6.5 \times 10^2$$

LO 6.5: Given data (tabular, graphical, etc.) from which the state of a system at equilibrium can be obtained, calculate the equilibrium constant, K.
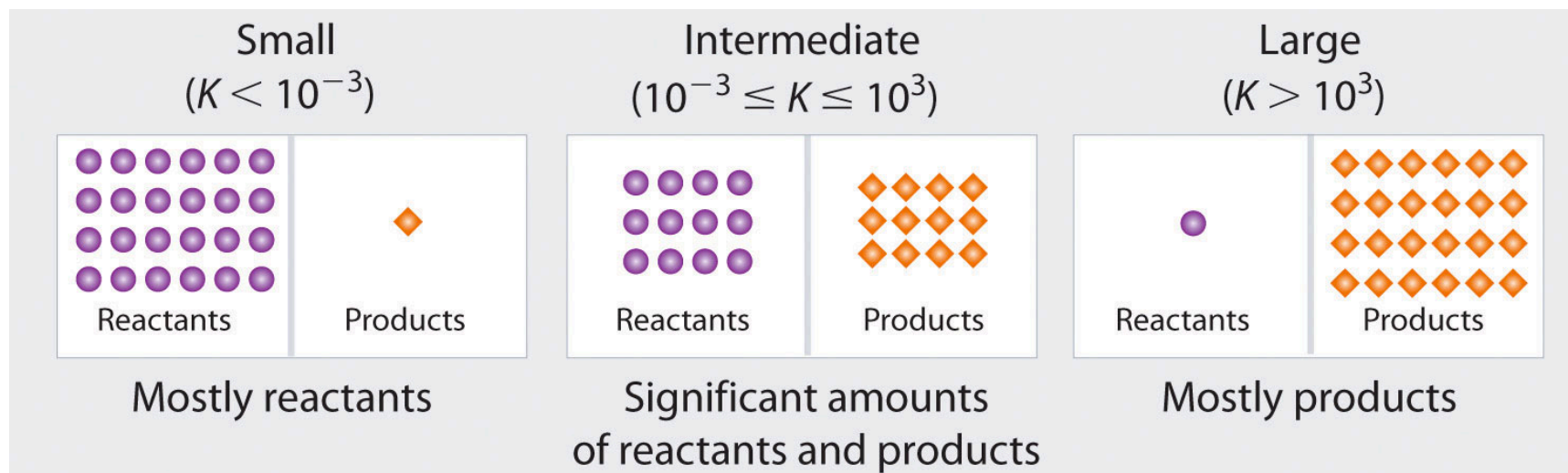
Calculating Equilibrium Concentrations with K

- Equilibrium concentrations can be calculated using a K expression, the K constant, and initial concentrations or partial pressures of substances.

- Steps:
  1) Write an equilibrium expression for the reaction
  2) Set up an ICE table and fill in "initial" quantities
  3) Determine "changes" in the system in terms of x needed for the system to achieve equilibrium
  4) Determine the "equilibrium" values for the system by adding the "initial" and "change" values together
  5) Solve for x using the K expression and the "equilibrium" values. Verify if the change in initial concentrations is negligible using the 5% rule.
  6) Determine all equilibrium quantities using the value of x

- Example: Given the following reaction at 1373 K: $Cl_2(g) \rightleftharpoons 2Cl(g)$, determine the equilibrium partial pressures of all species if 0.500 atm Cl_2 is present initially. $K = 1.13 \times 10^{-4}$ for the reaction at 1373 K.

Click reveals answer.

LO 6.6: Given a set of initial conditions (concentrations or partial pressures) and K, use stoichiometric relationships and the law of mass action (Q equals K at equilibrium) to determine qualitatively and/or quantitatively the conditions at equilibrium for a system involving a single reversible reaction.

Calculating Equilibrium Concentrations with K

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0.497 atm Cl_2 and

0.00752 atm Cl

LO 6.6: Given a set of initial conditions (concentrations or partial pressures) and K, use stoichiometric relationships and the law of mass action (Q equals K at equilibrium) to determine qualitatively and/or quantitatively the conditions at equilibrium for a system involving a single reversible reaction.

+ 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.

Small ($K < 10^{-3}$)		Intermediate ($10^{-3} \le K \le 10^{3}$)		Large ($K > 10^{3}$)	
Reactants	Products	Reactants	Products	Reactants	Products
Mostly reactants		Significant amounts of reactants and products		Mostly products	

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.

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 products
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.

+ 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)

$$Fe^{+3}(aq) + SCN^-(aq) \rightleftharpoons SCN^{2+}(aq)$$

$Fe^{3+}_{(aq)}$

$SCN^-_{(aq)}$

$FeSCN^{2+}_{(aq)}$

add some $Fe^{3+}_{(aq)}$

add some $SCN^-_{(aq)}$

$$Co(H_2O)_6^{2+}{}_{(aq)} + 4\,Cl_{(aq)} \rightleftharpoons CoCl_{4\,(aq)} + 6\,H_2O_{(l)}$$

(pink)   + HEAT   (blue) $\Delta H = +$

Δ

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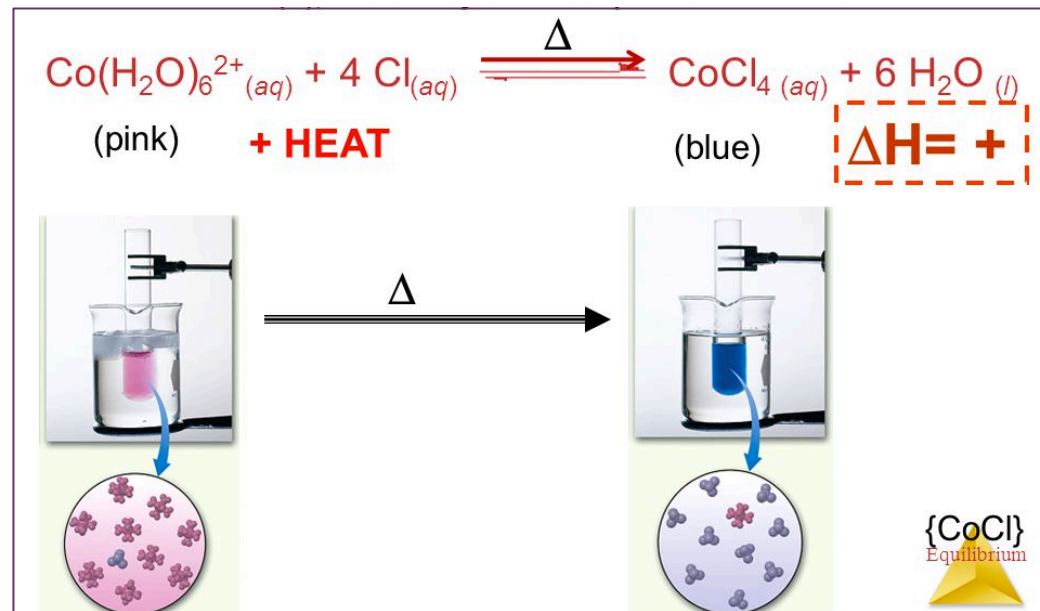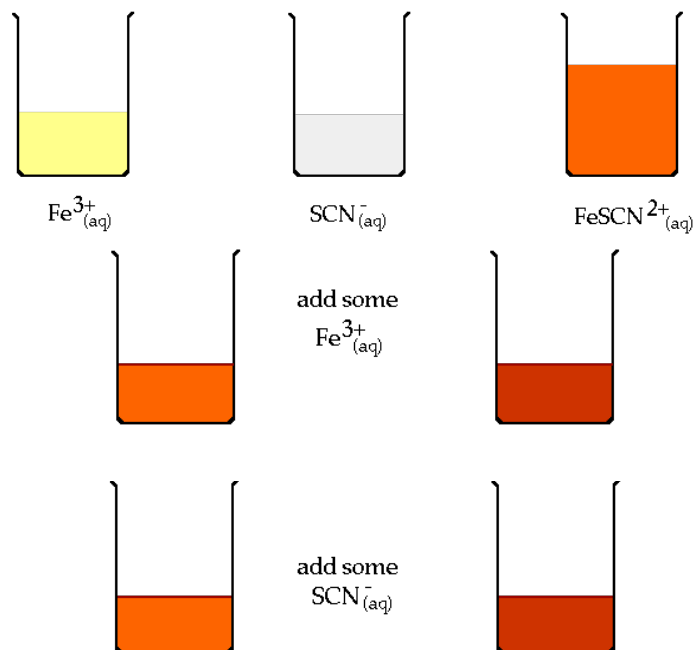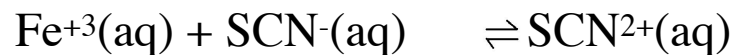
LO 6.9: The student is able to use LeChatelier's principle to design a set of conditions that will optimize a desired outcome, such as product yield.

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.

+ Acid/Base Particulates

General: HA + H_2O → A^- + H_3O^+

Strong: HA + → A^- H_3O^+
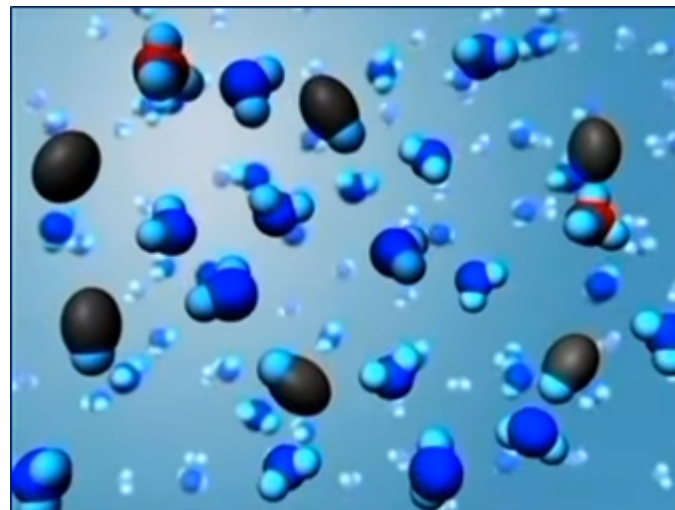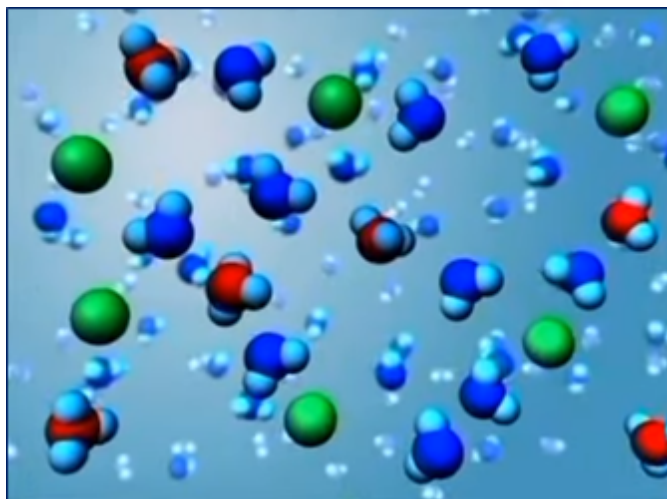
Weak: HA + ⇌ A^- + H_3O^+

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.

+pH of Weak or Strong Acid

Note the similar pH values of both monoprotic acids.

pH= 3.00

1L

pH= 3.00

1L

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

- This is a particulate picture of a weak acid whose [HA] = 1.00M and K_a = 1.00x10^{-6}.
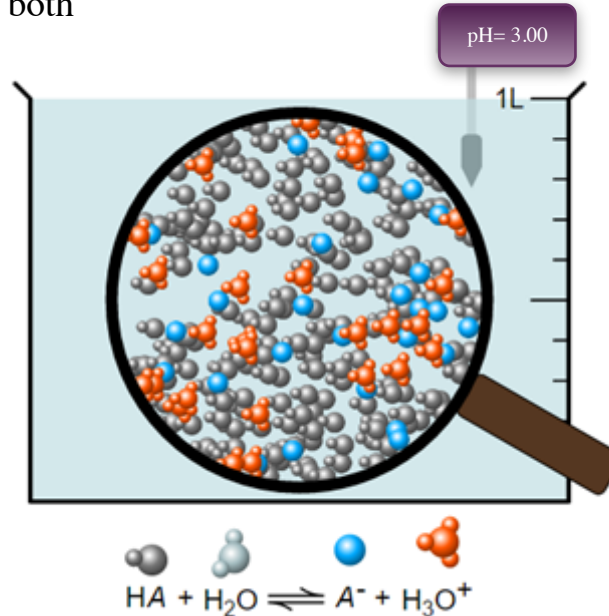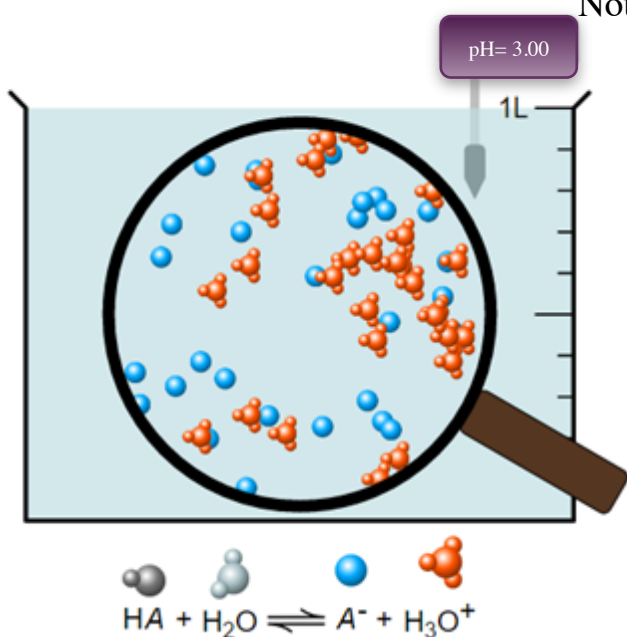
- This is a particulate picture of a strong acid whose [HA] = 0.00100M.
- Note the 100% ionization of this acid.

- pH is a measure of the [H$^+$] in solution. More moles of a weak acid are needed to achieve equivalent [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.

+ Titrations

This illustration shows the titration curve of a strong acid with a strong base.

Titration of 40.00 mL of 0.100 M CH₃CH₂COOH with 0.100 M NaOH

Phenolphthalein
pKₐ of CH₃CH₂COOH=4.89
pH = 8.80 at equivalence point
Buffer region
Methyl red
[CH₃CH₂COOH] = [CH₃CH₂COO⁻]
Volume of NaOH added (mL)
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Titration of 50.0 mL of 0.10 M Acid
$K_a = 10^{-10}$
$K_a = 10^{-8}$
$K_a = 10^{-6}$
$K_a = 10^{-4}$
$K_a = 10^{-2}$
Strong acid
Equivalence point
Volume 0.10 M NaOH added (mL)
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50.0 mL of 0.100 M HCl with 0.100 M NaOH
Equivalence point
Volume NaOH added (mL)
©NCSSM 2003

Video
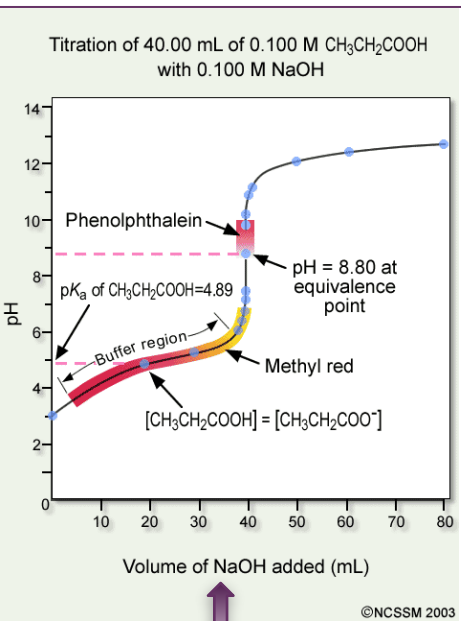
This illustration shows the titration curve of
a weak acid with a strong base
with indicator changes.
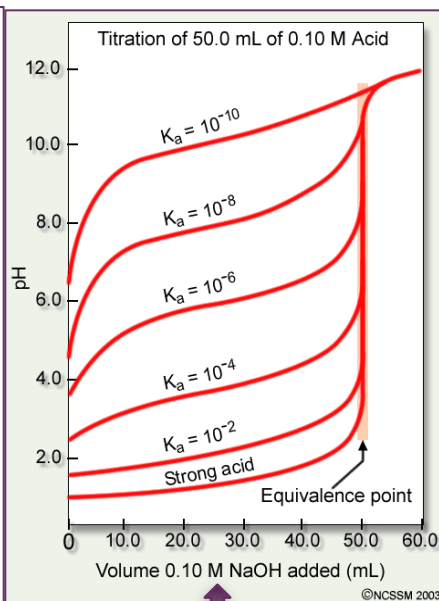
This illustration shows the titration curves
of several weak acids with a strong base

Titration of H₂A with NaOH
pH = 11.9
$pK_{a2} = 9.7$
[A²⁻]
2nd Equiv. pt.
[HA⁻] = [A²⁻]
2nd Half-Equiv. point
pH = 6.0
[HA⁻]
1st Equivalence point
$pK_{a1} = 2.3$
[H₂A] = [HA⁻]
1st Half-Equivalence point
Moles of OH⁻ added
©NCSSM 2003

Titration of 40.00 mL of 0.100 M NH₃ with 0.100 M NaOH
pOH of NH₃ = 4.75
Buffer region
Phenolphthalein
[NH₃] = [NH₄⁺]
pH = 5.27 at equivalence point
Methyl red
Volume of HCl added (mL)
©NCSSM 2003
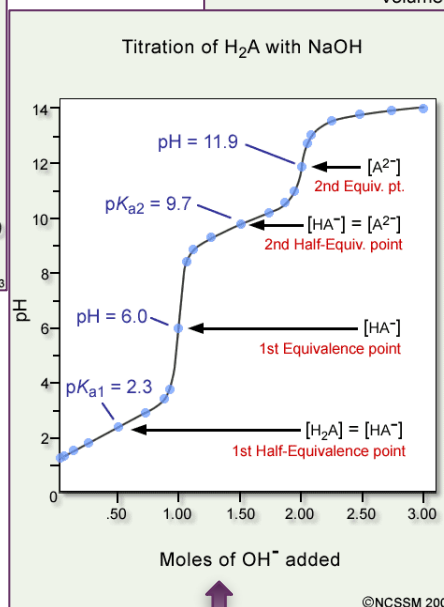
This illustration shows the titration curve of a polyprotic weak acid with a strong base.
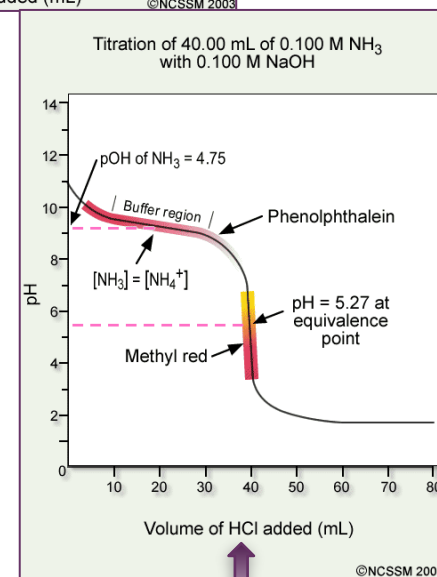
This illustration shows the titration curve of a weak base with a strong acid with indicator changes.

See Source link to review titration calculations.

LO 6.13: The student can interpret titration data for monoprotic or polyprotic acids involving titration of a weak or strong acid by a strong base (or a weak or strong base by a strong acid) to determine the concentration of the titrant and the pK_a for a weak acid, or the pK_b for a weak base.

$+\mathrm{K_w}$ and Temperature

$$K_w = [\mathrm{H^+}][\mathrm{OH^-}] = 1.0 \times 10^{-14} \text{ at } 25°\mathrm{C}$$

T (°C)	K_w (mol^2 dm^{-6})	pH
0	0.114 x 10^{-14}	7.47
10	0.293 x 10^{-14}	7.27
20	0.681 x 10^{-14}	7.08
25	1.008 x 10^{-14}	7.00
30	1.471 x 10^{-14}	6.92
40	2.916 x 10^{-14}	6.77
50	5.476 x 10^{-14}	6.63
100	51.3 x 10^{-14}	6.14

Video

$$E + H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

- As T increases, pH of pure water decreases. The water is NOT becoming more acidic. A solution is only acidic if [H+] > [OH-].
- At 50°C, the pH of pure water is 6.63, which is defined as "neutral", when [H+] = [OH-]. A solution with a pH of 7 at this temperature is slightly basic b/c it is higher than the neutral value of 6.63.
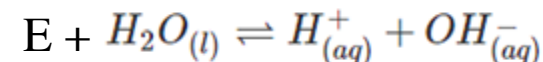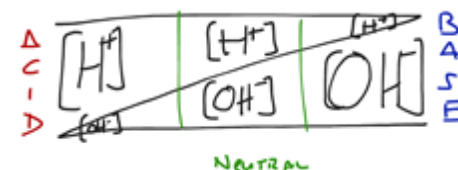
The dissociation of water is endothermic. An increase of energy will shift the reaction to the right, increasing the forward reaction, and increase the value of K_w.

LO 6.14: The student can, based on the dependence of K_w on temperature, reason that neutrality requires [H+] = [OH-] as opposed to requiring pH = 7, including especially the application to biological systems.

+ Acid/Base Mixtures and its pH

A 25 mL sample of hydrofluoric acid (HF) is titrated with 25 mL of 0.30M sodium hydroxide (NaOH). At the equivalence point of the titration, what would the pH of the solution be? Justify with a reaction.

a. pH < 7
b. pH = 7
c. pH > 7
d. pH = pK_a

Click reveals answer and explanation.

LO 6.15: The student can identify a given solution as containing a mixture of strong acids and/or bases and calculate or estimate the pH (and concentrations of all chemical species) in the resulting solution.

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a. $pH < 7$
b. $pH = 7$
c. $pH > 7$
d. $pH = pK_a$

The correct answer is "c" pH>7. At the equivalence point, the moles of acid equal the moles of base. The remaining species would be Na^+ and F^-. The conjugate base, F^- will hydrolyze with water, producing OH^- in solution: $F^-(aq) + H_2O(l) \leftrightarrows HF(aq) + OH^-(aq)$ Select the Source link to see more calculations in this titration.

LO 6.15: The student can identify a given solution as containing a mixture of strong acids and/or bases and calculate or estimate the pH (and concentrations of all chemical species) in the resulting solution.

+pH and Acid/Base Equilibria

1. Vinegar is 0.50M acetic acid, $HC_2H_3O_2$, with a $K_a = 1.8 \times 10^{-5}$. What would be the pH of this solution?

1st click reveals answer and explanation.

2. Identify and compare the relative strengths of the two acids and the two bases in this neutralization reaction: $OH^-(aq) + NH_4^+(aq) \leftrightarrows H_2O(l) + NH_3(aq)$.

2nd 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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$$HC_2H_3O_{2(aq)} + H_2O_{(l)} \rightleftharpoons C_2H_3O_{2(aq)}^- + H_3O_{(aq)}^+$$

	$HC_2H_3O_2$	H_2O	$C_2H_3O_2^-$	H_3O^+
Initial	0.5	---	0	0
Change	-x	---	+x	+x
Equilibrium	0.5 - x	---	x	x

For every acetic acid molecule that dissociates, one acetate ion and one hydronium ion is produced. This can be represented by subtracting "x" from the original acetic acid concentration, and adding "x" to the original concentrations of the dissociated ions.

You can create a modified equilibrium constant expression

$$K_a = \frac{[C_2H_3O_2^-][H_3O^+]}{[HC_2H_3O_2]}$$

and then plug in the concentration values you found in the ICE table

$$1.8 \times 10^{-5} = \frac{x^2}{0.5 - x}$$

so

$$x^2 + (1.8 \times 10^{-5})x - (9 \times 10^{-6}) = 0$$

then use the quadratic formula to calculate

$$x = 0.0030\ M = [H_3O^+]$$

which can be plugged into the formula

$$pH = -\log[H_3O^+]$$
$$-\log(0.0030) = pH = 2.5$$

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

2nd click reveals answer and explanation.

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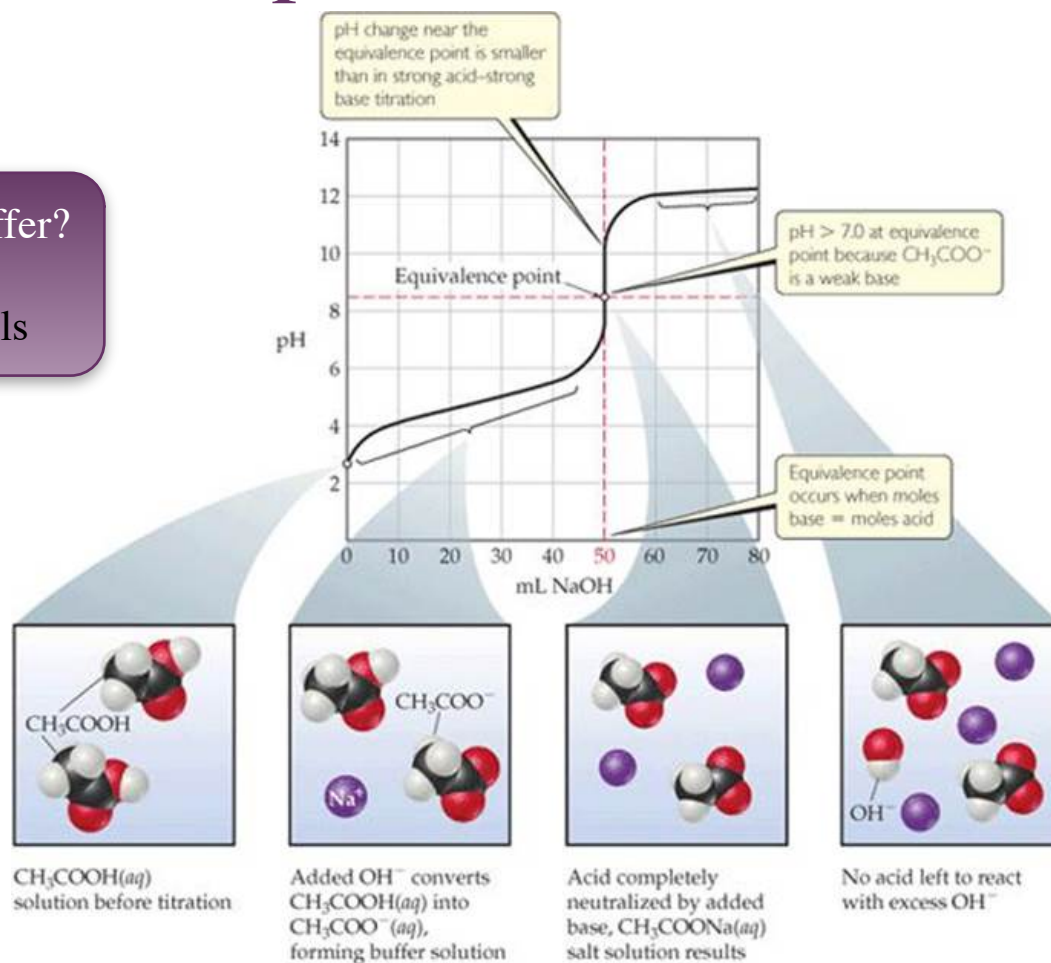
+pH and

$$HC_2H_3O_{2(aq)} + H_2O_{(l)} \rightleftharpoons C_2H_3O_{2(aq)}^- + H_3O_{(aq)}^+$$

	HC₂H₃O₂	H₂O	C₂H₃O₂⁻	H₃O⁺
Initial	0.5	---	0	0
Change	-x	---	+x	+x
Equilibrium	0.5 - x	---	x	x

1. Vinegar is 0.50M acetic acid, $HC_2H_3O_2$, with a $K_a =$ 1.8 x 10⁻⁵. What would be the pH of this solution?

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$$pH = -\log[H_3O^+]$$
$$= -\log(0.0030) = pH = 2.5$$

Answer: Hydroxide(OH⁻), and ammonia(NH₃) are the two bases, with ammonia being the weaker, while ammonium(NH₄⁺) and water are the acids, with water the weaker.

The correct formulation of acid strength is based on a comparison to the K_a's of hydronium (=1) and water (= 1 x 10⁻¹⁴). Any acid that is stronger than hydronium (e.g. HCl) is a strong acid and its conjugate base (chloride) has no effect on pH because it does not hydrolyze in water. Any acid whose strength is between hydronium and water (e.g. ammonium) is a weak acid, and its conjugate is a weak base. Similarly, for bases, any base with K_b greater than that of hydroxide, which is = 1, (e.g., oxide ion as K_2O) is a strong base, and its conjugate acid (K+) has no effect on pH because it does not hydrolyze in water. Any base with K_b between that of hydroxide and water (= 1 x 10⁻¹⁴) is a weak base, and its conjugate is a weak acid (e.g., acetate).

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.
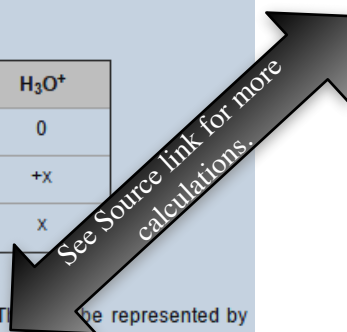
+ Acid/Base reaction species

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.

pH change near the equivalence point is smaller than in strong acid–strong base titration

pH > 7.0 at equivalence point because CH_3COO^- is a weak base

Equivalence point

Equivalence point occurs when moles base = moles acid

mL NaOH

CH_3COOH

CH_3COO^-

Na^+

OH^-

$CH_3COOH(aq)$ solution before titration

Added OH^- converts $CH_3COOH(aq)$ into $CH_3COO^-(aq)$, forming buffer solution

Acid completely neutralized by added base, $CH_3COONa(aq)$ salt solution results

No acid left to react with excess OH^-

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.

How to Build a Buffer:

Getting the pH correct:

- The pH of a buffer is primarily determined by the pKa 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 pKa.

- Choose a conjugate acid-base pair that has a pKa 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.

Weak Base – Strong Acid Titration
0.10 M NH₃ titrated with 0.10 M HCl

Buffered regime in effect

Equivalence Pt at 25.0 mL

Half Equiv Pt at 12.5 mL
$[NH_4^+] = [NH_3]$
so…
$pH = pK_a$
For any acid-base conjugate pair, choose a pair that has a pK_a near the target pH for the buffer.

NH3 0.1 mol/L – titrant = HCl 0.1 mol/L

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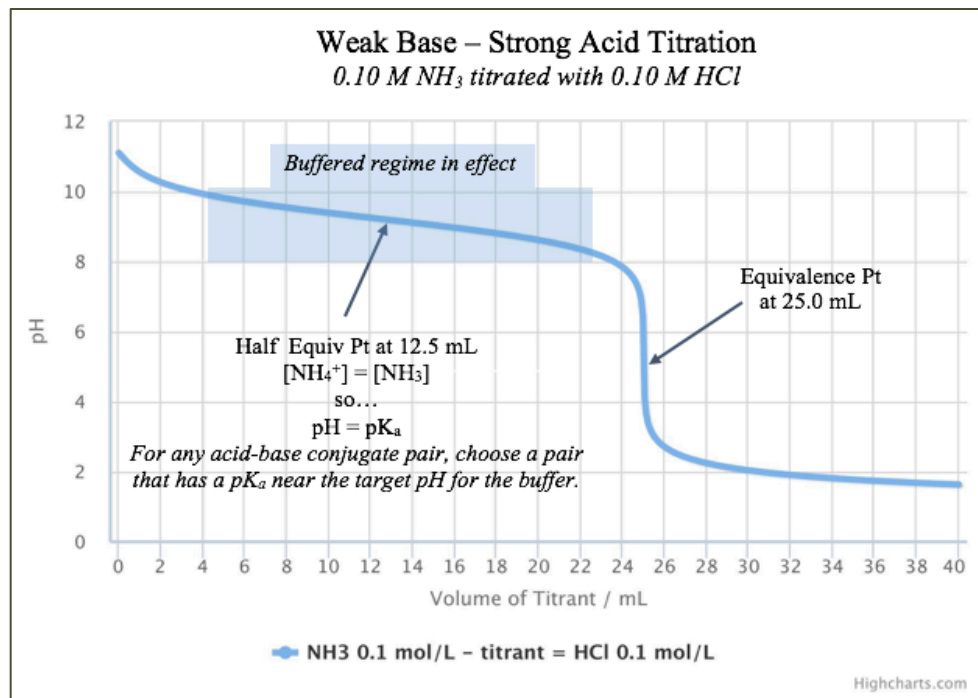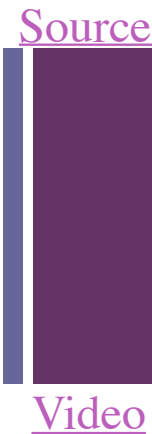
LO 6.18: The student can design a buffer solution with a target pH and buffer capacity by selecting an appropriate conjugate acid-base pair and estimating the concentrations needed to achieve the desired capacity.

How to Build a Buffer:
+

Getting the pH correct:

- The pH of a buffer is primar[ily]
  determined by the pKa of th[e]
  acid in the conjugate acid-b[ase]

- When both species in the co[njugate]
  acid-base pair have equal
  concentrations, the pH of th[e buffer is]
  equal to the pKa.

- Choose a conjugate acid-bas[e pair that]
  has a pKa closest to the pH [you want]
  and then adjust concentratio[ns to fine]
  tune from there.

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  members of the conjugate acid-base

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0.10 M NH_3 titrated with 0.10 M HCl

Buffered regime in effect

Equivalence
at 25.0 mL

Half Equiv Pt at 12.5 mL
$[NH_4^+] = [NH_3]$
so…
$pH = pK_a$
For any acid-base conjugate pair, choose a pair
that has a pK_a near the target pH for the buffer.

pH

Volume of Titrant / mL

NH3 0.1 mol/L – titrant = HCl 0.1 mol/L

LO 6.18: The student can design
selecting an appropriate conjugate
achieve the desired capacity.

+Finding the Major Species

- A 50.0 mL sample of 0.50 M $HC_2H_3O_2$ 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?

(pKa for $HC_2H_3O_2$ is 4.7)

a. $[HC_2H_3O_2] > [C_2H_3O_2{}^{1-}] > [\,H^+\,] > [\,OH^-\,]$

b. $[HC_2H_3O_2] = [C_2H_3O_2{}^{1-}] > [\,H^+\,] > [\,OH^-\,]$

c. $[HC_2H_3O_2] > [C_2H_3O_2{}^{1-}] = [\,H^+\,] > [\,OH^-\,]$

d. $[C_2H_3O_2{}^{1-}] > [HC_2H_3O_2] > [\,OH^-\,] > [\,H^+\,]$

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 pKa associated with the labile proton.

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  a. $[HC_2H_3O_2] > [C_2H_3O_2{}^{1-}] > [\,H^+\,] > [\,OH^-\,]$

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  d. $[C_2H_3O_2{}^{1-}] > [HC_2H_3O_2] > [\,OH^-\,] > [\,H^+\,]$

Option B is correct.

At the half equivalence point, the concentrations of the weak acid and its conjugate base are equal because the OH- ion has reacted with half of the original acetic acid. The pH of the buffer is equal to the pKa at that point, so the [H+] is $10^{-4.7}$ which is far lower than the concentrations of the conjugates but far higher than the [OH-] which has a value of $10^{-9.3}$.

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 pKa associated with the labile proton.

+ The Buffer Mechanism

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 H_3O^+ and 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.

If a strong acid is added to the HF/F- buffer, then the the added acid will react completely with the available base, F-. This results in a nearly unchanged $[H_3O^+]$ and a nearly unchanged pH.

$$H_3O^+{}_{(aq)} + F^-{}_{(aq)} \rightarrow HF_{(aq)} + H_2O_{(l)}$$
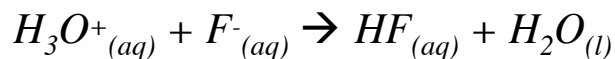
If a strong base is added to the HF/F- buffer, then the added base will react completely with the available acid, HF. This results in a nearly unchanged $[H_3O^+]$ and a nearly unchanged pH.

$$HF_{(aq)} + OH^-{}_{(aq)} \rightarrow F^-{}_{(aq)} + H_2O_{(l)}$$
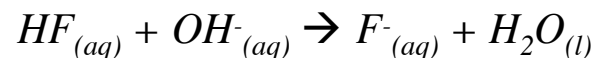
The slight shift in pH after challenge is governed by the hydrolysis equilibrium of HF, based on the new HF and F- concentrations:

$$HF_{(aq)} + H_2O_{(l)} \rightleftharpoons F^-{}_{(aq)} + H_3O^+{}_{(aq)}$$
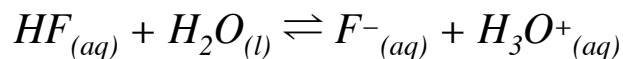
LO 6.20: The student can identify a solution as being a buffer solution and explain the buffer mechanism in terms of the reactions that would occur on addition of acid/base.

$+K_{sp}$ and Solubility Calculations

Question:

What is the maximum number of moles of AgBr that will fully dissolve in 1.0 L of water, if the Ksp value of silver bromide is 4.0×10^{-12}?

4.0 x 10^{-12} b. 2.0 x 10^{-12} c. 4.0 x 10^{-6} d. 2.0 x 10^{-6}

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 K_{sp} values.

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Answer:

The correct answer is "d" 2.0×10^{-6} . To determine the solubility of AgBr we need to determine the maximum concentrations of Ag+ and Br- that will equal the equilibrium constant. The Ksp equation is

Ksp = [Ag+][Br-] with [Ag+] = [Br-] = X, so to solve for X we need to take the square root of 4.0×10^{-12}

LO 6.21: The student can predict the solubility of a salt, or rank the solubility of salts, given the relevant K_{sp} values.

+ Find a K_{sp} from solubility data

Using a conductivity meter and a pH probe, a student determined the molar solubility of saturated solutions made by dissolving hydroxide salts in water. The student's data is shown in the table below:

Compound	Solubility (mol/L)
$Ba(OH)_2$	0.11 M
$Ca(OH)_2$	0.011 M
$Cr(OH)_3$	1.3×10^{-8} M
$Sn(OH)_2$	1.1×10^{-9} M

Which of the hydroxide salts above has the smallest K_{sp} value?

a. $Ba(OH)_2$ b. $Ca(OH)_2$ c. $Cr(OH)_3$ d. $Sn(OH)_2$

Click reveals answer and explanation.

LO 6.22: The student can interpret data regarding solubility of salts to determine, or rank, the relevant Ksp values.

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Which of the hydroxide salts above has the smallest K_{sp} value?

a. $Ba(OH)_2$ b. $Ca(OH)_2$ c. $Cr(OH)_3$ d. $Sn(OH)_2$

Option C is correct.

$Ba(OH)_2$, $Ca(OH)_2$ and $Sn(OH)_2$ all have the same Ksp expression $K = [X][2X]^2$ or $Ksp = 4[X]^3$
So the salt with the lowest solubility will have the smallest Ksp.
$\quad$ Ksp for $Sn(OH)_2 = (4)(1.1 \times 10^{-9})^3 = 5.4 \times 10^{-27}$
$Cr(OH)_3$'s Ksp expression is different. It is $Ksp = [X][3X]^3 = 27[X]^4$
$\quad$ Ksp for $Cr(OH)_3 = (27)(1.3 \times 10^{-8})^4 = 6.7 \times 10^{-31}$

$\quad$ Solving without a calculator... Ba, Ca and Sn all have the same Ksp expression, so the smallest solubility will have the smallest Ksp.
$\quad$ The contest is now between $Sn(OH)_2$ and $Cr(OH)_3$. You need to quickly establish that since $(10^{-8})^4 = 10^{-32}$ and $(10^{-9})^3 = 10^{-27}$ the Ksp of $Cr(OH)_3$ will be smaller than that of $Sn(OH)_2$.

LO 6.22: The student can interpret data regarding solubility of salts to determine, or rank, the relevant Ksp values.

+Common Ion Effect

The solubility of a sparingly soluble hydroxide can be greatly increased by the addition of an acid. For example, the hydroxide salt $Mg(OH)_2$ is relatively insoluble in water:

$$Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2OH^-_{(aq)} \qquad \text{With } Ksp = 5.61 \times 10^{-12}$$
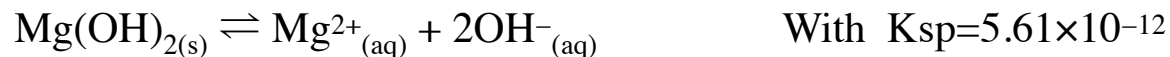
When acid is added to a saturated solution that contains excess solid $Mg(OH)_2$, the following reaction occurs, removing OH– from solution:

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$
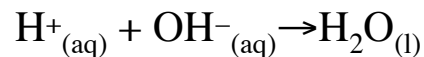
The overall equation for the reaction of $Mg(OH)_2$ with acid is thus

$$Mg(OH)_{2(s)} + 2H^+_{(aq)} \rightleftharpoons Mg^{2+}_{(aq)} + 2H_2O_{(l)} \qquad (18.7.7)$$
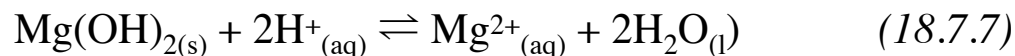
As more acid is added to a suspension of $Mg(OH)_2$, the equilibrium shown in Equation 18.7.7 is driven to the right, so more $Mg(OH)_2$ dissolves.

In contrast, the solubility of a sparingly soluble salt may be decreased greatly by the addition of a common ion. For example, if $MgCl_2$ is added to a saturated $Mg(OH)_2$ solution, additional $Mg(OH)_2$ will precipitate out. The additional Mg^{2+} ions will shift the original equilibrium to the left, thus reducing the solubility of the magnesium hydroxide.

LO 6.23: The student can interpret data regarding the relative solubility of salts in terms of factors (common ions, pH) that influence the solubility.

+ Salt dissolution: ΔH and ΔS
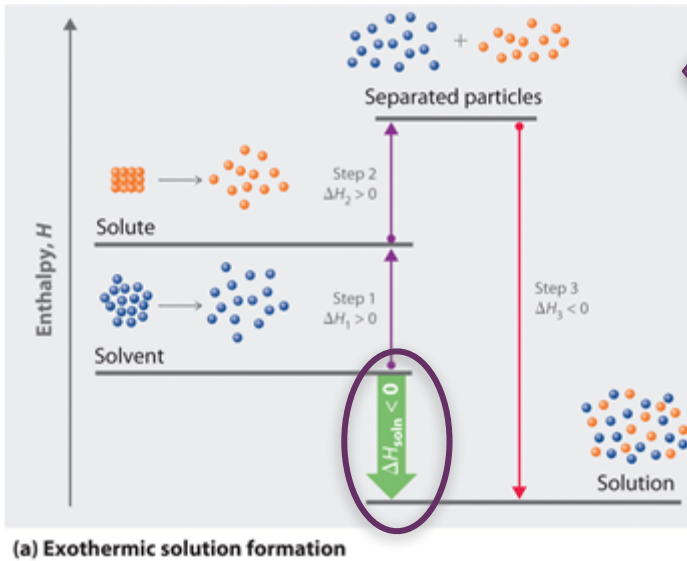
- The enthalpy (ΔH_{soln}) of dissolution is dependent upon the intermolecular forces of the solute and solvent.
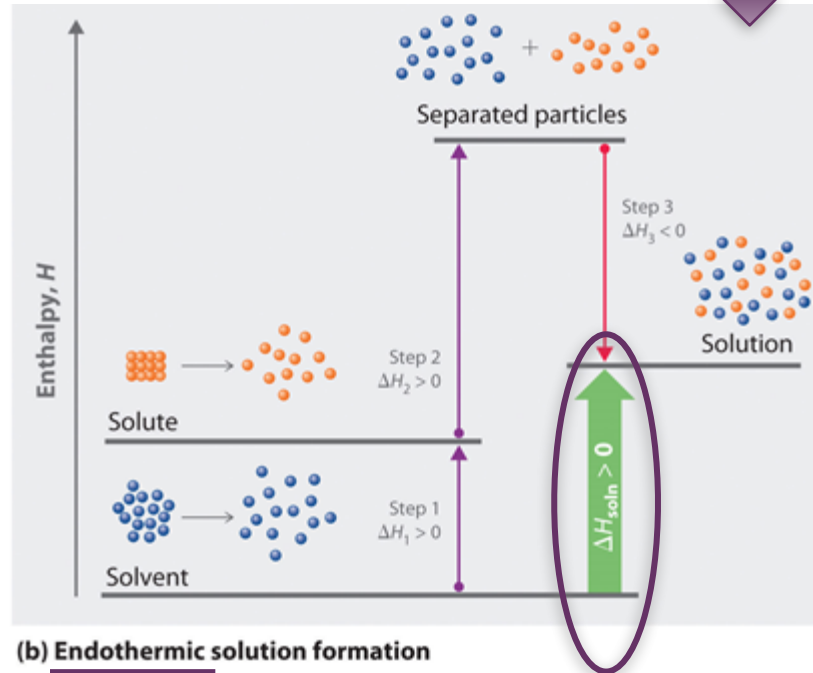
(a) Exothermic solution formation

(b) Endothermic solution formation
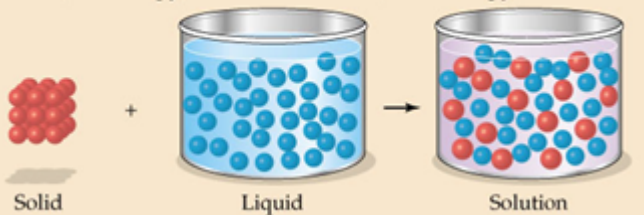
- The entropy (ΔS_{soln}) of dissolution generally increases the disorder of the system.

LO 6.24: The student can analyze the enthalpic and entropic changes associated with the dissolution of a salt, using particulate level interactions and representations.

+ K, ΔG° and thermodynamic favorability

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

$$= -RT \ln K$$

$$= -n\,F\,E°$$

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

$G°_{reactants}$

$\Delta G°rxn < 0$

$Q = 1,$
$m = \Delta G$

$G°_{products}$

G (free energy)

$Q < K_{eq}$

$Q = K_{eq}$

$Q > K_{eq}$

Extent of Reaction

$$Q = \frac{[HI]^2}{[H_2][I_2]}$$

$$K_{eq} = \frac{[HI]^2_{eq}}{[H_2]_{eq}[I_2]_{eq}} = 49.5$$

(440°C)

position of equilibrium corresponds to the <u>minimum</u> of free energy

At the minimum, the system is in <u>dynamic equilibrium</u> and $\Delta G = 0$.

$$\Delta G_{rxn} = \Delta G°_{rxn} + RT\ln Q$$
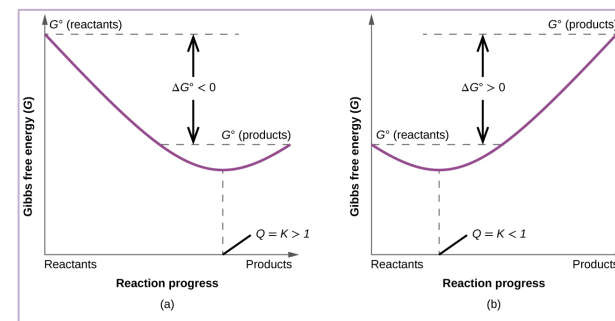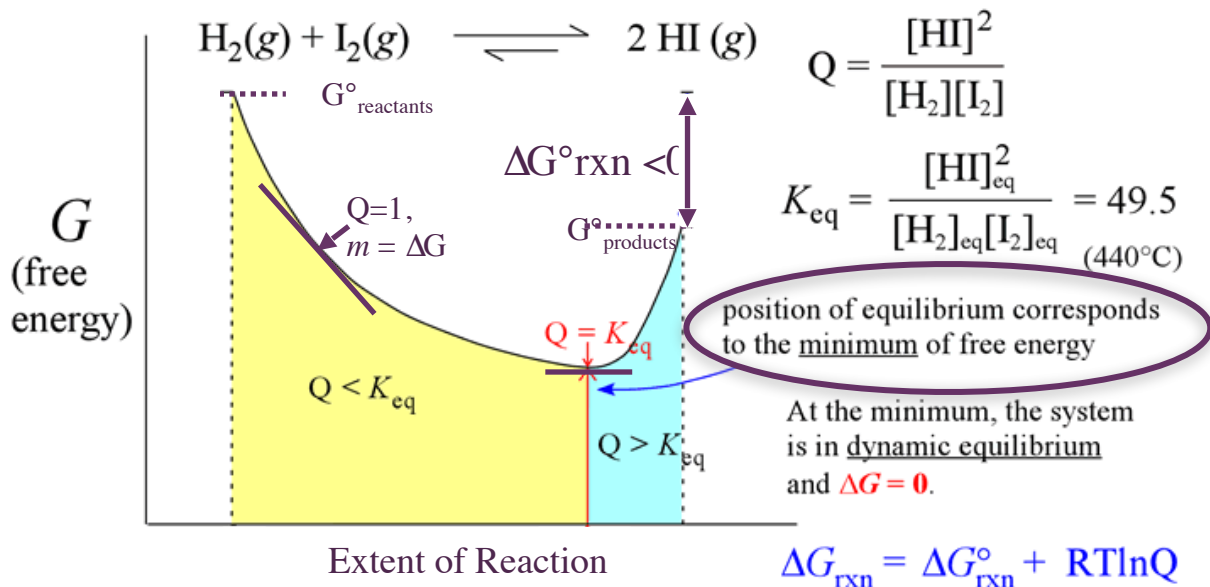
The key to understanding the relationship between ΔG° and K is recognizing that the magnitude of ΔG° tells us how far the standard-state is from equilibrium. The smaller the value of ΔG° , the closer the standard-state is to equilibrium. The larger the value of ΔG°, the further the reaction has to go to reach equilibrium.

LO 6.25: The student is able to express the equilibrium constant in terms of ΔG ° and RT and use this relationship to estimate the magnitude of K and, consequently, the thermodynamic favorability of the process.

Science Practices

Laboratory Exercises

+ Gravimetric Analysis

- What It Determines:
  - amount of analyte by mass measurements
  - % composition
  - empirical formulas

- How It Can Be Done:
  - Dehydration of a hydrate
  - Forming a precipitate, which is then isolated and massed

- Analysis:
  - Remember to ALWAYS go to moles!
  - use mole ratios to convert between various components

Step 1
Dissolve

Solid soluble salt containing
Pb^{2+}(●) and other
chemical species (●)

Solution with dissolved
Pb^{2+}(●) and other
chemical species (●)

Science Practices
1.5 The student can *re-express key elements* of natural phenomena across multiple representations in the domain.
2.2 The student can *apply mathematical routines* to quantities that describe natural phenomena.
4.2 The student can *design a plan* for collecting data to answer a particular scientific question.
5.1 The student can *analyze data* to identify patterns or relationships.
6.1 The student can *justify claims with evidence*.

Learning Objectives
1.3: The student is able to select and apply mathematical relationships to mass data in order to justify a claim regarding the identity and/or estimated purity of a substance.
1.17: The student is able to express the law of conservation of mass quantitatively and qualitatively using symbolic representations and particulate drawings.
1.19: The student can design, and/or interpret data from, an experiment that uses gravimetric analysis to determine the concentration of an analyte in a solution.

+ Gravimetric Analysis

Source

- What It Determines:
  - amount of analyte by mass measurements
  - % composition
  - empirical formulas

- How It Can Be Done:
  - Dehydration of a hydrate
  - Forming a precipitate, which is then isolated and massed

- Analysis:
  - Remember to ALWAYS go to moles!
  - use mole ratios to convert between various components

Video

Virtual Lab

Step 2
Add solution containing SO_4^{2-} (•)

Solution with dissolved Pb^{2+} (•) and other chemical species (•)

Solid $PbSO_4$ and solution with other chemical species (•) and left over SO_4^{2-} (•)

Science Practices
1.5 The student can *re-express key elements* of natural phenomena across multiple representations in the domain.
2.2 The student can *apply mathematical routines* to quantities that describe natural phenomena.
4.2 The student can *design a plan* for collecting data to answer a particular scientific question.
5.1 The student can *analyze data* to identify patterns or relationships.
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  - Forming a precipitate, which is then isolated and massed

- Analysis:

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  - use mole ratios to convert between various components

Step 3
Filter and weigh the solid $PbSO_4$

Solid $PbSO_4$ and solution with other chemical species (•) and left over SO_4^{2-}(•)

+ Gravimetric Analysis

- What It Determines:
  - amount of analyte by mass measurements
  - % composition
  - empirical formulas

- How It Can Be Done:
  - Dehydration of a hydrate
  - Forming a precipitate, which is then isolated and massed

- Analysis:
  - Remember to ALWAYS go to moles!
  - use mole ratios to convert between various components

Filter funnel
Filter paper
Solid $PbSO_4$
Mass This Solid
Erlenmeryer Flask
Filtration Set-up

Science Practices
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  - use mole ratios to convert between various components

Filter funnel
Filter paper
Solid $PbSO_4$
Mass This Solid
Erlenmeryer Flask
Filtration Set-up

Possible Source of Error	Contamination in solid	Incomplete Precipitation	Solid not fully dehydrated
Impact on Results	measured mass too large	Lose ion in filtrate – mass too small	measured mass too large

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+Gas Laws Labs

Determination of Molar Mass of a Volatile Liquid
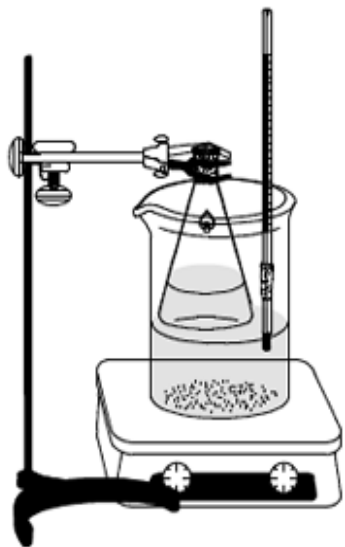
$$PV = nRT$$

$$mm = n/m$$

http://chemskills.com/?q=ideal_gas_law

Determination of Molar Volume of a Gas

acid

Mg

water

1.

Diffusion : Graham's Law Demo

$NH_{3(aq)}$ on cotton wool

white cloud of NH_4Cl

$HCl_{(aq)}$ on cotton wool

(c) doc b

Science Practices
1.4 The student can *use representations and models* to analyze situations or solve problems qualitatively and quantitatively.
2.2 The student can *apply mathematical routines* to quantities that describe natural phenomena.
2.3 The student can *estimate numerically* quantities that describe natural phenomena.
6.4 The student can *make claims and predictions about natural phenomena* based on scientific theories and models.

Learning Objectives
LO 2.4: The student is able to use KMT and concepts of intermolecular forces to make predictions about the macroscopic properties of gases, including both ideal and nonideal behaviors.
LO 2.6: The student can apply mathematical relationships or estimation to determine macroscopic variables for ideal gases.

+Gas Laws Labs

Determination of Molar Mass of a Volatile Liquid

- Volatile liquid heated until completely vaporized
- PV=nRT to solve for n:
  - Temperature of water bath=T
  - Small hole in stopper means Pressure = room pressure
  - Volume=volume of flask
- Divide Mass of recondensed unknown by moles, compare to known molar mass to ID unknown
- Assume vapor completely recondenses
- →If lose vapor, then mass would be too low, and moles would be low

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Mg

water

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Determination of Molar Volume of a Gas

hydrogen gas

Mg

water

2.

Diffusion : Graham's Law Demo

NH$_{3(aq)}$ on cotton wool   white cloud of NH$_4$Cl   HCl$_{(aq)}$ on cotton wool

(c) doc b

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Determination of Molar Volume of a Gas

hydrogen gas

dilute acid

water +
dilute acid + $MgCl_{2(aq)}$

3.

Diffusion : Graham's Law Demo

$NH_{3(aq)}$ on cotton wool   white cloud of NH_4Cl $HCl_{(aq)}$ on cotton wool

(c) doc b

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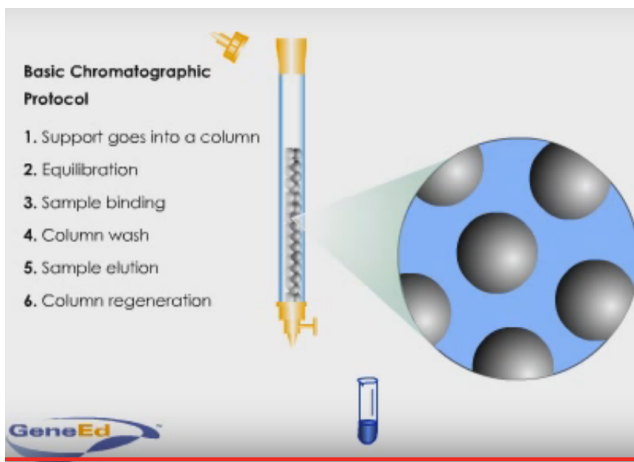
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Determination of Molar Volume of a Gas

After rxn, eudiometer lowered into water until levels equal so pressure inside room and tube are same

Use Dalton's Law to subtract P_{water}

Sources of error:

- Mg left: moles of H_2 too low

- Air bubble at start: volume of gas too high

Source 1

Source 2

Video 1

Video 2

Video 3

Diffusion : Graham's Law Demo

$NH_{3(aq)}$ on cotton wool — white cloud of NH_4Cl — $HCl_{(aq)}$ on cotton wool

(c) doc b

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Use Dalton's Law to subtract P_{water}

Sources of error:

- Mg left: moles of H_2 too low
- Air bubble at start: volume of gas too high

Diffusion : Graham's Law Demo

- How It's Done/Analysis:
  - Ends of glass tube plugged with soaked cotton
  - White ring is NH_4Cl ppt

  - Ppt will not be exactly in middle…

- Molar mass of NH_3 is lower than MM of HCl, so ring will be toward right side of tube
- Graham's Law can be used to establish ratios which can be applied to distances

---

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+Gas Laws Labs

After rxn, eudiometer lowered into water until levels equal

Source 1

Question:

A sealed gas cylinder has a mixture of three gasses, 0.25 moles of He, 0.25 moles of Ne and 0.50 moles of Kr. If the total pressure in the cylinder was 100 mmHg, what would be the partial pressure of Ne in the cylinder?

a. 0.25 mmHg
b. 0.50 mmHg
c. 25 mmHg
d. 50 mmHg
e. 100 mmHg

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+ Chromatography

Chromatography

All chromatographic techniques flow the mixture, that is to be separated, through a material that **retains some components more than others**.

This causes different components to flow through the material at different speeds, so they separate.

(includes nice discussion of biological applications)

Basic Chromatographic Protocol

1. Support goes into a column
2. Equilibration
3. Sample binding
4. Column wash
5. Sample elution
6. Column regeneration

GeneEd

Column Chromatography

- Column chromatography: technique that uses an adsorbent packed in a glass column, and a solvent that moves down slowly through the packed column.
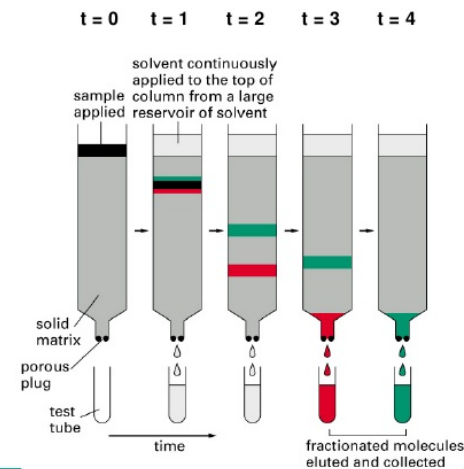
t = 0   t = 1   t = 2   t = 3   t = 4

solvent continuously applied to the top of column from a large reservoir of solvent

sample applied

solid matrix

porous plug

test tube

time

fractionated molecules eluted and collected

Advantage: We can collect and use the fractions

Science Practices
4.2 The student can *design a plan* for collecting data to answer a particular scientific question.
5.1 The student can *analyze data* to identify patterns or relationships.
6.2 The student can *construct explanations of phenomena based on evidence* produced through scientific practices.
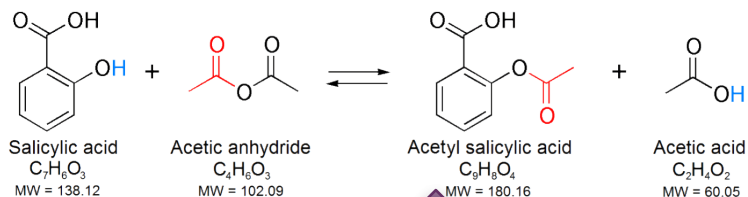
Learning Objectives
LO 2.7: The student is able to explain how solutes can be separated by chromatography based on intermolecular interactions.
LO 2.10: The student can design and/or interpret the results of a separation experiment (filtration, paper chromatography, column chromatography, or distillation) in terms of the relative strength of interactions among and between the components.

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Chromatograph

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Click here to watch animation explaining column chromatography

Chromatographic
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...rt goes into a column
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Source (includes nice discussion of biological applica...

t = 0   t = 1   t = 2   t = 3   t = 4

solvent continuously applied to the top of
sample column from a large
applied reservoir of solvent

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solid matrix

porous plug

test tube

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Column Chromatography

- Column chromatography: technique that uses an adsorbent pa... glass column, and a solvent that moves down slowly through t... column.

[Source](#) (includes nice discussion of biological applica...

- Main Error:
  - Incomplete Separation

- Can be caused by:
  - Inconsistent spotting
  - Overloading
  - Improper packing (column)
  - Poor solvent choice

Advantage: We can collect and use the fractions

t = 0   t = 1   t = 2   t = 3   t = 4

solvent continuously applied to the top of column from a large reservoir of solvent

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+ Synthesis
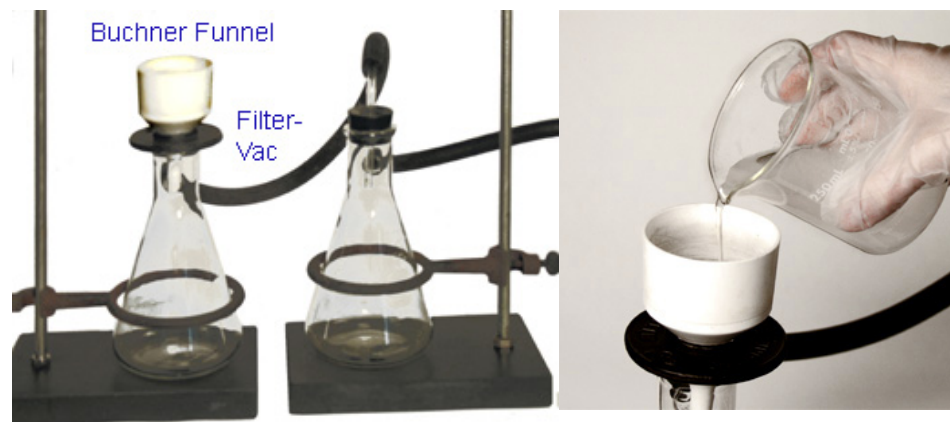
- Inorganic Synthesis Examples:
  - Synthesis of Coordination Compound
  - Synthesis of Alum from aluminum

- Organic Synthesis Example:
  - Synthesis of Aspirin

Salicylic acid
$C_7H_6O_3$
MW = 138.12

Acetic anhydride
$C_4H_6O_3$
MW = 102.09

Acetyl salicylic acid
$C_9H_8O_4$
MW = 180.16

Acetic acid
$C_2H_4O_2$
MW = 60.05

- Syntheses are done in solution, and require purification by filtration, recrystalization, column chromatography or a combination

- % Yield is calculated; analysis is done by melting point, NMR, IR

Synthesizing Alum Procedure:

Source of aluminum is reacted with KOH

Possible Error Sources: impurity in Al (such as plastic coating) prevents complete rxn

LO:

+ Synthesis

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- Syntheses are done in solution, and require purification by filtration, recrystalization, column chromatography or a combination

- % Yield is calculated; analysis is done by melting point, NMR, IR

Synthesizing Alum Procedure:

Mixture heated until no Al(s) is left

Possible Error Sources: some Al(s) remains undissolved

LO:

+ Synthesis
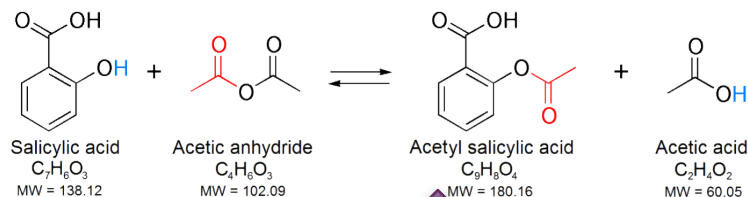
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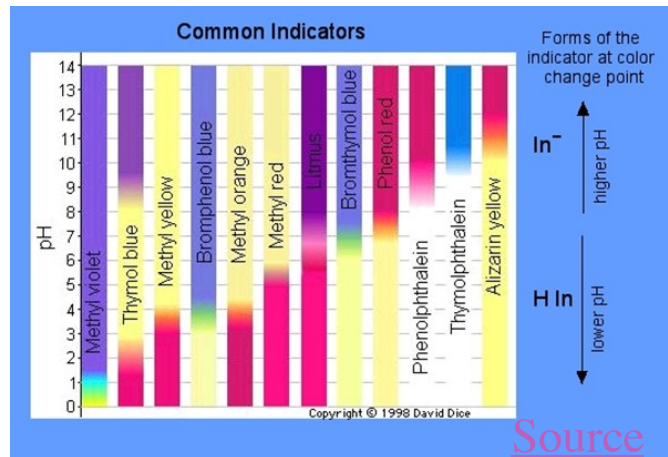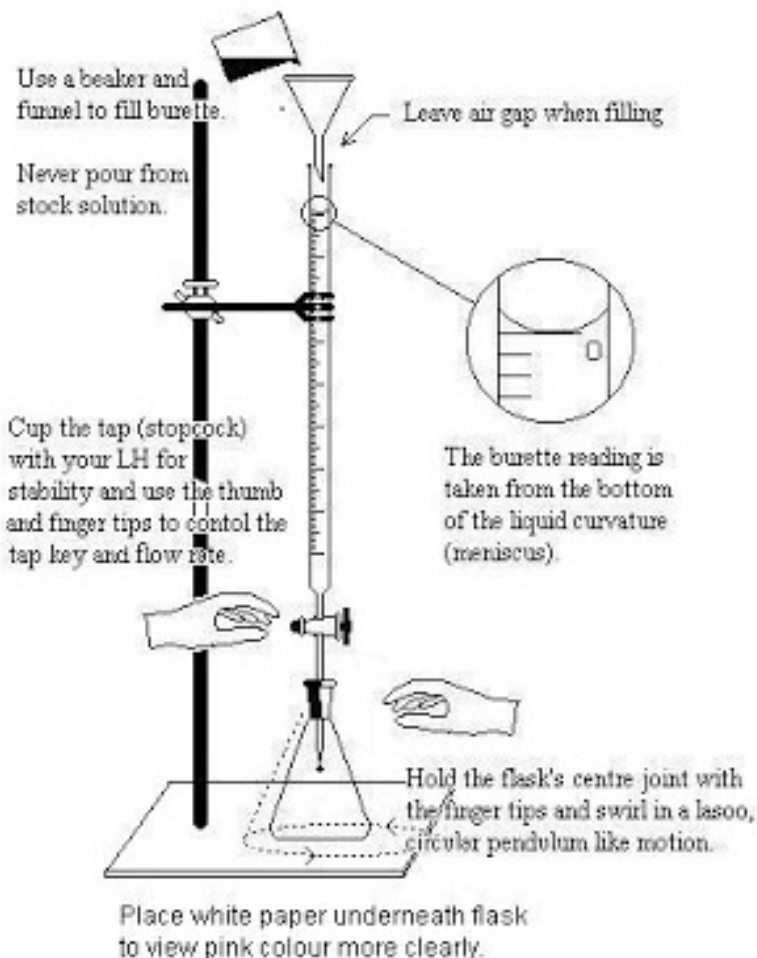H_2SO_4 is added to ppt $Al(OH)_3$

Possible Error Sources: incomplete precipitation
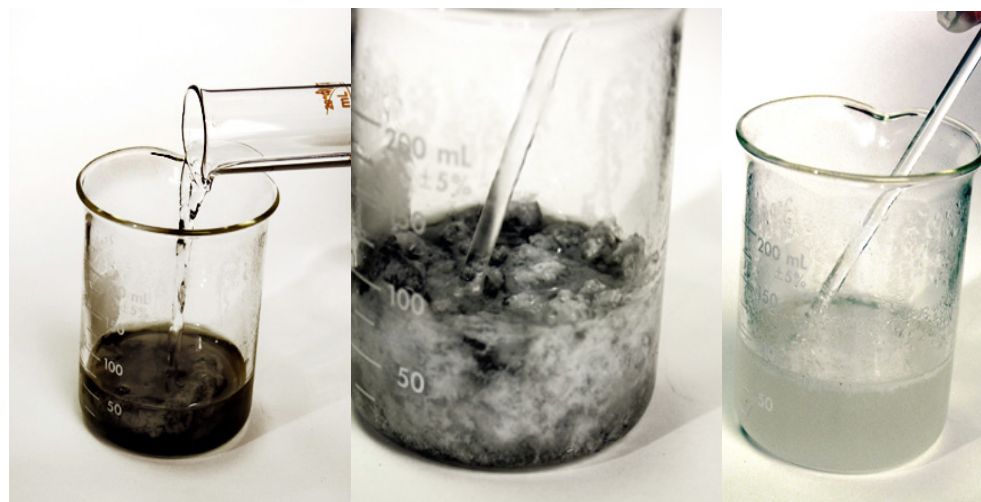
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- % Yield is calculated; analysis is done by melting point, NMR, IR

Synthesizing Alum Procedure:

Recrystallize alum in ice bath

Possible Error Sources: crystals form too quickly, incomplete recrystallization

Science Practices
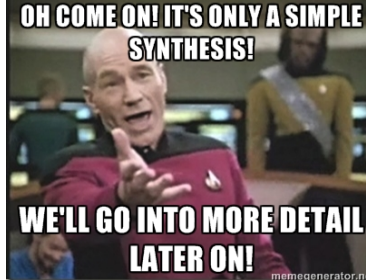
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6.1 The student can *justify claims with evidence*.

LO:

Learning Objectives

LO 3.5: The student is able to design a plan in order to collect data on the synthesis or decomposition of a compound to confirm the conservation of matter and the law of definite proportions.
LO 3.6: The student is able to use data from synthesis or decomposition of a compound to confirm the conservation of matter and the law of definite proportions.
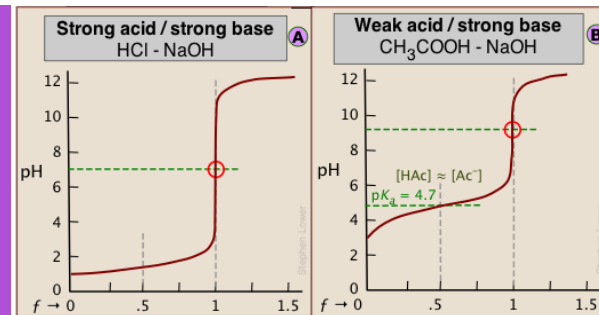
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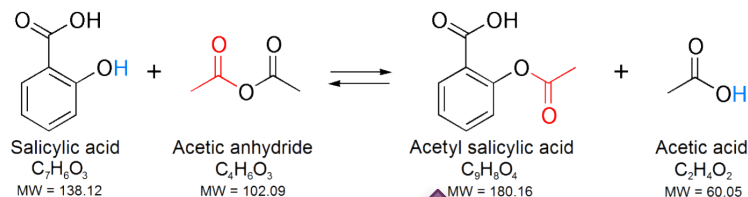
Synthesizing Alum Procedure:

Filter and collect alum crystals

Possible Error Sources: crystals escape to filtrate, crystals not washed well and remain wet

LO:

+ Synthesis

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Synthesizing Alum Procedure:

<table>
<tr><td>

Science Practices

2.1 The student can *justify the selection of a mathematical routine* to solve problems.

2.2 The student can *apply mathematical routines* to quantities that describe natural phenomena.

4.2 The student can *design a plan* for collecting data to answer a particular scientific question.

6.1 The student can *justify claims with evidence*.

</td><td>

Learning Objectives

LO 3.5: The student is able to design a plan in order to collect data on the synthesis or decomposition of a compound to confirm the conservation of matter and the law of definite proportions.

LO 3.6: The student is able to use data from synthesis or decomposition of a compound to confirm the conservation of matter and the law of definite proportions.

</td></tr>
</table>

LO:

+ Titration- Acid/Base

Common Indicators

Forms of the indicator at color change point

Copyright © 1998 David Dice

Use a beaker and funnel to fill burette.

Leave air gap when filling

Never pour from stock solution.

The burette reading is taken from the bottom of the liquid curvature (meniscus).

Cup the tap (stopcock) with your LH for stability and use the thumb and finger tips to control the tap key and flow rate.

Hold the flask's centre joint with the finger tips and swirl in a lasso, circular pendulum like motion.

Place white paper underneath flask to view pink colour more clearly.

Strength of Acids affects shape of graph:

Strong acid / strong base
HCl - NaOH (A)

Weak acid / strong base
CH_3COOH - NaOH (B)

$[HAc] \approx [Ac^-]$
$pK_a = 4.7$

Polyprotic acids have multiple end points:

pH = 10.3

pH = 6.4

$[H_2CO_3^+] \approx [HCO_3^-]$

$[HCO_3^-] \approx [CO_3^{2-}]$

H_2CO_3 titrated with NaOH
$K_{a1} = 10^{-6.4}$, $K_{a2} = 10^{-10.3}$

equivalent fraction of base added

$[CO_3^{2-}] \approx [HCO_3^-]$

Na_2CO_3 titrated with HCl
$K_{b1} = 10^{-7.6}$, $K_{b2} = 10^{-3.7}$

pH = 7.6

$[HCO_3^-] \approx [H_2CO_3]$

pH = 3.7

equivalent fraction of acid added

Science Practices
1.4 The student can *use representations and models* to analyze situations or solve problems qualitatively and quantitatively.
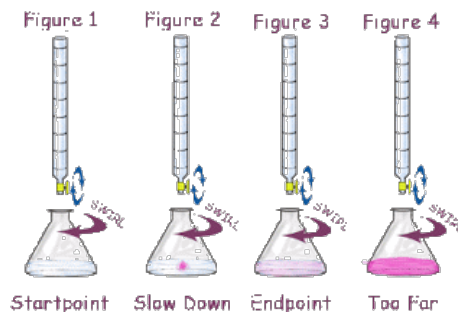5.1 The student can *analyze data* to identify patterns or relationships.

Learning Objectives
LO 6.12: The student can 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.
LO 6.13: The student can interpret titration data for monoprotic or polyprotic acids involving titration of a weak or strong acid by a strong base (or a weak or strong base by a strong acid) to determine the concentration of the titrant and the pKa for a weak acid, or the pKb for a weak base.
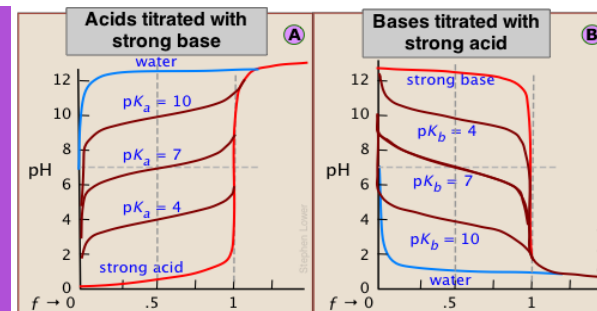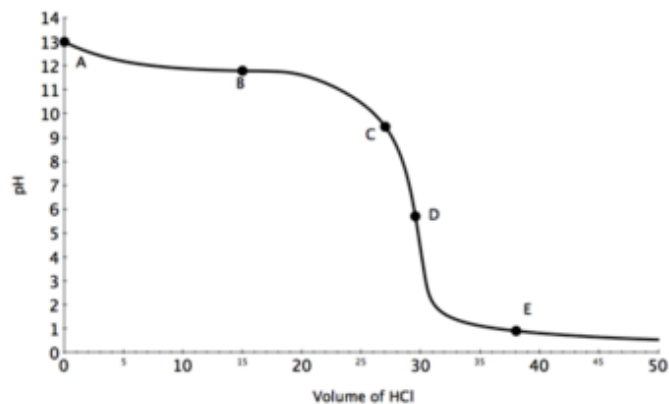
+Titration- Acid/Base

Titration of an Acid with a Base
using phenolphthalein indicator

Figure 1 Figure 2 Figure 3 Figure 4

Startpoint Slow Down Endpoint Too Far

SWIRL SWIRL SWIRL SWIRL

Use a beaker and funnel to fill burette.

Never pour from stock solution.

Leave air gap when filling

Cup the tap (stopcock) with your LH for stability and use the thumb and finger tips to control the tap key and flow rate.

The burette reading is taken from the bottom of the liquid curvature (meniscus).

Hold the flask's centre joint with the finger tips and swirl in a lasoo, circular pendulum like motion.

Place white paper underneath flask to view pink colour more clearly.

Strength of Acids affects shape of graph:

Strong acid / strong base
HCl - NaOH   A

Weak acid / strong base
CH_3COOH - NaOH   B

$[HAc] \approx [Ac^-]$
$pK_a = 4.7$

Polyprotic acids have multiple end points:

pH = 10.3
pH = 6.4
$[H_2CO_3^*] \approx [HCO_3^-]$
$[HCO_3^-] \approx [CO_3^{2-}]$
H_2CO_3 titrated with NaOH
$K_{a1} = 10^{-6.4}$, $K_{a2} = 10^{-10.3}$
equivalent fraction of base added

$[CO_3^{2-}] \approx [HCO_3^-]$
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pH = 3.7
equivalent fraction of acid added

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+ Titration- Acid/Base

- Assumption: Endpoint is equivalence point
  - This is not true – we actually "overshoot" before indicator changes

- Possible Sources of Error:
  - Overshoot Endpoint
    - Moles of titrant (and therefore analyte) too high
  - Not reading to bottom of meniscus
    - Moles of titrant too low
  - Concentration of titrant not what expected
    - Be sure to rinse buret with titrant first to control for this

Titration of an Acid with a Base
using phenolphthalein indicator

Figure 1   Figure 2   Figure 3   Figure 4

Startpoint   Slow Down   Endpoint   Too Far

Strength of Acids affects shape of graph:

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HCl - NaOH

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equivalent fraction of acid added

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Titration of an Acid with a Base using phenolphthalein indicator

Figure 1 Figure 2 Figure 3 Figure 4

Startpoint Slow Down Endpoint Too Far

Strength of Acids affects shape of graph:

Acids titrated with strong base (A)

Bases titrated with strong acid (B)

Polyprotic acids have multiple end points:

H_2CO_3 titrated with NaOH $K_{a1} = 10^{-6.4}$, $K_{a2} = 10^{-10.3}$

Na_2CO_3 titrated with HCl $K_{b1} = 10^{-7.6}$, $K_{b2} = 10^{-3.7}$

+ Titration- Acid/Base

Question:

The graph below is of the titration of a weak base with hydrochloric acid. Based on the graph which point would represent the region where the pH is dominated by the molarity of the hydrochloric acid being added?

a. A
b. B
c. C
d. D
e. E

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REDOX Titration

ACID-BASE TITRATION
VERSUS
REDOX TITRATION

Oxidation — Compound A loses electrons

Reduction — Compound B gains electrons

In an acid-base titration, the species involved are acids and bases.	Redox titrations are titrations that take place among redox species.
In an acid-base titration, the species take part in a neutralization reaction forming water molecules.	In redox titrations, the species react through oxidation and reduction reactions
Weak acids and weak bases are used as indicators for acid-base titrations.	Some redox species act as self-indicators and for most cases special redox indicators are used.
Acid-base titrations are more common as it can take place between any form of acid and base/ weak and strong.	Redox titrations are commonly seen among the 'd' block elements.

PEDIAA.COM

Applications/Methods of REDOX Titrations:

Vitamin C Content

Solution of KIO_3 of know concentration

Food sample containing ascorbic acid with added KI, HCl and starch

Concentration of a redox species

$KMnO_4$ → $KMnO_4$

Potassium dichromate

indicator
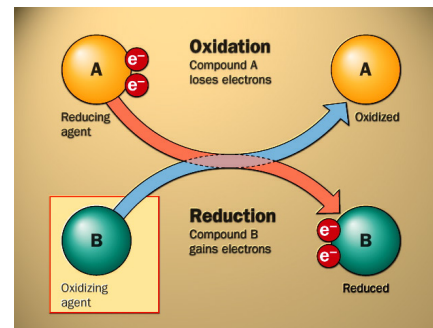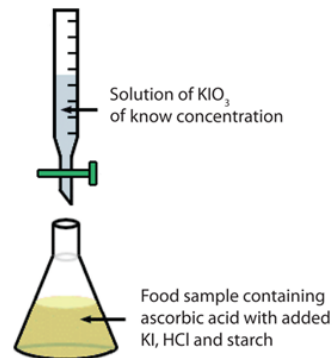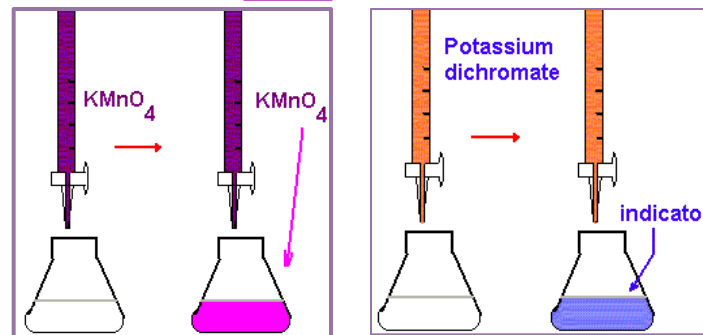
Back Titrations

Done when the endpoint can be hard to ID – add an excess, and then back titrate to determine how much is in excess

---

Science Practices
4.2 The student can *design a plan* for collecting data to answer a particular scientific question.
5.1 The student can *analyze data* to identify patterns or relationships.

Learning Objectives
LO 1.20: The student can design, and/or interpret data from, an experiment that uses titration to determine the concentration of an analyte in a solution.
LO 3.9: The student is able to design and/or interpret the results of an experiment involving a redox titration.
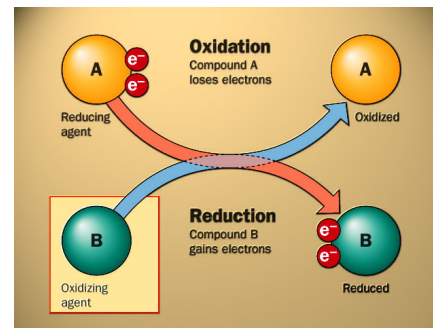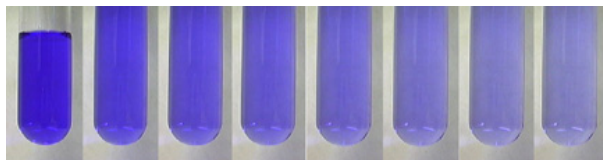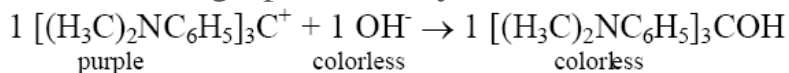
REDOX Titration

- Endpoint can be determined by potentiometer:

Titration of Fe^{2+} with Ce^{4+}

Potentiometer

Buret Ce^{4+}

Ag-AgCl electrode

Pt

Fe^{2+}

©NCSSM 2004

Oxidation Compound A loses electrons

Reducing agent

A

Oxidized

Reduction Compound B gains electrons

B

Oxidizing agent

Reduced

Applications/Methods of REDOX Titrations:

Video

Virtual Lab

Vitamin C Content	Solution of KIO_3 of know concentration
	Food sample containing ascorbic acid with added KI, HCl and starch
	Source
Concentration of a redox species	$KMnO_4$ $KMnO_4$ Potassium dichromate indicator
	Source
Back Titrations	Done when the endpoint can be hard to ID – add an excess, and then back titrate to determine how much is in excess

REDOX Titration

- Endpoint can be determined by potentiometer:

In_{ox} — indicator is color of In_{ox}

$E = E^o_{In_{ox}/In_{red}}$ — indicator's color transition range

In_{red} — indicator is color of In_{red}

Applications/Methods of REDOX Titrations:

Vitamin C Content	Solution of KIO_3 of know concentration Food sample containing ascorbic acid with added KI, HCl and starch Source
Concentration of a redox species	$KMnO_4$ $KMnO_4$ Potassium dichromate indicator Source
Back Titrations	Done when the endpoint can be hard to ID – add an excess, and then back titrate to determine how much is in excess

REDOX Titration

- Or an indicator that shows the presence of a particular species:

Source

- Starch indicates presence of iodine

Applications/Methods of REDOX Titrations:

Vitamin C Content	Solution of KIO₃ of know concentration Food sample containing ascorbic acid with added KI, HCl and starch Source
Concentration of a redox species	KMnO₄ → KMnO₄ Potassium dichromate → indicator Source
Back Titrations	Done when the endpoint can be hard to ID – add an excess, and then back titrate to determine how much is in excess

Kinetics

- Using Spectrometry:

$$1 \, [(H_3C)_2NC_6H_5]_3C^+ + 1 \, OH^- \rightarrow 1 \, [(H_3C)_2NC_6H_5]_3COH$$
purple   colorless   colorless

| Time (s) | 0 | 90 | 180 | 270 | 360 | 450 | 540 | 600 |

- Data:

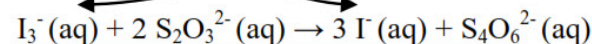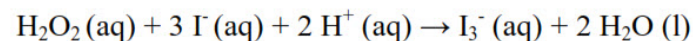| Zero Order Plot	1st Order Plot	2nd Order Plot

- Analysis
  - rate law from straight-line graph
  - k from integrated rate law
  - E_a from Arrhenius Equation

- Clock Reactions

  - Reactions that have a delayed physical change due to mechanism which only has a later step show color change

  - Concentration vs. time data can be gathered

$+ 2 S_2O_3^{2-}$
$+ 4 \times 10^{-4} \, mol$

$- 2 S_2O_3^{2-}$
$- 4 \times 10^{-4} \, mol$

$2 I^- + S_2O_8^{2-} \rightarrow I_2 + SO_4^{2-}$

$2 I^- + S_2O_8^{2-} \rightarrow I_2 + SO_4^{2-}$
$I_2 + 2 S_2O_3^{2-} \rightarrow 2 I^- + S_4O_6^{2-}$

$2 I^- + S_2O_8^{2-} \rightarrow I_2 + SO_4^{2-}$

A   B   C

+ Kinetics

- Using Spectrometry:

$$1 \; [(H_3C)_2NC_6H_5]_3C^+ + 1 \; OH^- \rightarrow 1 \; [(H_3C)_2NC_6H_5]_3COH$$
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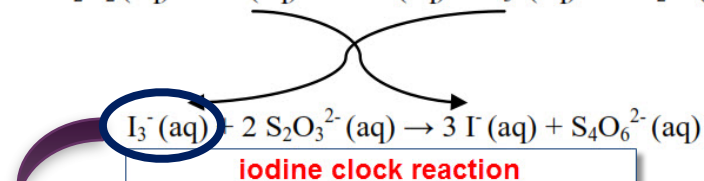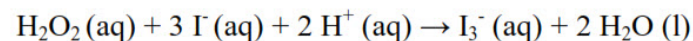| Zero Order Plot	1st Order Plot	2nd Order Plot

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    - It is important that there is a relatively low $[S_2O_3^-]$ so that the I_3^- will accumulate and show the color change

$$H_2O_2 \, (aq) + 3 \; I^- \, (aq) + 2 \; H^+ \, (aq) \rightarrow I_3^- \, (aq) + 2 \; H_2O \, (l)$$

$$I_3^- \, (aq) + 2 \; S_2O_3^{2-} \, (aq) \rightarrow 3 \; I^- \, (aq) + S_4O_6^{2-} \, (aq)$$

iodine clock reaction

Kinetics

- Using Spectrometry:
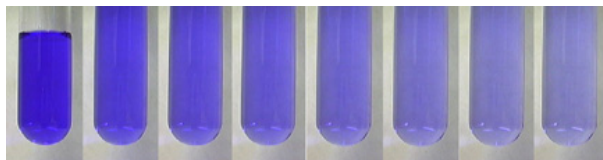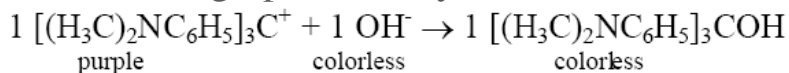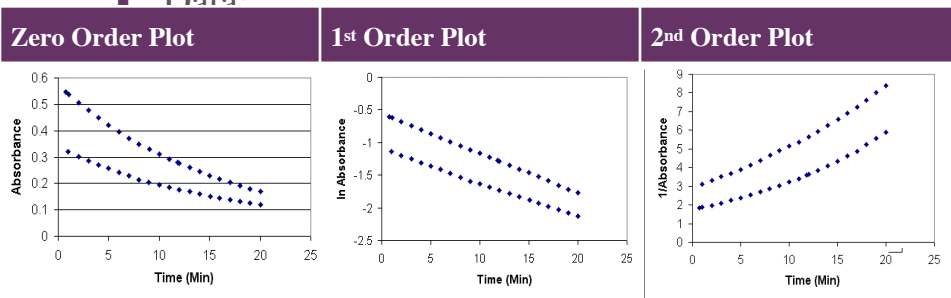
$$1\ [(H_3C)_2NC_6H_5]_3C^+ + 1\ OH^- \rightarrow 1\ [(H_3C)_2NC_6H_5]_3COH$$
purple   colorless   colorless

| Time (s) | 0 | 90 | 180 | 270 | 360 | 450 | 540 | 600 |

- Data:

Zero Order Plot	1st Order Plot	2nd Order Plot

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$$H_2O_2\ (aq) + 3\ I^-\ (aq) + 2\ H^+\ (aq) \rightarrow I_3^-\ (aq) + 2\ H_2O\ (l)$$

$$I_3^-\ (aq) + 2\ S_2O_3^{2-}\ (aq) \rightarrow 3\ I^-\ (aq) + S_4O_6^{2-}\ (aq)$$

iodine clock reaction

Blue in the presence of starch

Science Practices
2.1 The student can *justify the selection of a mathematical routine* to solve problems.
2.2 The student can *apply mathematical routines* to quantities that describe natural phenomena.
5.1 The student can *analyze data* to identify patterns or relationships.

Learning Objectives
LO 4.2: The student is able to analyze concentration vs. time data to determine the rate law for a zeroth-, first-, or second-order reaction.
LO 4.3: The student is able to connect the half-life of a reaction to the rate constant of a first-order reaction and justify the use of this relation in terms of the reaction being a first-order reaction.
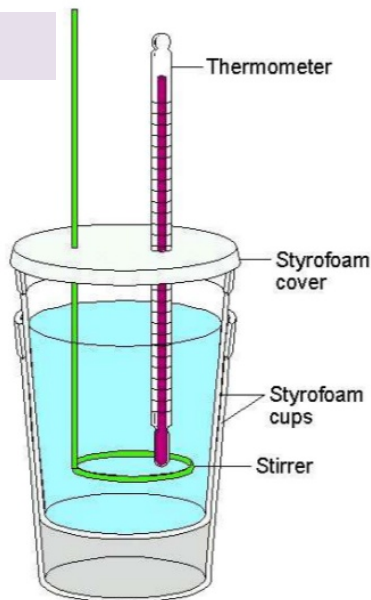
\+
Kinetics

Question:

Which of the following would increase the rate of a chemical reaction.

    a. decreasing the temperature
    b. increasing the concentration of the products
    c. decreasing the concentration of the products
    d. increasing the concentration of the reactants
    e. decreasing the concentration of the reactants

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+ Calorimetry

Application of <u>Law of Conservation of Energy</u>: All heat produced/consumed during reaction (system) is exchanged with the surroundings.
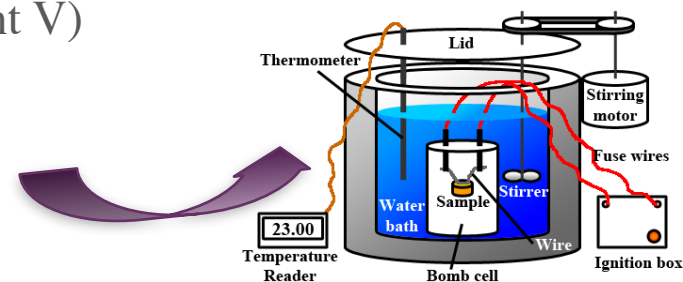
Applications:

- Specific Heat of Material
  - Can be used to ID unknown

- Heat of reaction

- Energy content of food
  - This is usually done in a bomb calorimeter (constant V)

Video

Virtual Lab

Source

Coffee Cup Calorimeter

Applications

A calorimeter is used to measure the heat absorbed or released in a chemical (or other) process by measuring the temperature change of an insulated mass of water.

Constant P

Thermometer

Styrofoam cover

Styrofoam cups

Stirrer

Reaction occurs in solution.
Temperature increases or decreases.
Insulating cup traps heat or keeps out heat from the surroundings.

Source

Thermometer
Lid
Stirring motor
Fuse wires
Water bath
Sample
Stirrer
Wire
Ignition box
23.00
Temperature Reader
Bomb cell

+ Calorimetry

Application of <u>Law of Conservation of Energy</u>: All heat produced/consumed during reaction (system) is exchanged with the surroundings.
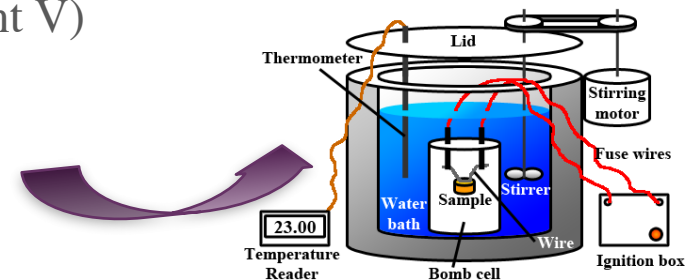
Applications:

- Specific Heat of Material
  - Can be used to ID unknown

- Heat of reaction

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  - This is usually done in a bomb calorimeter (constant V)

Coffee Cup Calorimeter

Assumption:
•**the calorimeter is isolated**
•**so the surroundings are only the calorimeter setup, which includes the water**
•**the calorimeter itself has a heat capacity, as it will absorb some heat.**
•**So…**

$$q_{surr} = -q_{rxn}$$
$$q_{surr} = q_{cal} + q_{H_2O+sys}$$
$$q_{cal} = C_{cal}\Delta T$$

Therefore:

$$-q_{rxn} = C_{cal}\Delta T + m_{H_2O+sys}c\Delta T$$

Then we can use q_{rxn} find ΔH_{rxn}:

$$\Delta H_{rxn} = q_{rxn}/mol_{react}$$

Thermometer — Lid — Stirring motor — Fuse wires — Water bath — Sample — Stirrer — Wire — Ignition box — Temperature Reader — 23.00 — Bomb cell
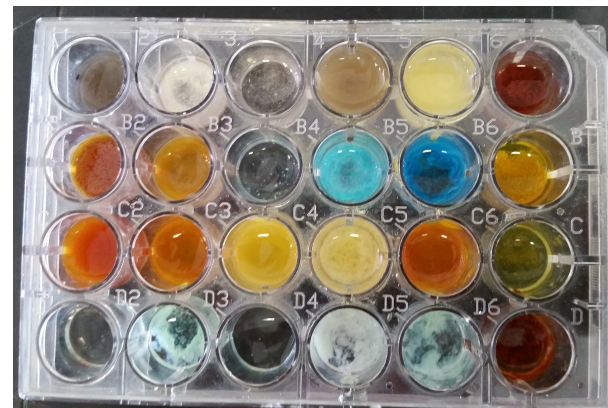

Qualitative Analysis

METAL ION FLAME TESTS

A flame test is an analytical procedure used by chemists to detect the presence of particular metal ions, based on the colour of the flame produced.
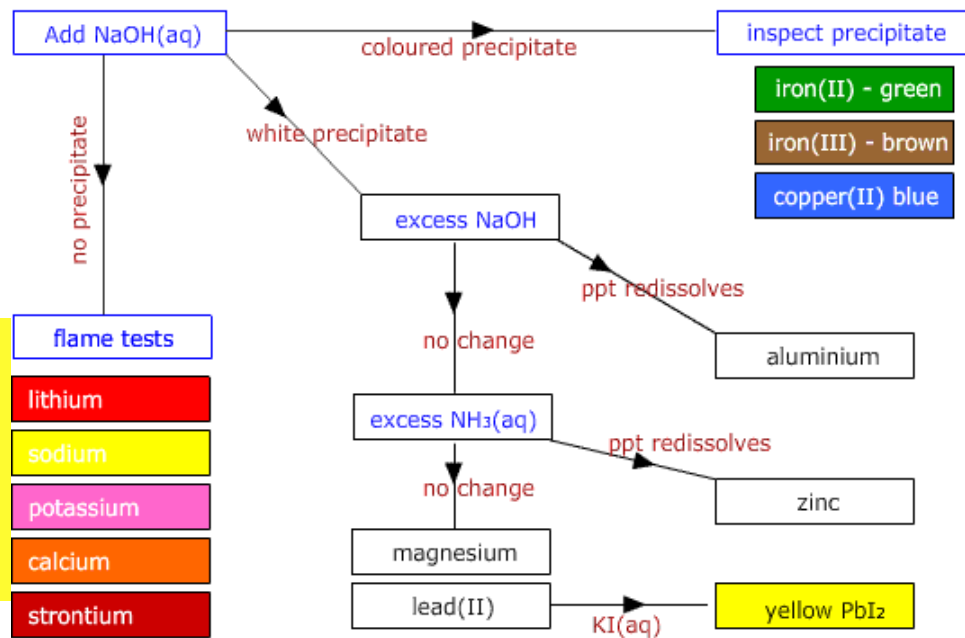
ABSORPTION

EMISSION

When heated, the electrons in the metal ion gain energy and can jump into higher energy levels. Because this is energetically unstable, the electrons tend to fall back down to where they were before, releasing energy as they do so. This energy is released as light energy, and as these transitions vary from one metal ion to another, it leads to the characteristic colours given by each metal ion.

2014 COMPOUND INTEREST WWW.COMPOUNDCHEM.COM

LITHIUM Li⁺ | SODIUM Na⁺ | POTASSIUM K⁺ | RUBIDIUM Rb⁺ | CAESIUM Cs⁺ | CALCIUM Ca²⁺

STRONTIUM Sr²⁺ | BARIUM Ba²⁺ | RADIUM Ra²⁺ | COPPER Cu²⁺ | IRON Fe²⁺/Fe³⁺ | BORON B³⁺

INDIUM In³⁺ | LEAD Pb²⁺ | ARSENIC As³⁺ | ANTIMONY Sb³⁺/Sb⁵⁺ | SELENIUM Se²⁺/Se⁴⁺ | ZINC Zn²⁺

Remember that the lower the K_{sp}, the less soluble the substance. Qualitative analysis then also allows a ranking of salts by K_{sp}, and demonstrates the effect of pH on solubility.

lithium
sodium
potassium
calcium
strontium

Analysis of cations (positive ions)

Add NaOH(aq) → coloured precipitate → inspect precipitate

iron(II) – green
iron(III) – brown
copper(II) blue

white precipitate

excess NaOH → ppt redissolves → aluminium

no precipitate

flame tests

no change

excess NH₃(aq) → ppt redissolves → zinc

no change

magnesium
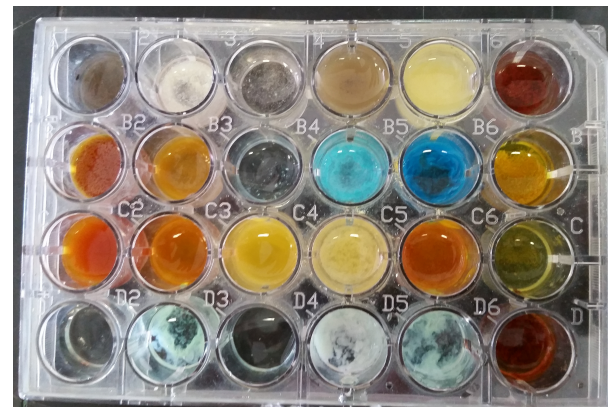
lead(II) — KI(aq) → yellow PbI₂

Qualitative Analysis

METAL ION FLAME TESTS

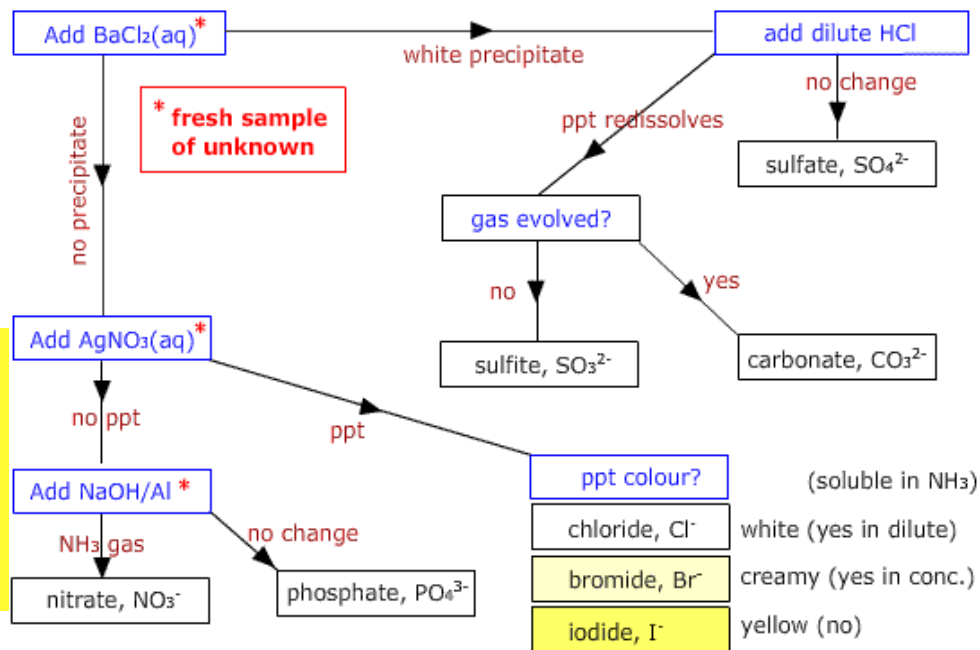A flame test is an analytical procedure used by chemists to detect the presence of particular metal ions, based on the colour of the flame produced.

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INDIUM In³⁺ LEAD Pb²⁺ ARSENIC As³⁺ ANTIMONY Sb³⁺/Sb⁵⁺ SELENIUM Se²⁺/Se⁴⁺ ZINC Zn²⁺

Remember that the lower the K_{sp}, the less soluble the substance. Qualitative analysis then also allows a ranking of salts by K_{sp}, and demonstrates the effect of pH on solubility.

Analysis of anions (negative ions)

Add BaCl₂(aq)* → white precipitate → add dilute HCl
 → no change → sulfate, SO_4^{2-}
 → ppt redissolves → gas evolved?
   → no → sulfite, SO_3^{2-}
   → yes → carbonate, CO_3^{2-}

* fresh sample of unknown

no precipitate → Add AgNO₃(aq)*
 → no ppt → Add NaOH/Al*
   → NH₃ gas → nitrate, NO_3^-
   → no change → phosphate, PO_4^{3-}
 → ppt → ppt colour?   (soluble in NH₃)
   chloride, Cl⁻   white (yes in dilute)
   bromide, Br⁻   creamy (yes in conc.)
   iodide, I⁻   yellow (no)

Now…

Just for Fun:
Some "Harry" Problems

$$2Fe(OH)_3 \ (s) + 3H_2SO_4 \ (aq) \rightarrow Fe_2(SO_4)_3 \ (aq) + 6H_2O \ (l)$$

- a. Ron Weasley had to perform the above reaction in Professor Snape's potions class. Ron mixed 45.0 g iron III hydroxide with 45.0 ml 2.00 M sulfuric acid in a cauldron, leaving the lid off. The heat capacity of his cauldron was 645 J/K.

-    i. What other information would Ron need to know or measure experimentally to determine the molar change in enthalpy of the reaction, $\Delta H°rxn$?

-    ii. Unbeknownst to Ron, Draco Malfoy dropped a 100 g sneakoscope (assume this is unreactive and at room temperature) into Ron's cauldron before Ron measured his temperature but after the reaction was initiated. Explain in which direction this would alter Ron's experimental value of $\Delta H°rxn$.

- b. Hermione Granger also performed this reaction. She mixed 45.0 g iron III hydroxide with 450 ml 2.00 M sulfuric acid in her cauldron, and kept the lid on, using a spell to enable her to measure temperature (revelio thermo).

-    i. How would you expect her temperature change to differ from Ron's, if at all? For this comparison, assume that Ron's reaction was performed with the lid on and with no sneakoscope.

-    ii. Hermione repeated the experiment using all the same measurements, but used aluminum hydroxide instead of iron III hydroxide. Assuming that both reactions have the same $\Delta H°rxn$, would her temperature change be smaller, the same, or greater in her second experiment.

- c. Given the following values for absolute entropies, what would $\Delta S°rxn$ be?

	$Fe(OH)_3 \ (s)$	$Fe^{3+} \ (aq)$	$H_2SO_4 \ (aq)$	$SO_4^{2-} \ (aq)$	$H_2O \ (l)$
S°, J/mol·K	107	-315.9	20.08	20.1	69.91

Just for Fun… Answers

- ai. $q_{rxn} = -(C_{cal}\Delta T + c_{(mixture)}m_{(mixture)}\Delta T)$; $\Delta H°rxn = q_{rxn}$ / moles rxn

- Ron would need to measure the starting and final temperatures, know (or measure) the specific heat capacity and mass of the reaction mixture, and the number of moles of reaction. In this case,

- 45.0 g $Fe(OH)_3$ / 106.8 g/mole = 0.421 moles; 0.045 L x 2 M = 0.09 moles H_2SO_4 (limiting), so 0.03 moles reaction (to those who dislike this concept, I apologize).

- aii. Because the sneakoscope would absorb heat, ΔT would be lower, so the heat of the reaction would appear to be lower as would $\Delta H°rxn$.

- bi. For Hermione, the $Fe(OH)_3$ is now limiting, as there are now 0.9 moles H_2SO_4. So, there are more moles of reaction, about 0.21, a seven-fold increase. This would increase the temperature change. However, there is also a significant increase in mass of the reaction mixture, from about 90 g to 500 g. This would decrease the temperature change. So the exact ΔT outcome, increase or decrease, depends on the specific heat capacity of the reaction mixture.

- bii. 45.0 g $Al(OH)_3$ / 78 g/mole = 0.577 mole. This is still limiting, but now there are about 0.288 moles of reaction, so more heat is produced. As the total mass doesn't change, and the specific heat capacity is unlikely to change dramatically, it is reasonable to predict that ΔT would be larger.

- c. $\Delta S°rxn$ = sum product S° - sum reactant S°

- $\Delta S°rxn = 6(69.91) + 2(-315.9) + 3(20.1) - 2(107) - 3(20.08) = -426.3$ J/ mole*K.