5.112 EXAM STUDY GUIDE
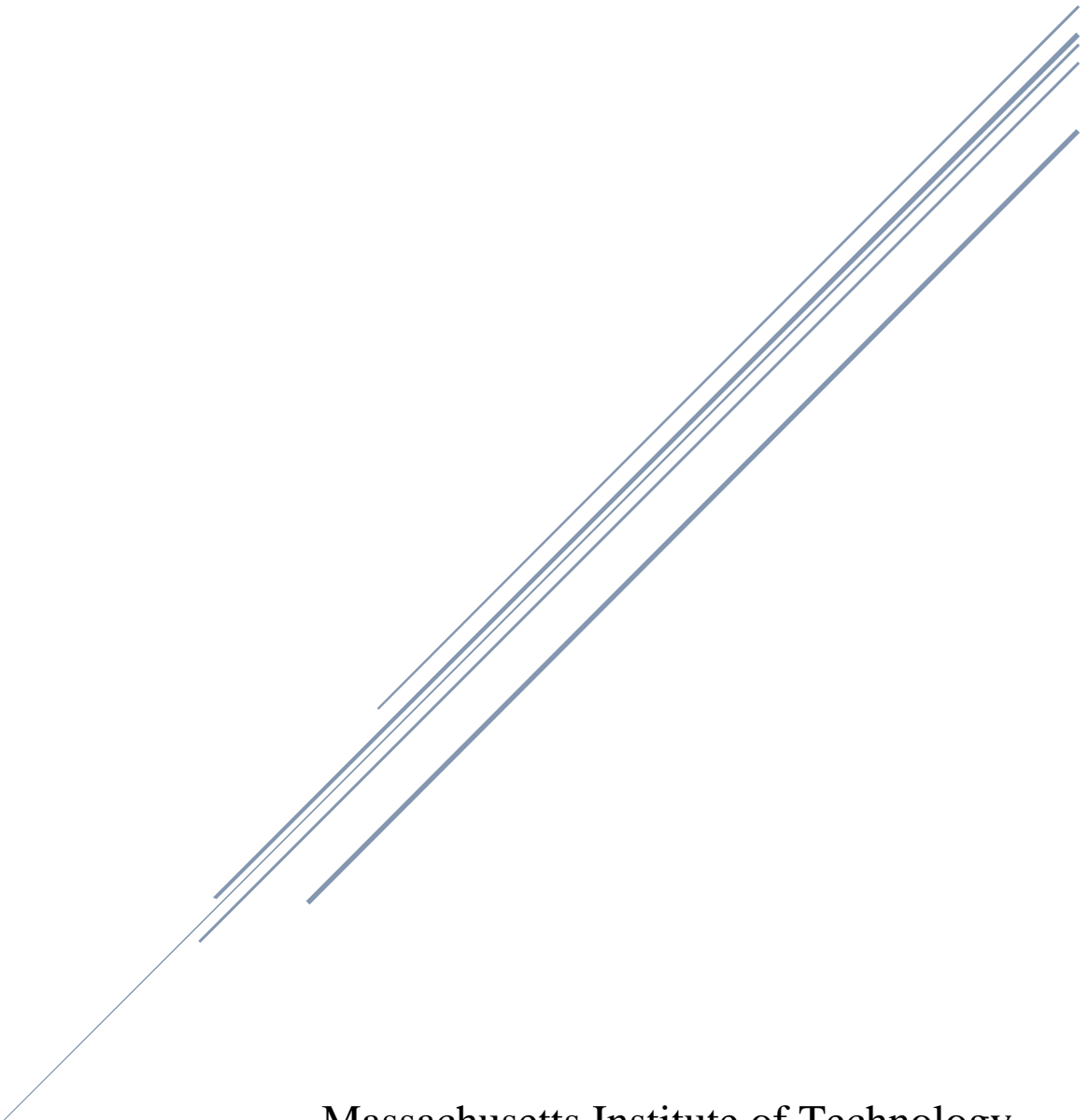
UNIT III

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5.112

TOPICS

ACID-BASE DEFINITIONS

A Review of Equilibrium

- A chemical reaction never truly goes to completion—instead, a reaction is said to be in **equilibrium** when the rates of the forward and reverse reactions are equal and there is no net change in composition.
- It is **dynamic**, meaning that the reactions are still happening and respond to external changes.
- We can also explain this process thermodynamically:
  - ➢ If a reaction mixture contains excess reactants to reach equilibrium, the spontaneous reaction is the forward reaction, so $\Delta G < 0$ for the forward reaction.
  - ➢ If a reaction mixture contains excess products, the reverse reaction is spontaneous, so $\Delta G > 0$ for the forward reaction.
  - ➢ Once a reaction has reached equilibrium, there is no tendency for spontaneous change in either the forward or reverse reaction, so $\Delta G = 0$.
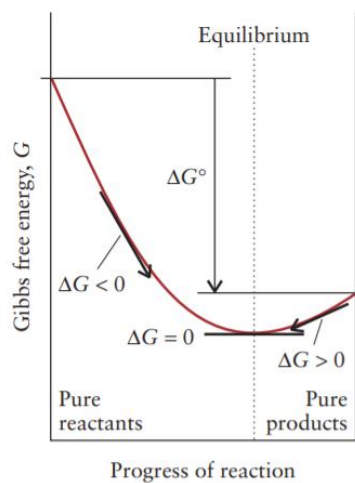

FIGURE 10.4 The variation of Gibbs free energy of a reaction mixture with composition. A reaction mixture has a spontaneous tendency to change in the direction of decreasing Gibbs free energy. Note that ΔG is the *slope* of the line at each composition, whereas $\Delta G°$ is the difference between the standard Gibbs free energies of the pure reactants and the pure products.

  - ➢ A system will tend to the lowest state of free energy (think of a ball naturally rolling down a valley)

- The **equilibrium constant**, K, is useful in determining how much product will be formed when a reaction is at equilibrium, and is defined by:
  - ➢ When K > 1, there is high products.
  - ➢ When K < 1, there is low products.
- What happens to a system in equilibrium when it is disturbed?
- **Le Chatelier's Principle**—when a stress is applied to a system in dynamic equilibrium tends to adjust to minimize the effects of the stress.
- This principle can be used to predict the direction of change of a system under external perturbation.
- For example, if a reaction has reached equilibrium and you add in more reactant, more product will form in order to minimize the stress of the system.
  - ➢ You have too much reactant, so the system wants to use up the excess reactant by making product in order to reestablish equilibrium.

Classification of Acids and Bases

- Acids and bases are two of the most important classes of compounds in chemistry, as they are involved in countless reactions and in living organisms.
- Arrhenius originally developed a definition for acids and bases, but this was later generalized further by Johannes **Brønsted** and Thomas **Lowry**.
  - ➢ A Brønsted-Lowry **acid** is a substance that **donates** a proton (H^+ ion).

$$\text{For } aA + bB \rightleftharpoons cC + dD \qquad K_c = \left\{ \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} \right\}_{eq.}$$
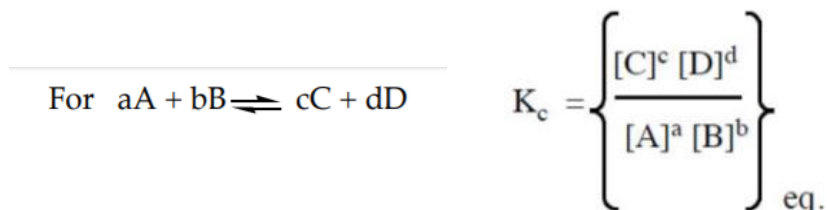
  - ➢ A Brønsted-Lowry **base** is a substance that **accepts** a proton.
- A substance can only act as an acid, for instance, if there is a base present to accept its proton (it doesn't just simply eject a proton).
- Let's look at HCl in water:

$$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

- In this reaction, HCl donates a proton to a water molecule, so HCl is the acid, while H_2O is the base (proton acceptor).
- The H_3O^+ ion is called a **hydronium ion.**
- We should remember that this reaction is in dynamic equilibrium, but lies strongly toward the products, so we only wrote a single forward arrow for simplicity.
  - ➢ A **strong** acid is fully deprotonated (ionized/dissociated) in solution.
  - ➢ A **weak** acid is only partially deprotonated in solution.

- ➢ For this unit, we will mostly only be using water as our solvent.
- The species formed by this reaction (H_3O^+ and Cl^-) can also in turn donate and accept a proton, respectively (because the reverse reaction also happens).
  - ➢ A **conjugate base** is the species left when an acid donates a proton.
  - ➢ A **conjugate acid** is the species left when a base accepts a proton.
  - ➢ In this reaction, Cl^- is the conjugate base of HCl, while H_3O^+ is the conjugate acid of H_2O.
- **Amphoteric** molecules can act as both an acid or a base, depending on reaction conditions (ex. H_2O can act as a base and become H_3O^+, or it can act as an acid and become OH^-, a **hydroxide ion**).
- Acid and base definitions can be further generalized, enter **Lewis acids/bases**:
  - ➢ A Lewis acid is an **electron pair acceptor**.
  - ➢ A Lewis base is an **electron pair donor**.
- For instance, an H^+ ion accepts an electron pair from a molecule (a Lewis base) to form a bond, so it is a Lewis acid.
- Furthermore, this definition can include metal atoms or ions as acids, even though there is no protons involved and as such are not Brønsted acids.
- We will not focus too much on Lewis acids and bases in this unit.

CHEMISTRY OF ACIDS AND BASES

Acid-Base Chemistry of Water

- As mentioned previously, water will be our solvent of choice for this unit, and it is amphoteric.
- Let's then look at the proton exchange of water molecules in pure water:

$$2\ H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

- The equilibrium constant for this reaction is $K_w = 1.0 \times 10^{-14}$ at 298 K. This value is very small, so it means that only a very small amount of water molecules are ionized.
- Since we are in pure water and it is also our solvent, we do not include it in the equilibrium expression, giving us this relation.

$$K_w = [H_3O^+][OH^-]$$

- Chemists use something called the **pH scale** in order to evaluate the concentration of hydronium ions in solution:

$$pH = -log[H_3O^+]$$

- The higher the hydronium concentration of a solution, the lower the pH:
  - ➢ The pH of pure water is 7
  - ➢ The pH of a basic solution is greater than 7.
  - ➢ The pH of an acidic solution is less than 7.
- A less commonly used scale is the **pOH scale**, which measures the concentration of hydroxide ions:
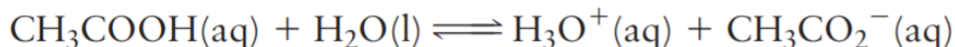
$$pOH = -log[OH^-]$$

- In general:

$$pX = -logX$$

- We can then derive the following expressions using K_w:

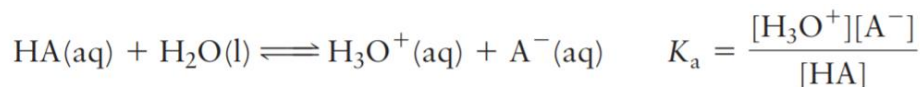$$pK_w = pH + pOH = 14 \text{ at 298 K}$$
$$pK_a + pK_b = 14$$

Weak Acids and Bases

- Most acids and bases found in nature are weak, so it is important to place emphasis on them.
- Take for example acetic acid:

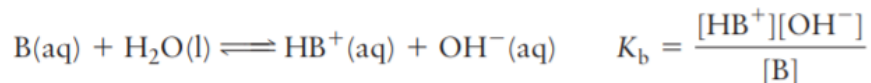$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

- Let's calculate the **acid ionization constant, or K$_a$** of acetic acid, remembering that we do not include water in the equilibrium expression:

$$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3COOH]}$$

- The K$_a$ of acetic acid is around 1.8×10^{-5} at 25°C. This means that only a very small proportion of CH$_3$COOH molecules dissociate and donate a proton to water (around 1 out of every 100).
- In general, for any acid in water:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- And similarly, for any base in water:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq) \qquad K_b = \frac{[HB^+][OH^-]}{[B]}$$

FIGURE 11.15 In a solution of a weak acid, only some of the acidic hydrogen atoms are present as hydronium ions (the red sphere), and the solution contains a high proportion of the original acid molecules (HA, gray spheres). The green sphere represents the conjugate base of the acid and the blue spheres are water molecules. The inset at the left shows only the solute species.

- A strong acid/base will have a K$_a$/K$_b$ > 1, and will ionize almost completely, while a weak acid/base will have a K$_a$/K$_b$ < 1, and will not ionize that much.
- The **pK$_a$** (equal to -log(K$_a$)) of solutions is of particular interest because it cleanly describes the strength of acids (rather than using K$_a$ values which are either extremely small or extremely large)
  - ➢ The larger the pK$_a$, the weaker the acid. The smaller the pK$_a$ (or more negative), the stronger the acid.
- Similarly (but less commonly), in terms of base strength, we use pK$_b$.
- What about the strength conjugate acids/bases of the acids/bases?
  - ➢ The stronger the acid, the **weaker** its conjugate base
  - ➢ The weaker the acid, the **stronger** its conjugate base
- This makes sense when thinking about equilibrium because, for instance, a strong acid will push the equilibrium towards the products for complete ionization (large K$_a$), so the reverse reaction will have a much smaller K$_b$.

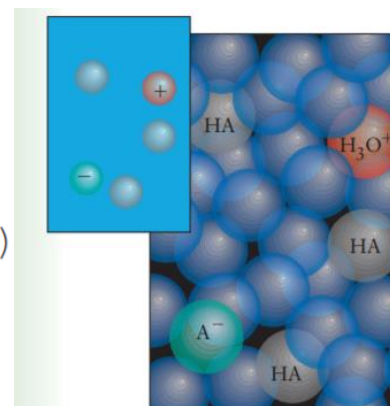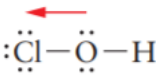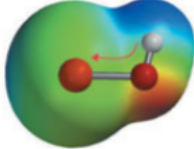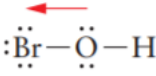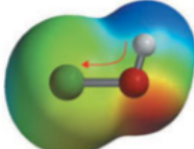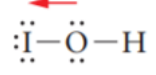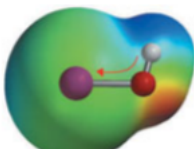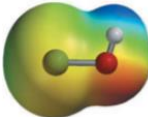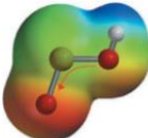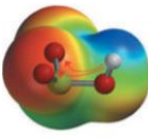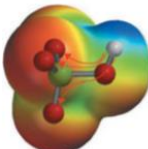*Molecular Explanation for Strength of Acids and Bases*

- When thinking about this in terms of stability (especially useful when thinking about organic acids and bases), a stronger acid is one that is more stable in its deprotonated (conjugate base) form, so it will not want to accept a proton and return to its state of lower stability. The conjugate base of this acid is weak and more stable.
- It is also important to consider the electronegativity of atoms in the molecule as well as general patterns of electron density.

TABLE 11.5 Correlation of Acid Strength and Electronegativity

Acid, HXO	Structure*	Electronegativity of atom X	pK_a	
hypochlorous acid, HClO	:Cl̈—Ö—H	3.2	7.53	
hypobromous acid, HBrO	:B̈r—Ö—H	3.0	8.69	
hypoiodous acid, HIO	:Ï—Ö—H	2.7	10.64	

*The red arrows indicate the direction of the shift of electron density away from the O—H bond.

- Here, we see that as the electronegativity of the X atom increases, so does the strength of the acid HXO.
  - Because Cl is more electronegative than I, it withdraws electron density from the O—H bond. This polarizes and weakens the bond, making it easier for the molecule to donate its proton.
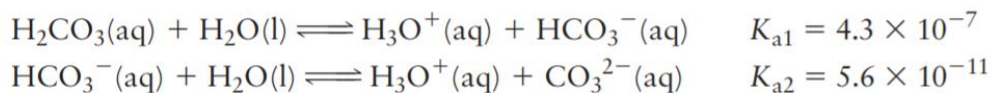
TABLE 11.6 Correlation of Acid Strength and Oxidation Number

Acid	Structure*	Oxidation number of Cl atom	pK_a
hypochlorous acid, HClO	:Cl̈—Ö—H	+1	7.53
chlorous acid, HClO₂	:Cl̈—Ö—H (with =O)	+3	2.00
chloric acid, HClO₃	:Cl—Ö—H (with two =O)	+5	strong
perchloric acid, HClO₄	O=Cl—Ö—H (with three =O)	+7	strong

- Since a proton is bonded to an atom that is donating its lone pair of electrons, that atom will carry a negative charge when the proton leaves. This implies that a strong acid will be one that is able to spread that negative charge throughout the molecule to other electronegative atoms (thereby stabilizing the molecule) when it has donated its proton.
- For instance, perchloric acid, $HClO_4$, is bonded to 4 electronegative oxygens, so once it donates its H^+, the remaining negative charge on the oxygen can be spread to the other 3 oxygens through **resonance**, making this more stable than hypochlorous acid, which is somewhat polar.

Polyprotic Acids and Bases

- A **polyprotic acid** is one that can donate more than one proton. For example, H_2SO_4 and H_2CO_3 can both donate 2 protons.
- In turn, a **polyprotic base** is one that can accept more than one proton, such as CO_3^{2-}.
- This proton donation/acceptance happens successfully, so an H_2SO_4 molecule will donate a proton and become HSO_4^-, which can then donate a proton and become SO_4^{2-}.
- Let's look at carbonic acid H_2CO_3, an important acid in nature:

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \qquad K_{a1} = 4.3 \times 10^{-7}$$
$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq) \qquad K_{a2} = 5.6 \times 10^{-11}$$

The conjugate base of H_2CO_3 in the first equilibrium, HCO_3^-, acts as an acid in the second equilibrium. That ion produces in turn its own conjugate base, CO_3^{2-}.

Protons are donated successively by polyprotic acids, with the acidity constant decreasing significantly, usually by a factor of about 10^3 or more, with each proton lost (Table 11.10):

$$K_{a1} \gg K_{a2} \gg K_{a3} \gg \cdots$$

- Why is $K_{a1} \gg K_{a2} \gg K_{a3}$? As an H^+ ion is removed from the neutral molecule, the remaining species is negatively charged, so it resists losing a positively charged proton and becoming even more negatively charged (remember, the more neutral a molecule, the more stable).
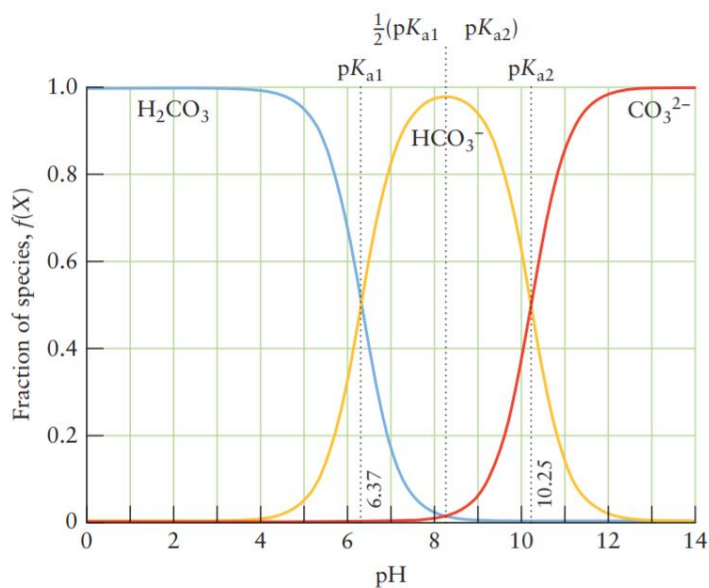

FIGURE 11.21 The fractional composition of the species in carbonic acid as a function of pH. Note that the more fully protonated species are dominant at lower pH.

TITRATIONS AND BUFFERS

Buffers

- A **buffer** solution is a solution that resists changes in pH with small additions of acid or base.
    - ➢ An acid buffer consists of a weak acid and its conjugate base, supplied as salt.
    - ➢ A base buffer consists of a weak base and its conjugate acid, supplied as salt.
- Buffers are particularly important in biology, as organisms need to stay at a constant pH, even with environmental changes, or they'll die.
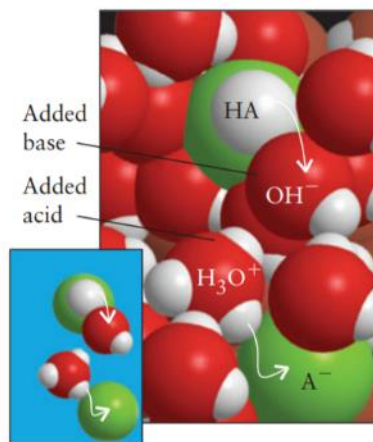

FIGURE 12.1 A solution can act as a buffer if it contains a weak acid, HA, which donates protons when a strong base is added, and the conjugate base, A⁻, which accepts protons when a strong acid is added. In the inset, for clarity water molecules are represented by the blue background.
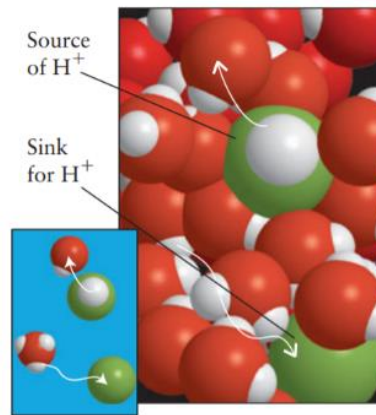
FIGURE 12.2 A buffer solution contains a weak base that acts as a sink for the protons supplied by a strong acid and a weak acid that acts as a source of protons to supply to a strong base being added. The joint action of the source and sink keeps the pH constant when strong acid or base is added. The inset highlights the buffer action by representing the water molecules as a blue background.

- A buffer solution will maintain its pH because it is able to both donate a proton when a strong base is added to **neutralize** it, or accept a proton when a strong acid donates one.
- How would you design a buffer?
    - ➢ Consider the ratio of [HA] to [A⁻]
    - ➢ pK_a
    - ➢ pH
- An important equation in making a buffer is the **Henderson-Hasselbach equation:**

$$pH \cong pk_a - log(\frac{[HA]_o}{[A^-]_o})$$

- ➢ It is important to note that in this formula, we are making the assumption that the initial concentration of HA and A⁻ is approximately equal to their equilibrium concentrations.
- ➢ This equation only applies to buffers!
- ➢ A buffer solution is most effective in the range of pH = $pK_a \pm 1$

Titrations of Strong Acids and Bases

- A **titration** is the addition of a solution called the titrant from a burette to a sample called the analyte.
- Titrations are used to determine the amount of acid or base present in a solution.
- The addition of a strong acid to a strong base (or vice versa) results in the following net ionic equation:

$$H_3O^+(aq) + OH^-(aq) \longrightarrow 2\,H_2O(l)$$
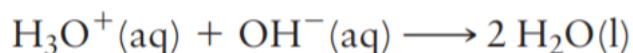
- It's important, however, to look at the full chemical equation to ensure that your stoichiometric amounts are correct.
- Let's take a look at a **pH curve**:
- Titrations of strong bases with strong acids have this general shape.
- The point S is called the **stoichiometric point** or **equivalence point** and is the **theoretical** volume at which the moles of base added is equal to the moles of acid present in the analyte.
- The **end point** is the **experimentally determined** volume at which the moles of base added equals the moles of acid present.
- The end point should equal the equivalence point.
- To know when you have reached the end point, you use what is called an **indicator** (a compound that changes color depending on pH), and pay attention to when the indicator just begins to change color.
- An indicator should be chosen so that its end point is close to the equivalence point of the titration.
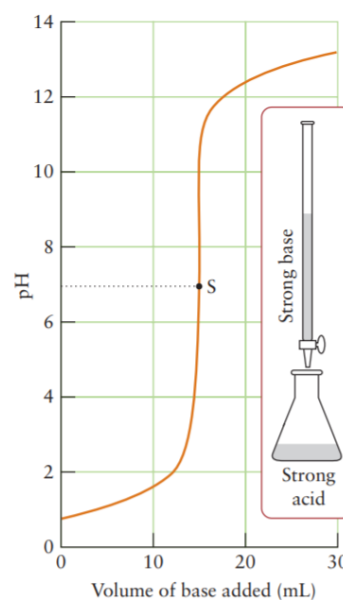- The equivalence point for a strong acid and strong base titration will always be at pH=7.

FIGURE 12.5 The variation of pH during a typical titration of a strong acid (the analyte) with a strong base (the titrant). The stoichiometric point (S) occurs at pH = 7.

Titrations of Weak Bases with Strong Acids or Weak Acids with Strong Bases

- The titrations involving weak acids in bases is a little bit less straightforward, as it requires the use of equilibrium charts.
- The pH curves of these titrations also look slightly different than with strong acid/base titrations:
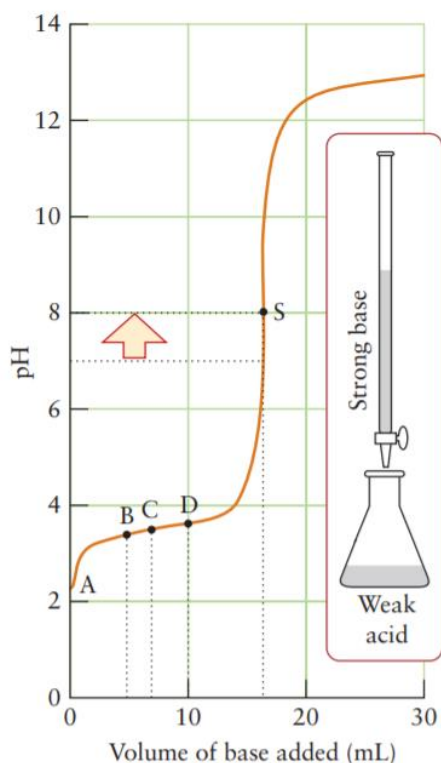
FIGURE 12.6 The pH curve for the titration of a weak acid with a strong base: 25.00 mL of 0.100 M HCOOH(aq) with 0.150 M NaOH(aq). The stoichiometric point (S) occurs at pH > 7 because the anion HCO_2^- is a base. The other points on the curve are explained in the text and in Example 12.6.

- The region around B,C and D is known as the **buffer region**, and this region is absent in strong acid and base titrations because they do not form good buffers.
- While the definition of the equivalence point is the same, the pH at that point might not be at pH = 7.
- In the case of a weak acid with strong base titration, the equivalence point is at pH > 7 because some of the weak acid is converted into its conjugate base.
- Point C is the **half-equivalence point** is the point where half the volume and half the number of moles needed to reach the equivalence point have been added (so [HA] = [A⁻])
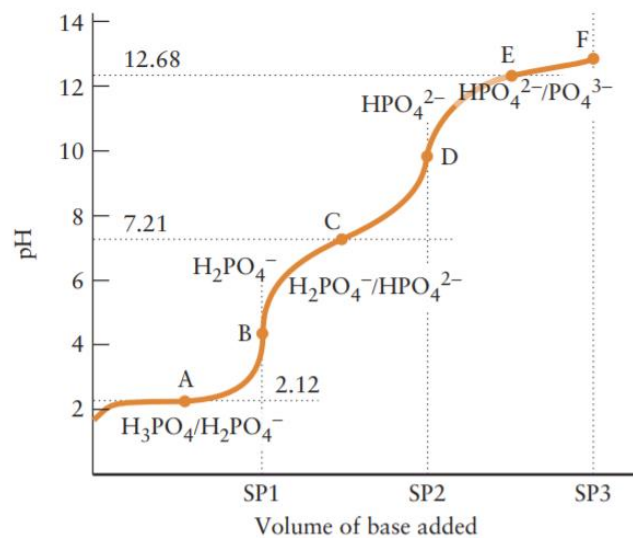
FIGURE 12.13 The variation of the pH of the analyte solution during the titration of a triprotic acid (phosphoric acid). The major species present in solution at the first two stoichiometric points (B and D) and at points when half the titrant required to reach a stoichiometric point has been added (A, C, and E) are shown. Compare this diagram with Fig. 11.22. The labels SP1, SP2, and SP3 denote the volumes of base required to reach the three stoichiometric points. Points A through F are explained in the text.

- The titration of polyprotic acids and bases is very similar to that of monoprotic acids and bases, but in this case, there are several equivalence points (B,D, and E) rather than just one.
- This requires setting up various equilibrium charts, depending on the problem.

ELECTROCHEMISTRY

*Oxidation and Reduction—Redox*

- The study of **electrochemistry** is crucial because it may one day lead to an inexhaustible form of energy.
- This study of the relationship between electricity and chemical reactions has its core on the movement of electrons, as you should expect:
    - ➢ A substance that undergoes **oxidation loses electrons** in a reaction.
    - ➢ A substance that undergoes **reduction gains electron**.
    - ➢ A great mnemonic device is OIL RIG: **o**xidation **i**s **l**oss, **r**eduction **i**s **g**ain.
    - ➢ Furthermore, an **oxidizing agent** is one that accepts electrons, and is reduced.
    - ➢ A **reducing agent** is one that donates electron, and is itself oxidized.
- A **redox reaction** is one in which there is an exchange of electrons from species to another.
- **Oxidation numbers** help us keep track of electrons in a chemical reaction, and there are guidelines for assigning oxidation numbers:
    - ➢ Since electrons carry a negative charge, a **positive** oxidation number indicates that electrons were lost (i.e. +2, +4 etc.), while a **negative** oxidation number indicates that electrons were gained (-2, -1).
    - ➢ Free elements have an oxidation number of **zero**.
    - ➢ Ions composed of only one atom (monatomic ions) have an oxidation number equal to their charge (Li^{1+} ions have an oxidation number of +1).
    - ➢ When elements are bonded together covalently, the element with the greater electronegativity is assigned the electrons in the bond.
    - ➢ In an element-element bond (N-N, C-C etc.), the electrons are shared equally.
    - ➢ Oxidation numbers can be fractional (as in -0.5 per O in $[O_2]^-$).
    - ➢ O generally has an oxidation number of -2, with a few exceptions such as in peroxides, while H generally has an oxidation number of +1 (also with some exceptions).
    - ➢ The sum of all the oxidation numbers in a molecule must equal the net charge of the molecule.

Balancing Redox Reactions

- A key in balancing redox reactions is to consider the reduction and oxidation processes separately, that is, splitting the overall reaction into two **half-reactions**: one for oxidation and one for reduction.
- Let's consider the following reaction:

$$Zn(s) + Ag^+(aq) \rightarrow Zn^{2+}(aq) + Ag(s)$$
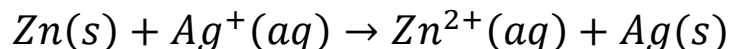
- The first step in balancing a redox reaction is to identify the species being oxidized and the species being reduced.
- Since Zn goes from an oxidation number of 0 to an oxidation number of +2, it lost electrons and is oxidized, while Ag is reduced.
- Now, we need to make half reactions for each, including the electrons that are lost or gained:

$$\text{Oxidation: } Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$
$$\text{Reduction: } Ag^+(aq) + e^- \rightarrow Ag(s)$$
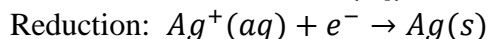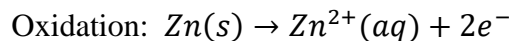
- Zn/Zn^{2+} and Ag/Ag^+ are each known as **redox couples**.
- Now that we have the two half-reactions, we must multiply each equation so that both have the same number of electrons. In this case, that would mean multiplying the reduction equation by 2.

$$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$$
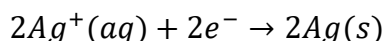
- After doing so, add the two equations together, and cancel out the electrons and spectator ions.

$$Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$$
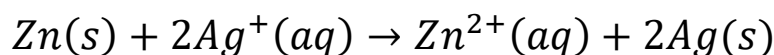
- We now have a balanced redox equation.
- What if the reaction happens in **acidic or basic conditions**, or if there is water or oxygen involved?
- Let's balance the following equation in basic solution:
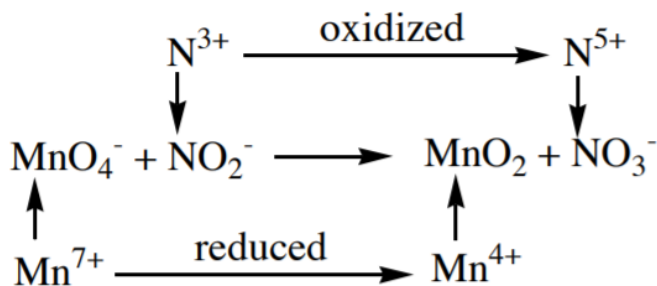
- Since we have identified the oxidized and reduced species, we can now write our half reactions:

$$\text{Reduction: } MnO_4^- + 3e^- \rightarrow MnO_2$$

$$\text{Oxidation: } NO_2^- \rightarrow NO_3^- + 2e^-$$
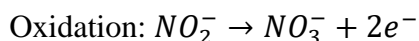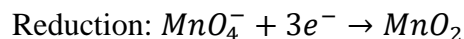
- Notice the problem? The number of oxygens is not consistent for either half-reaction!
- To balance the number of oxygens, rather than single oxygens (oxygen rarely exists in monatomic form), we add H_2O to the side of the reaction that lacks oxygen. This effectively adds whatever number of oxygens needed per water molecule:

$$\text{Reduction: } MnO_4^- + 3e^- \rightarrow MnO_2 + 2H_2O$$
$$\text{Oxidation: } NO_2^- + H_2O \rightarrow NO_3^- + 2e^-$$
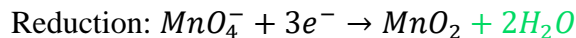
- Oxygens are now balanced, but now we added hydrogens to one side by adding water, while the other side does not have any!
- We take care of this by simply adding the needed number of H^+ to balance the hydrogens:

$$\text{Reduction: } MnO_4^- + 3e^- + 4H^+ \rightarrow MnO_2 + 2H_2O$$
$$\text{Oxidation: } NO_2^- + H_2O \rightarrow NO_3^- + 2e^- + 2H^+$$
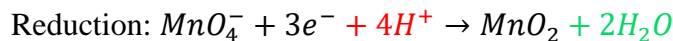
- Now, we do as usual and multiply the equations so that the electrons are equal to each other:
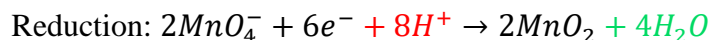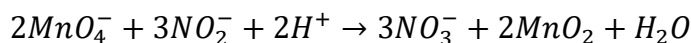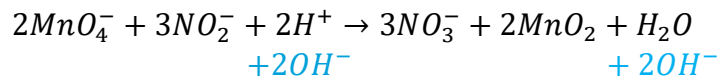
$$\text{Reduction: } 2MnO_4^- + 6e^- + 8H^+ \rightarrow 2MnO_2 + 4H_2O$$
$$\text{Oxidation: } 3NO_2^- + 3H_2O \rightarrow 3NO_3^- + 6e^- + 6H^+$$

- Adding the two equations yields:

$$2MnO_4^- + 3NO_2^- + 2H^+ \rightarrow 3NO_3^- + 2MnO_2 + H_2O$$

- Though this equation is balanced, remember that we were in basic conditions, so we cannot have H^+. Remove the H^+'s by adding the needed number of OH⁻ ions **on both sides** (you do not want to disturb the balance again). Note that adding OH⁻ to H^+ makes H_2O:

$$2MnO_4^- + 3NO_2^- + 2H^+ \rightarrow 3NO_3^- + 2MnO_2 + H_2O$$
$$+2OH^- \qquad\qquad\qquad + 2OH^-$$

- Finally, this yields:

$$2MnO_4^- + 3NO_2^- + H_2O \rightarrow 3NO_3^- + 2MnO_2 + 2OH^-$$
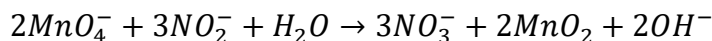
Electrochemical Cells

- An **electrochemical cell** is a device in which electron current is either:
  - ➢ Produced by a spontaneous chemical reaction (a **galvanic/voltaic cell**) or
  - ➢ Used to bring about a non-spontaneous reaction (an **electrolytic cell**)
- A **battery** is a collection of galvanic cells in series.
- **Electrodes** are conductors through which electrons can travel.
- Let's look at a galvanic cell:

Salt bridge | Voltmeter
Electrons | +1.10 V

Ions

Anode | Cathode

Oxidation: | Reduction:
$Zn(s) \rightarrow$ | $Cu^{2+}(aq) + 2\ e^-$
$Zn^{2+}(aq) + 2\ e^-$ | $\rightarrow Cu(s)$
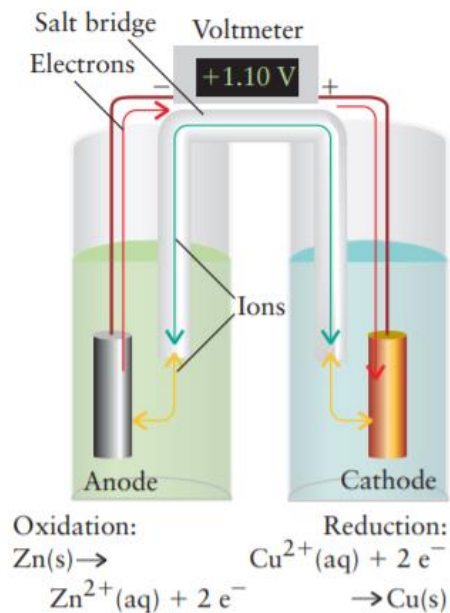
> ➢ At the **anode**, oxidation is occurring, and electrons produced from this process flow out.
> ➢ At the **cathode**, electrons flow in (from the anode) and allow for reduction to take place.
> ➢ Zinc solid is oxidized to Zn^{2+} ions, which go into solution
> ➢ Cu^{2+} ions at the cathode are reduced to copper solid, which is plated on the electrode.
> ➢ The **voltmeter** measures the flow of electric current.
> ➢ There is a **salt bridge** (usually composed of a gel) connecting the two half-cells so that ions can flow and maintain neutrality in the solutions (as we are generating +ions on the left and losing +ions on the right)

- Rather than drawing out the cell each time, we can write a shorthand:

$$Zn(s)\ |\ Zn^{2+}(aq)\ ||\ Cu^{2+}(aq)\ |\ Cu(s)$$

> ➢ A single line indicates a phase boundary (solid vs. aqueous), while a double line indicates the salt bridge.
> ➢ If there is no phase transition, use a comma instead of a line.

- In this cell, zinc metal is consumed and copper is deposited in a quantity that is proportional to the charge passed. This is known as **Faraday's Law.**
- How would we go about determining this amount?
> ➢ First, determine the amount of charge that has passed through the circuit:

$$Q\ = I \times t$$

> o Q is the magnitude of charge, measured in Coulombs (C)
> o I is the current, measured in amperes (A)
> o t is time, in seconds

- ➢ Then, we determine the number of moles of electrons that this charge is equivalent to by dividing by Faraday's constant (1 Faraday = 96,485 C/mol).
- ➢ Calculate the number of moles consumed and number of moles deposited, using stoichiometry.

Cell Potential and Spontaneity

- **Cell potential**, **E**$_{cell}$, is a way to measure how much voltage exists between two cells in a battery.
  - ➢ **Standard cell potential, E^o,** is the cell potential measured at standard conditions:
  - ➢ Atmospheric pressure is at 1 atm
  - ➢ Concentration of the solutions is 1M
- Each half-reaction has its own standard cell potential, which is usually listed on a table in textbooks.
- By convention, only the **standard reduction potentials** (cell potential for the reduction half-reaction) are listed, although one can easily find the oxidation potential by flipping the equation **and the sign** of the reduction potential:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s), \ E^o_{red} = +0.34 \, V$$

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-, \ E^o_{ox} = -0.34 \, V$$
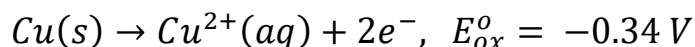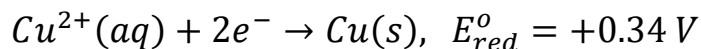
- To measure the potential for a single half-cell, measure it against a **standard hydrogen electrode**, which has a cell potential of 0.
- The overall cell potential, when considering both the oxidation and reduction reactions occurring, can be found using the following formula:

$$E^o_{cell} = E^o(cathode) - E^o(anode)$$

- ➢ Use this equation if the values that you are using are only the standard reduction potentials (tables generally only list standard reduction potentials anyway).
- ➢ $E^o(cathode)$, for instance, means that you are using the standard reduction potential for the **couple** (redox couple) at the cathode.
- A more intuitive (in my opinion) version of this formula is:

$$E^o_{cell} = E^o_{red} + E^o_{ox}$$

- ➢ With this equation, once you identify the oxidation and reduction half-reactions, figure out E^o_{ox} and E^o_{red} for those reaction, respectively.
- ➢ Note that tables usually only list values for E^o_{red}, so you will have to find E^o_{ox} by flipping the equation and the sign of the given voltage.
- Once you have figured out the cell potential, how would you know if the flow of electrons is spontaneous?

- Remember that spontaneity relates to ΔG. It turns out that there is a formula relating E_{cell} and ΔG:

$$\Delta G_{cell} = -nFE_{cell}$$

  - ➢ Where n is the number of electrons involved in the reaction
  - ➢ F is Faraday's constant
- Remembering that a negative ΔG implies a spontaneous reaction,
  - ➢ A positive E_{cell} means that the flow of electrons is spontaneous.
  - ➢ A negative E_{cell} means that the flow of electrons is non-spontaneous.
  - ➢ A large positive E_{red}^o means that the element is easy to reduce, (because ΔG will be more negative).

- A battery is said to be **exhausted** when its cell potential has reached 0 V (dead battery), and this means that it has reached equilibrium.
- How does cell potential change with cell composition?
- Remember back from thermodynamics the following formula:

$$\Delta G = \Delta G^0 + RT \ \ln Q$$

- Knowing that $\Delta G = -nFE_{cell}$ and $\Delta G^o = -nFE_{cell}^o$, we can make substitutions and obtain the **Nernst equation:**
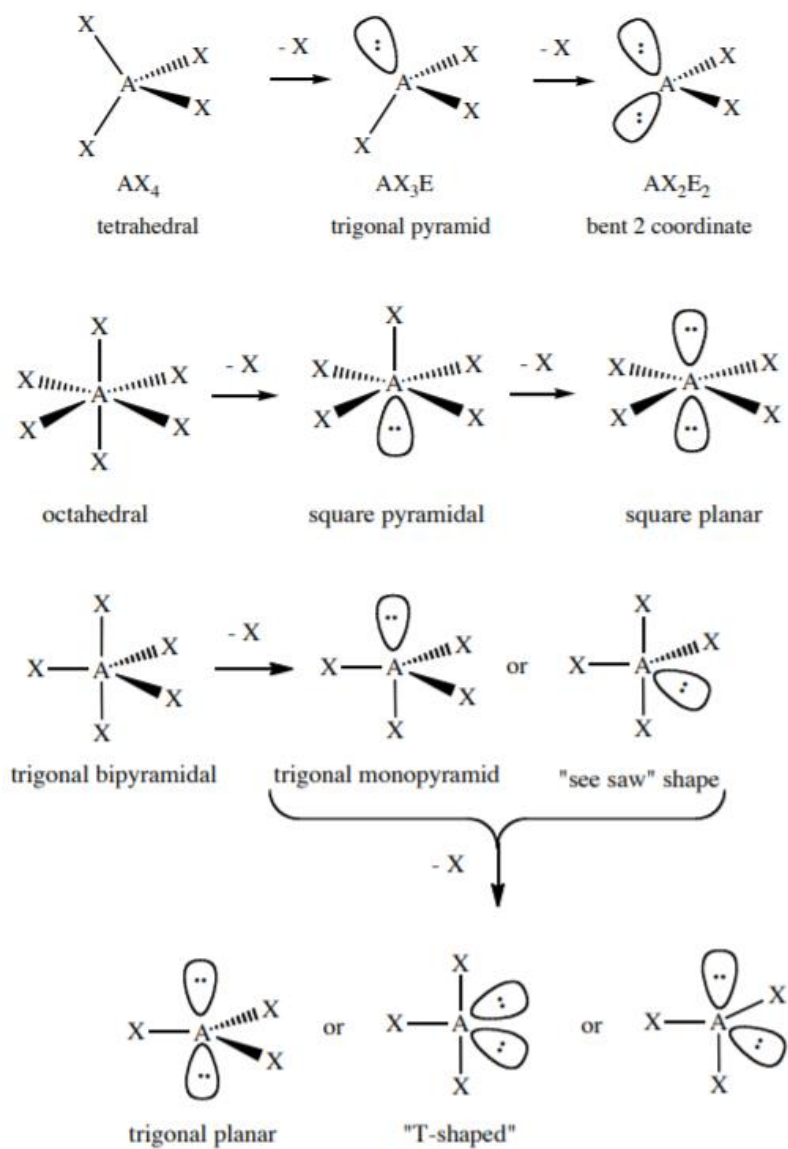
$$E = E^o - \frac{RT}{nF} \ln Q$$

- This equation allows us to calculate the potential for a cell that is not in standard conditions, as is the case for a discharged battery.
- If two cells are of identical types, but **different concentrations**, there *will* be a cell potential. These cells are called **concentration cells** and their cell potential is calculated using the Nernst equation.
- If more than one reaction is possible, the most favorable reaction is the one with the largest E^o.

THEORY OF MOLECULAR SHAPES

VSEPR Theory

- **V**alence **S**hell **E**lectron **P**air **R**epulsion is a way to predict the shapes of molecules based on the fact that electron pairs repel each other. In doing so, they will arrange themselves such that repulsion is minimized and electron density is spread out.
- Lone pairs of electrons occupy more space than bonded electrons (and hence affect the bond angles), and are not counted in the structure description.
- In minimizing high-energy electronic structure, molecules form the following shapes, depending on the number of bonded atoms and lone pairs:


AX_4	AX_3E	AX_2E_2
tetrahedral	trigonal pyramid	bent 2 coordinate

octahedral	square pyramidal	square planar

trigonal bipyramidal	trigonal monopyramid	"see saw" shape

trigonal planar	"T-shaped"

VALENCE BOND THEORY

Development of Valence Bond Theory

- In the Lewis model of a bond, we are assuming that an electron pair is localized between two atoms.
- We know, however, that this is quantum mechanically not entirely correct, as we can't describe the location of an electron in an atom in a precise position.
- Heitler, London, Slater, and Pauling developed **valence bond theory**, which goes beyond VSEPR theory and Lewis theory by considering the quantum mechanical properties of electrons.

Sigma (σ) and Pi (π) Bonds

- Let's look at a simple molecule: H_2:


Atomic orbitals
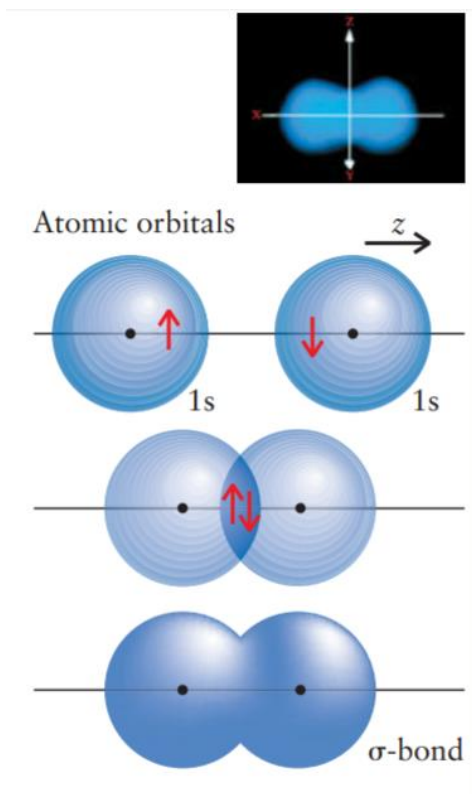
- Each H atom has an electron in its 1s orbital, and as they get closer to each other, there is a region of **overlap** and constructive interference of the 1s orbital wavefunctions.
- This pair of electrons is put into an orbital that is **cylindrically symmetric**, called a **σ bond** and has no nodes between the **internuclear axis**.

- There can also be an overlap of p orbitals between two atoms, called a **π bond**, and looks like this:


2p$_x$ 2p$_x$

z

π-bond
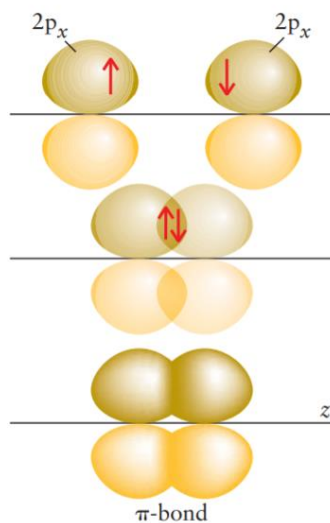
- There is overlap between the lobes of the p orbital **above and below** the internuclear axis. This bond has a node between the internuclear axis.
- Not all p orbitals form π bonds exclusively: using the similar overlap patterns in a σ bond between two s orbitals, there can be sigma bonds between a p orbital and an s orbital, or two p orbitals, as so:

2p$_x$ 2p$_z$ 2p$_x$

z

σ-bond
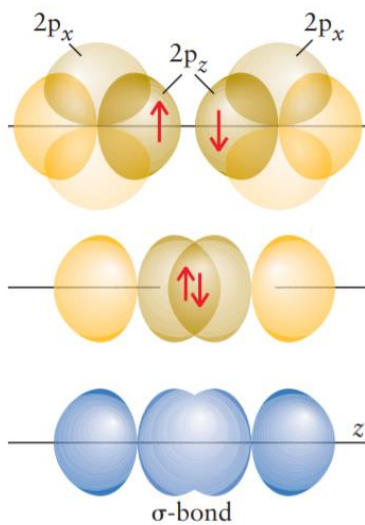
- In general:
  - ➤ A single bond is a σ bond.
  - ➤ A double bond is a σ bond plus one π bond.
  - ➤ A triple bond is a σ bond plus two π bonds.

Hybridization

- Sigma and pi bonds seem simple enough, but a molecule will rarely contain only one bond (whether that be single, double, or triple). A molecule of CH_4, for example, contains 4 σ bonds; however, even though carbon does have 4 orbitals (a 2s and 3 2p orbitals), it has a tetrahedral geometry, and the orbitals alone simply do not complement this bonding geometry.
- How would we construct several bonds that are all identical to each other so that we may have multiple σ bonds?
- We can combine, or **hybridize**, s and p orbitals so that they may form whatever number of identical orbitals (sp, sp^2, or sp^3 orbitals) that we need for the bonds in the molecule.
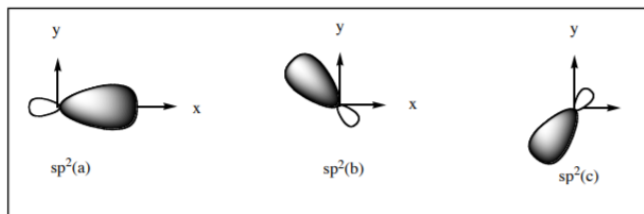- Let's make hybrid orbitals for BH_3, a trigonal planar molecule.
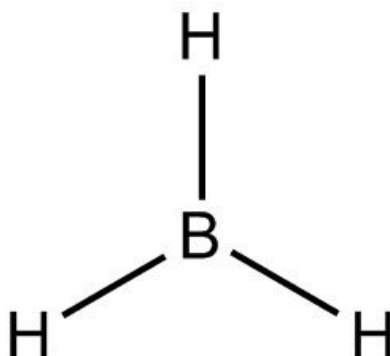
  - ➢ This molecule contains 3 σ bonds, so we need to combine a boron 2s orbital and 2 boron 2p orbitals to create 3 identical sp^2 hybrid orbitals.
  - ➢ Take this molecule to be in the xy plane.
- We obtain the following:

$$sp^2(a) = \frac{1}{\sqrt{3}}2s + \frac{\sqrt{2}}{\sqrt{3}}2p_x$$

$$sp^2(b) = \frac{1}{\sqrt{3}}2s - \frac{1}{\sqrt{6}}2p_x + \frac{1}{\sqrt{2}}2p_y$$

$$sp^2(c) = \frac{1}{\sqrt{3}}2s - \frac{1}{\sqrt{6}}2p_x - \frac{1}{\sqrt{2}}2p_y$$

Note that the sum of squared coefficients in a given equation and between equations is 1. The three lie in a plane 120° to one another. Note also that the "unused" (empty) orbital is $2p_z$.

  - ➢ The coefficients on the 2s and 2p orbitals represent the contribution the hybrid orbital.
  - ➢ The sum of the squares of the coefficients must add up to 1 across a row. Recall from unit 1 that the probability that an electron is at a point is given by the square of the wavefunction.