CHEM 30 REVIEW

ORGANIC

Organic or Inorganic??

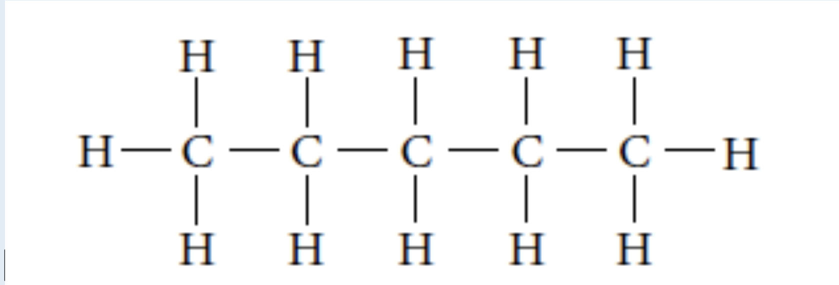
Formula	Organic or Inorganic?
$CaCO_{3(s)}$	Inorganic (carbonate ion)
$C_{25}H_{52(s)}$	Organic
$Ca_2C_{(s)}$	Inorganic (carbide ion)
$CCl_{4(l)}$	Organic
$CH_3COOH_{(l)}$	Organic
$CO_{2(g)}$	Inorganic (oxide)
$KCN_{(s)}$	Inorganic (cyanide)
$C_{12}H_{22}O_{11(s)}$	Organic

Four Types of Formulas

1. Molecular Formulas $C_5H_{10(g)}$

Not very useful for organic compounds because so many isomers can exist

2. Structural Formulas

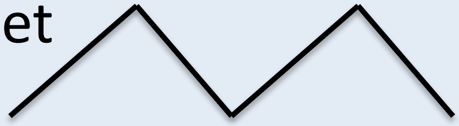


$$\begin{array}{ccccccccccccc} & & H & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & \end{array}$$

3. Condensed Structural For

$CH_3-(CH_2)_3-CH_3$

4. Line Diagrams
   – end of line segment represents carbon
   – it is assumed to satisfy each carbon's octet



Naming Organic Compounds

- Aliphatic Hydrocarbons – contains only hydrogen and carbon atoms
  - Straight line chains of carbon atoms
  - Alicyclic hydrocarbons have carbon atoms forming a closed ring. Still considered aliphatic

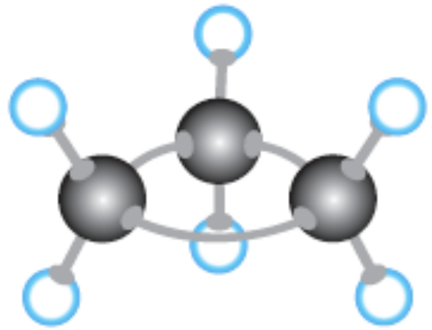
Alkanes	Alkenes	Alkynes
Only **single** C-C bonds	**Double** C-C Bond present	**Triple** C-C bond present
General formula C_nH_{2n+2}	General formula: C_nH_{2n}	General formula: C_nH_{2n-2}
Saturated	**Unsaturated**	**Unsaturated**

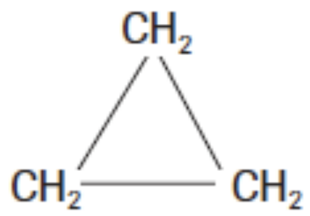
Summary of Naming Alkanes

1. Find the **parent chain.** Use the appropriate root and suffix.
2. Number the parent chain carbon atoms, starting from the end closest to the branch(es) so that the numbers are the **lowest** possible
3. Identify any **branches** and their location number on the parent chain (us the suffix –yl for branches)
4. If more than one of the same branch exist, use a **multiplier (di, tri)** to show this. Remember to include all numbers
5. If different branches exist, name them in alphabetical order
6. Separate numbers from numbers using **commas**, and numbers from words using **dashes** (**no extra spaces**)

CYCLOALKANES

- Based on evidence, chemists believe that organic carbon compounds sometimes take the form of cyclic hydrocarbons:
- Cycloalkanes: Alkanes that form a closed ring
  - General Formula C_nH_{2n}
    - Two less hydrogens are present than in straight chain alkanes because the two ends of the molecule are joined
    - Are these considered **saturated**?? Yes, because they have only single bonds and the max amount of hydrogen's bonded to the carbons
    - Cyclo-compounds will have a **higher** boiling point than their straight chain partners (because there is an additional bond present)





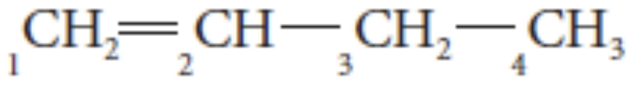
cyclopropane

Naming Alkenes and Alkynes

1. Find the parent chain. It MUST contain the multiple bond.
    - If the bond is a double, the suffix for the parent chain will be -ene
    - If the bond is a triple, the suffix for the parent chain will be –yne

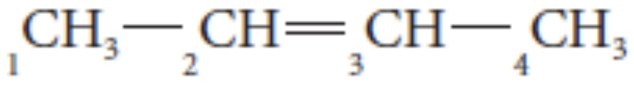
2. Count carbon atoms so that the **multiple bond** will be on the **lowest** possible number. Indicate the **number** that the multiple bond falls on directly <u>before</u> the suffix

3. Name branches as before



$${}_{1}\mathrm{CH_2}{=}{}_{2}\mathrm{CH}{-}{}_{3}\mathrm{CH_2}{-}{}_{4}\mathrm{CH_3}$$

but-1-ene



$${}_{1}\mathrm{CH_3}{-}{}_{2}\mathrm{CH}{=}{}_{3}\mathrm{CH}{-}{}_{4}\mathrm{CH_3}$$

but-2-ene

Naming Alkenes and Alkynes

4. It is possible for a molecule to have more than one double bond. These are called **alkadienes** and have the same general formula as alkynes (C_nH_{2n-2})
   - If this is the case, indicate both numbers where the double bond is formed, and change the suffix to **–diene**.

a) Draw buta-1,3-diene: $CH_2=CH-CH=CH_2$

b) What is the IUPAC name for the following:

$CH_2=C=CH-CH_3$ buta-1,2-diene

Structural Isomerism

- Compound with the same molecular formula but different structures
  - They will have different chemical and physical properties – based on their different structures

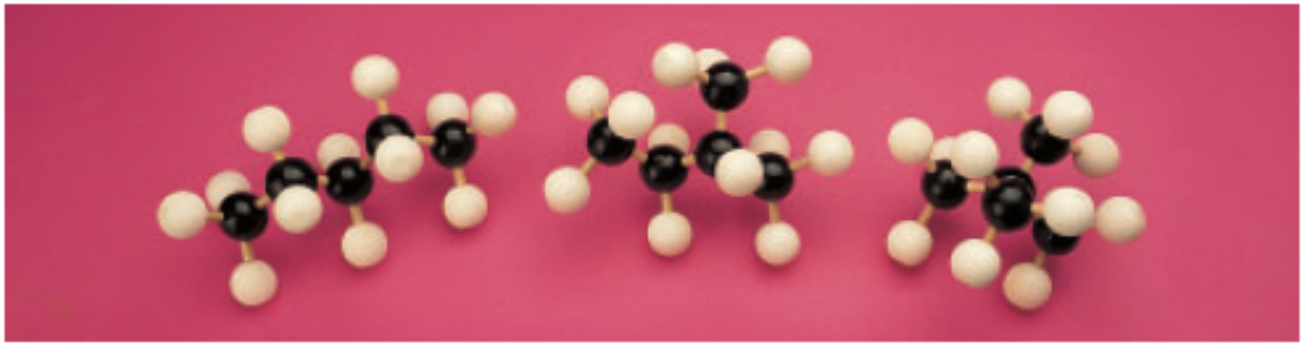
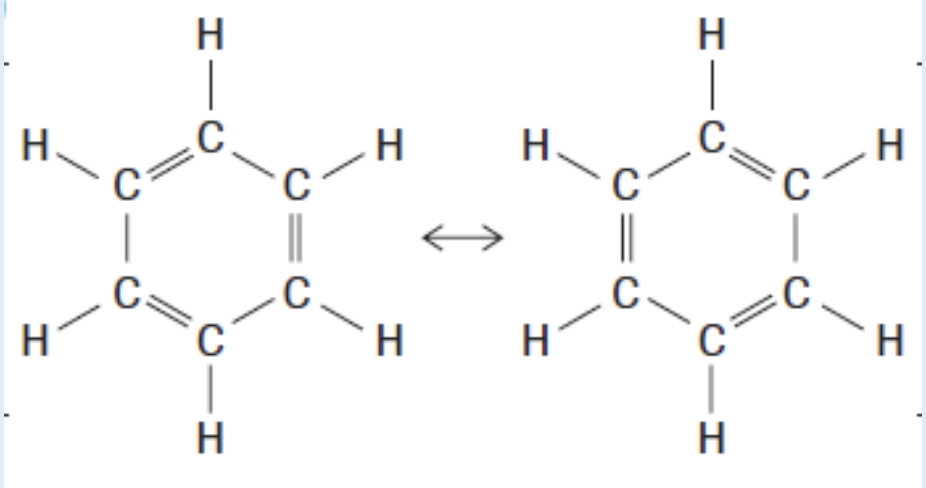
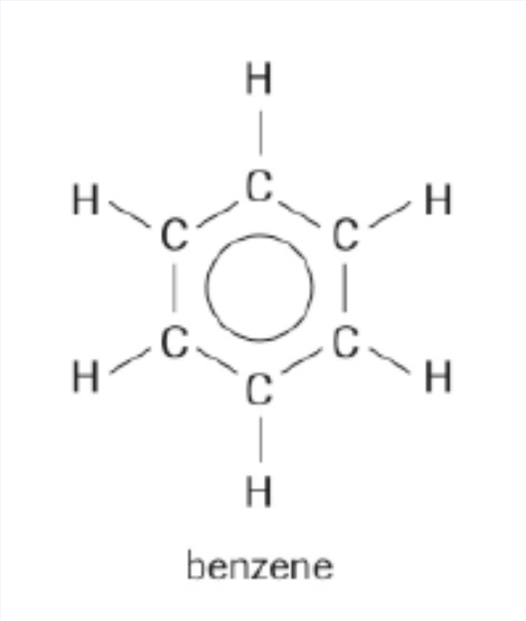


Figure 9
Each of the three isomers of C_5H_{12} has different physical and chemical properties.

- **What do we know about benzene?**
  - Formula is C_6H_6 (3D link)
  - Unreactive – so **no true** double or triple bonds
  - Carbon-carbon bonds are the same length and strength
  - Each carbon is bonded to a hydrogen
  - So what does benzene look like??



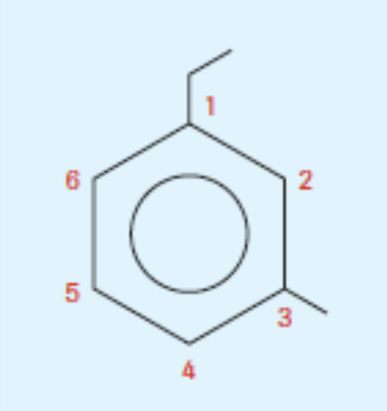
The three double bonds **resonate** resulting in an overall bond length somewhere **in between a single and a double bond**, explaining benzene's stability



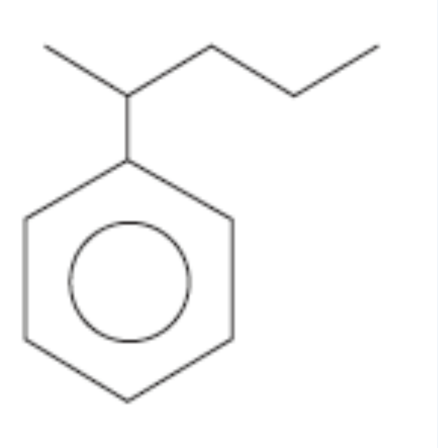
compounds

Practice Naming Aromatics

- Draw the line structural formula for 1-ethyl-3-methylbenzene



- Draw the line structural formula for 2-phenylpentane

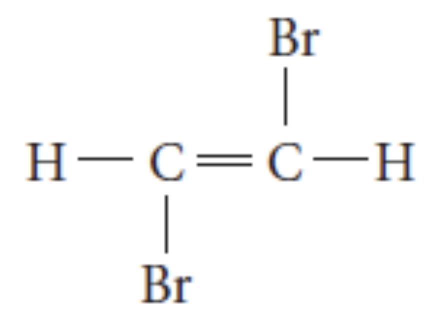


Practice Naming Organic Halides

- Name the following:

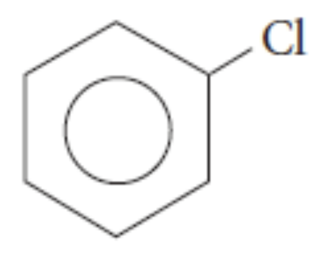
CH_2Cl_2

dichloromethane



1,2-dibromoethene

Bonus: Try 1,2-dibromo-1,2-dichloroethene

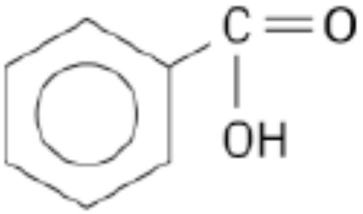


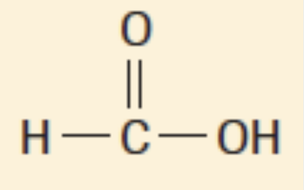
chlorobenzene

Carboxylic Acids

- A **carboxyl** group is composed of a carbon atom double bonded to an oxygen atom and bonded to a hydroxyl group (-COOH)
  - Note: Because the carboxyl group involves three of the carbon atom's four bonds, the carboxyl is always at the end of a carbon chain or branch

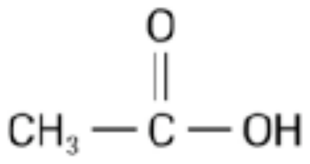
Examples:





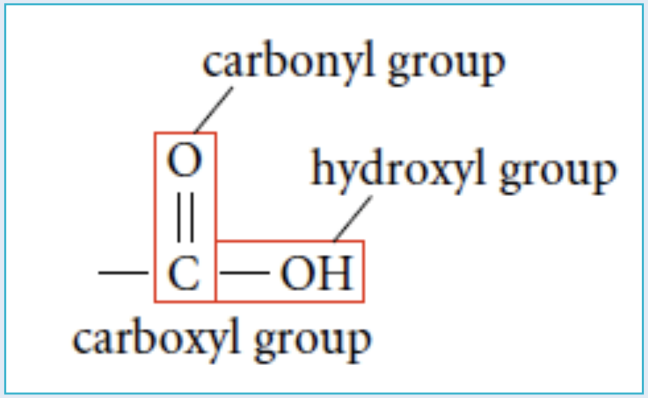
$H-\overset{\overset{\displaystyle O}{\|}}{C}-OH$

methanoic acid



$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$

ethanoic acid



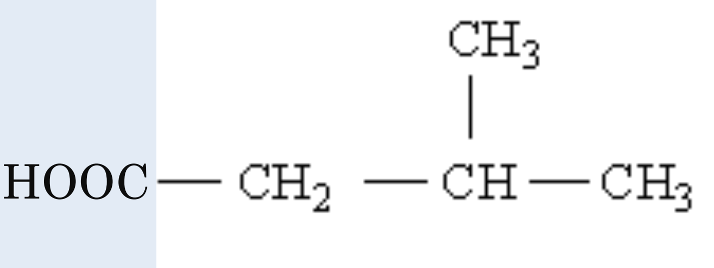
Carboxylic acids are weak organic acids

Naming Carboxylic Acids

1. Name the parent alkane
2. Replace the –e at the end of the name of than parent alkane with –oic acid
3. The carbon atoms of the carboxyl group is always given position number 1. Name and number the branches that are attached to the compound.

Draw 3-methylbutanoic acid

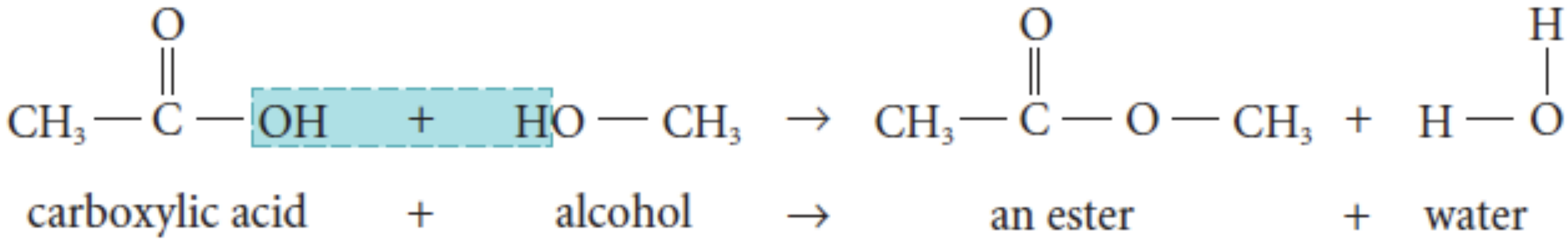
Remember COOH or HOOC can also represent the carboxyl group



$$HOOC-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

Esters

- The reaction between a carboxylic acid and an alcohol produces an ester molecule and a molecule of water
  - This reaction is known as a **condensation** or **esterification** reaction



$$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-\boxed{OH\quad+\quad H}O-CH_3 \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-O-CH_3 + H-\overset{\overset{H}{|}}{O}}$$

  - The ester functional group –COO– is similar to that of a carboxylic acid, except that the H atom of the carboxyl group has been replaced by a hydrocarbon branch.
  - Esters are responsible for natural and artificial fragrance and flavourings in plants and fruits.

Naming Esters

- Name the following ester and the acid and alcohol from which it can be prepared.

A strong acid catalyst, such as $H_2SO_{4(aq)}$ is used along with some heating to increase the rate of the organic reaction

$$\mathrm{CH_3{-}CH_2{-}CH_2{-}COOH + HO{-}CH_2{-}CH_3 \xrightarrow{H_2SO_4}}$$

butanoic acid **ethanol**

$$\mathrm{CH_3{-}CH_2{-}CH_2{-}COO{-}CH_2{-}CH_3 \quad + H_2O}$$

ethyl butanoate **water**

Tip: The branch attached to the oxygen (of the –CO**O**) comes first in the name, the chain attached to the carbon (of the –**C**OO) comes second

Physical Properties of Simple Hydrocarbons

Alkanes	Non-polar molecules Only intermolecular forces are London Force Boiling point and melting point **increase with number of carbons** All **insoluble** in water (like dissolves like) – nonpolar and polar don't mix 1-4Cs = gas, 5-16Cs = liquid 17 and up = solid at SATP
Alkenes	Non-polar molecules, therefore **insoluble** in water Boiling points slightly **lower than alkanes** with the same number of carbons due to less electrons (unsaturated), resulting in lower London Forces
Alkynes	Non-polar molecules, therefore **insoluble** in water **Higher boiling points than alkanes and alkenes** with similar C #s Accepted explanation: Linear structure around triple bond allows electrons to come closer together than in alkanes/enes, resulting in greater London Force
Branching	The **more branching, the less significant the London Force (~lower b.p.)** - more surface area in straight chain hydrocarbons allows more separation of charge, resulting in greater London Force - see Table #3 pg. 378 (i.e. pentane (with 5Cs) has a b.p. of 36^{o}C which is much higher than dimethylpropane (5Cs) -12^{o}C) = because branching decreased the strength of the London force

Physical Properties of Hydrocarbon Derivatives

Alcohols	**Much higher boiling points than hydrocarbons** (1-12Cs are liquids at SATP) due to hydrogen bonding between hydroxyl groups of adjacent molecules **Small** alcohols are **totally miscible in water**, but the larger the hydrocarbon part of the alcohol (nonpolar part), the more nonpolar the alcohol is
Carboxylic Acids	Like alcohols they have hydrogen bonding, but is more significant due to the C=O. This means **greater bps and solubility than alcohols** with same number of Cs. Carboxylic acids with 1-4Cs are **completely miscible in water**
Esters	Fruity odour in some cases Polar but they lack the –OH bond therefore do not have hydrogen bonding, so **lower bps than both alcohols and carboxylic acids** Esters with **few carbons** are polar enough to be **soluble** in water

Compound	Boiling Point (^{o}C)
butane	-0.5
butan-1-ol	117.2
butanoic acid	165.5

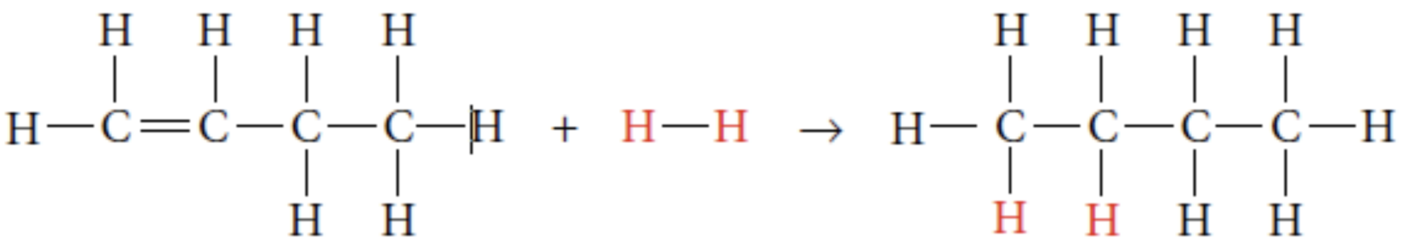
Combustion Reactions

- Burning of hydrocarbons in the presence of oxygen
  - **Complete Combustion**: abundant supply of oxygen; products are carbon dioxide, water vapour and heat
    - Ex. $C_3H_{8(l)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(g)}$
  - **Incomplete Combustion**: limited supply of oxygen; products are carbon monoxide, soot (pure carbon) or any combination of carbon dioxide, carbon monoxide and soot in addition to water vapour and heat
    - Ex. $2C_8H_{18(l)} + 17O_{2(g)} \rightarrow 16CO_{(g)} + 18H_2O_{(g)}$
    - OR $2C_8H_{18(l)} + 9O_{2(g)} \rightarrow 16C_{(s)} + 18H_2O_{(g)}$

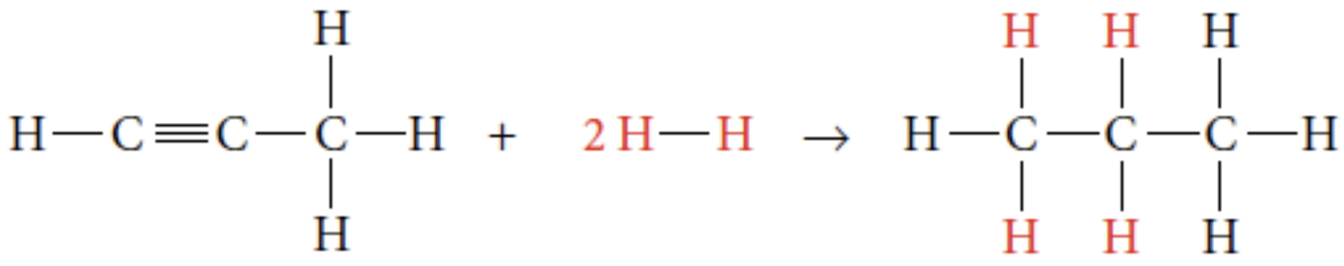
** Assume complete combustion unless specified otherwise

1. **Addition Reactions**: reaction of alkenes and alkynes with hydrogen gas, a halogen compound, or a hydrogen halide compound.
   - Addition reactions usually occur in the presence of a catalyst

a) Addition with $H_{2(g)}$ (also called **hydrogenation**)



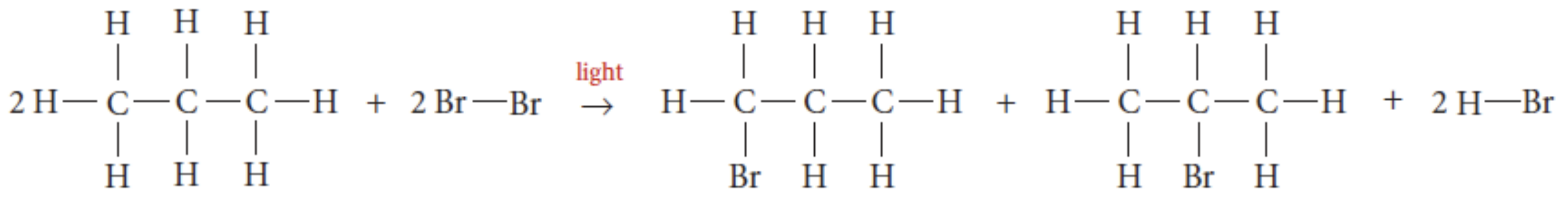
but-1-ene + hydrogen → butane



propyne + excess hydrogen → propane

2. **Substitution** Reactions – breaking of a C-H bond in an alkane or an aromatic ring and replacing it with another atom or group of atoms
   - Usually occur slowly at room temperature, so **light** may be necessary as a catalyst
   - Often substitutes a halogen for a hydrogen
   - No change in saturation

$$C_3H_8(g) + Br_2(g) \xrightarrow{\text{light}} C_3H_7Br(l) + HBr(g)$$

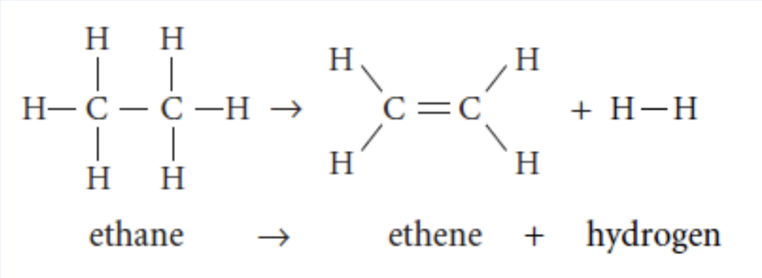


propane + bromine $\xrightarrow{\text{light}}$ 1-bromopropane + 2-bromopropane + hydrogen bromide

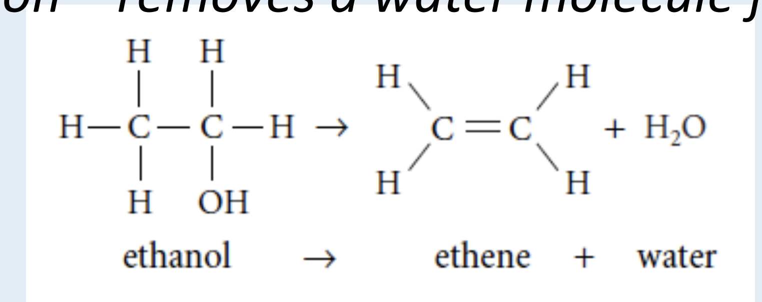
Propane contains hydrogen atoms bonded to end carbons and the middle carbon atom, so two different products (isomers) are formed, in unequal proportions

3. **Elimination** Reactions – involves eliminating atoms or groups of atoms from adjacent carbon atoms; decreases the level of saturation

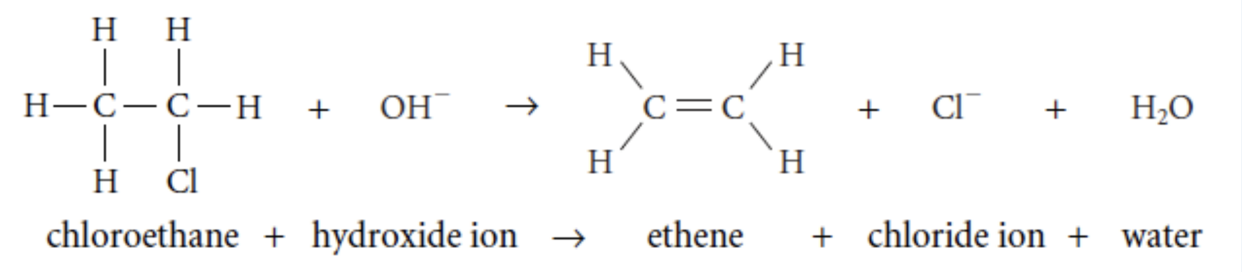
   a) Alkane <u>cracked</u> into an **alkene** (uses high temperatures)



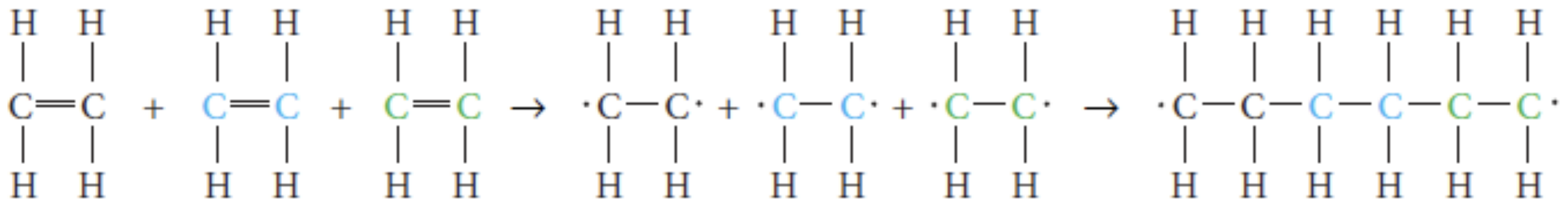
   b) <u>Alcohol</u> is reacted with a catalyst to produce an **alkene** and water (*dehydration – removes a water molecule from the alcohol*)



   c) <u>Alkyl halide</u> reacts with a hydroxide ion (OH$^-$) to produce an **alkene** (*dehydrohalogenation – removes a hydrogen and halogen atom*)

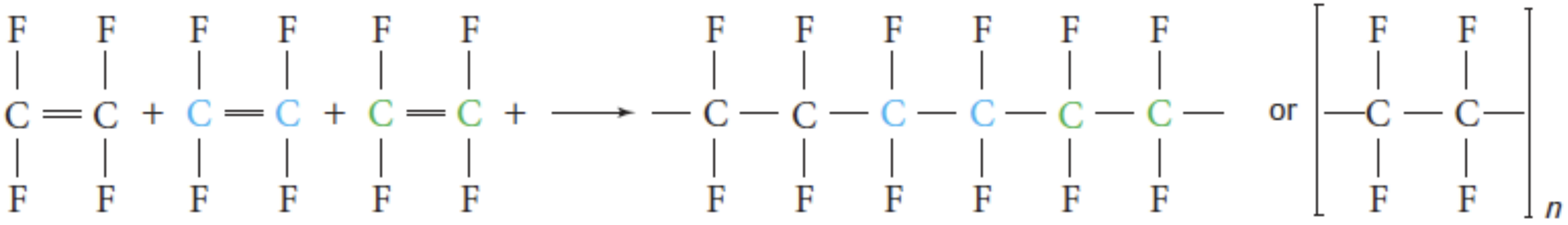


- **Addition Polymerization** always results in **one** product, the polymer
- Requires <u>unsaturated</u> hydrocarbon monomers and bond saturation occurs when the polymer is made
- Common polymers produced by addition polymerization:



ethene (ethylene)

part of polyethene (polyethylene)

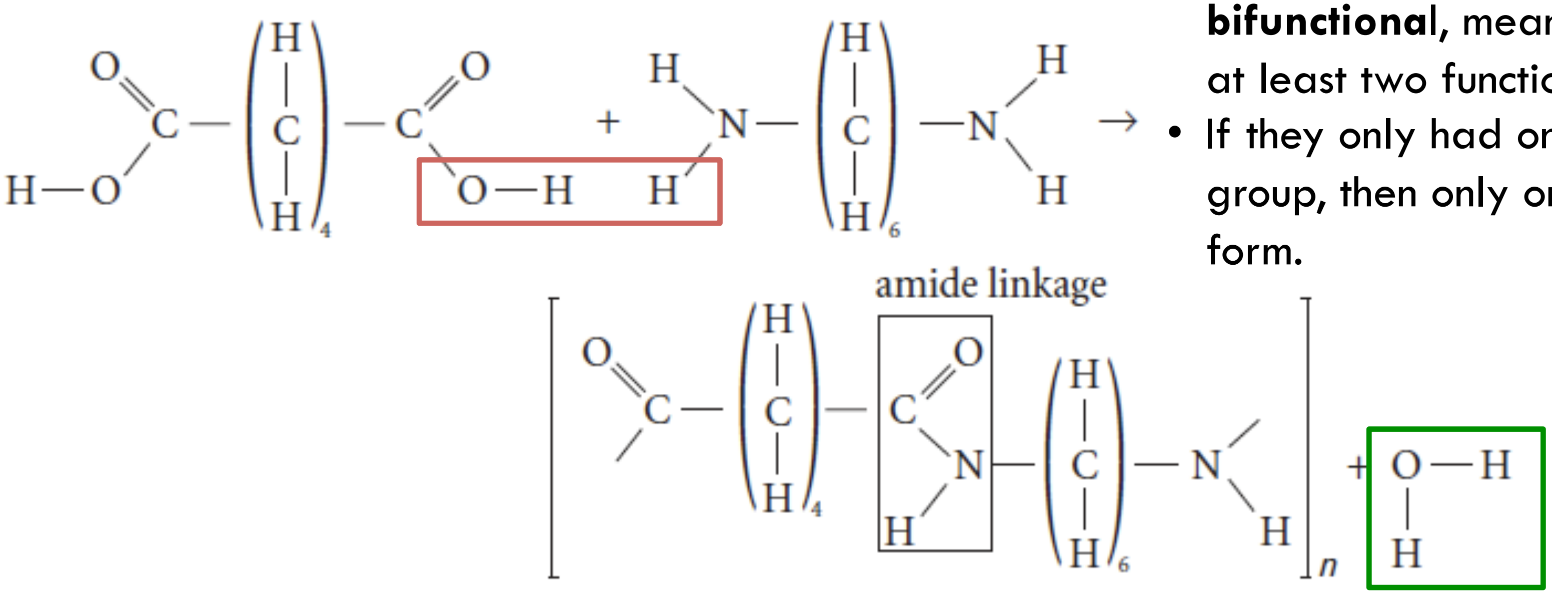


tetrafluoroethene

polytetrafluoroethene (Teflon)

Condensation Polymerization

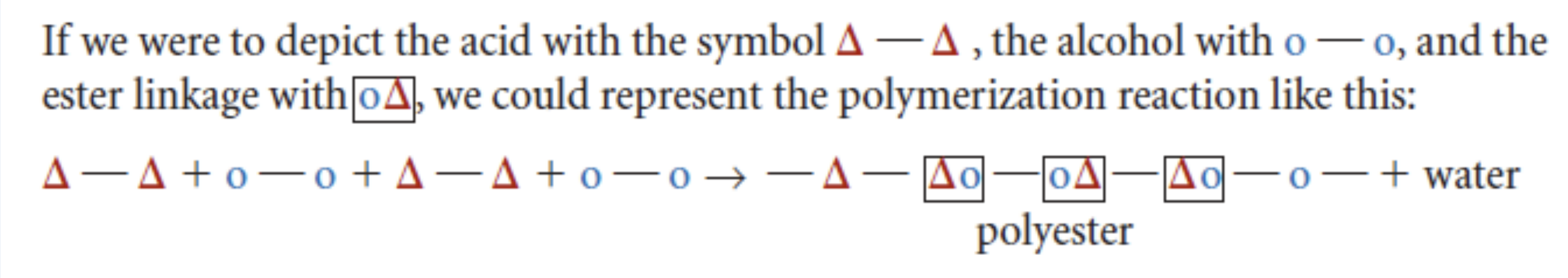
- Monomers combine to form a polymer and a bi-product. Each time a bond forms between monomers, small molecules, such as water, ammonia, or HCl are "condensed" out.
- The polymerization of nylon:



- For condensation polymerization to occur, monomers must be **bifunctional**, meaning they have at least two functional groups.
- If they only had one functional group, then only one bond would form.

Polyester

- When a carboxylic acid reacts with an alcohol in an esterification reaction, a water molecule is eliminated and a single ester molecule is formed.
- This esterification reaction can be repeated so many esters are joined in a long chain… a **polyester**
  - This is created using a <u>dicarboxylic</u> acid (an acid with a carboxyl group at each end) and a <u>diol</u> (an alcohol with a hydroxyl group at each end)
  - The ester linkages are formed end to end between alternating acid and alcohol molecules



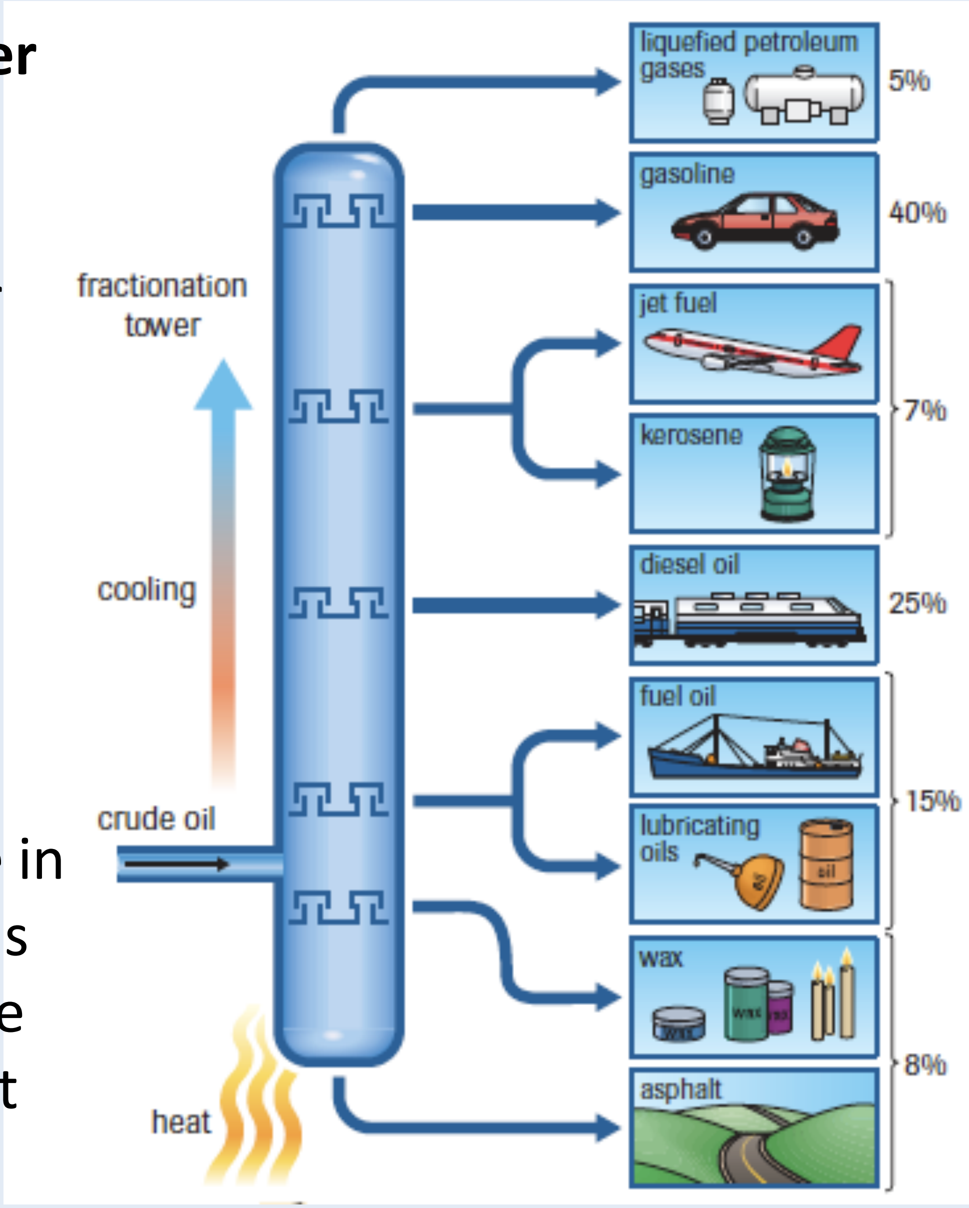
If we were to depict the acid with the symbol $\Delta - \Delta$, the alcohol with $o - o$, and the ester linkage with $\boxed{o\Delta}$, we could represent the polymerization reaction like this:

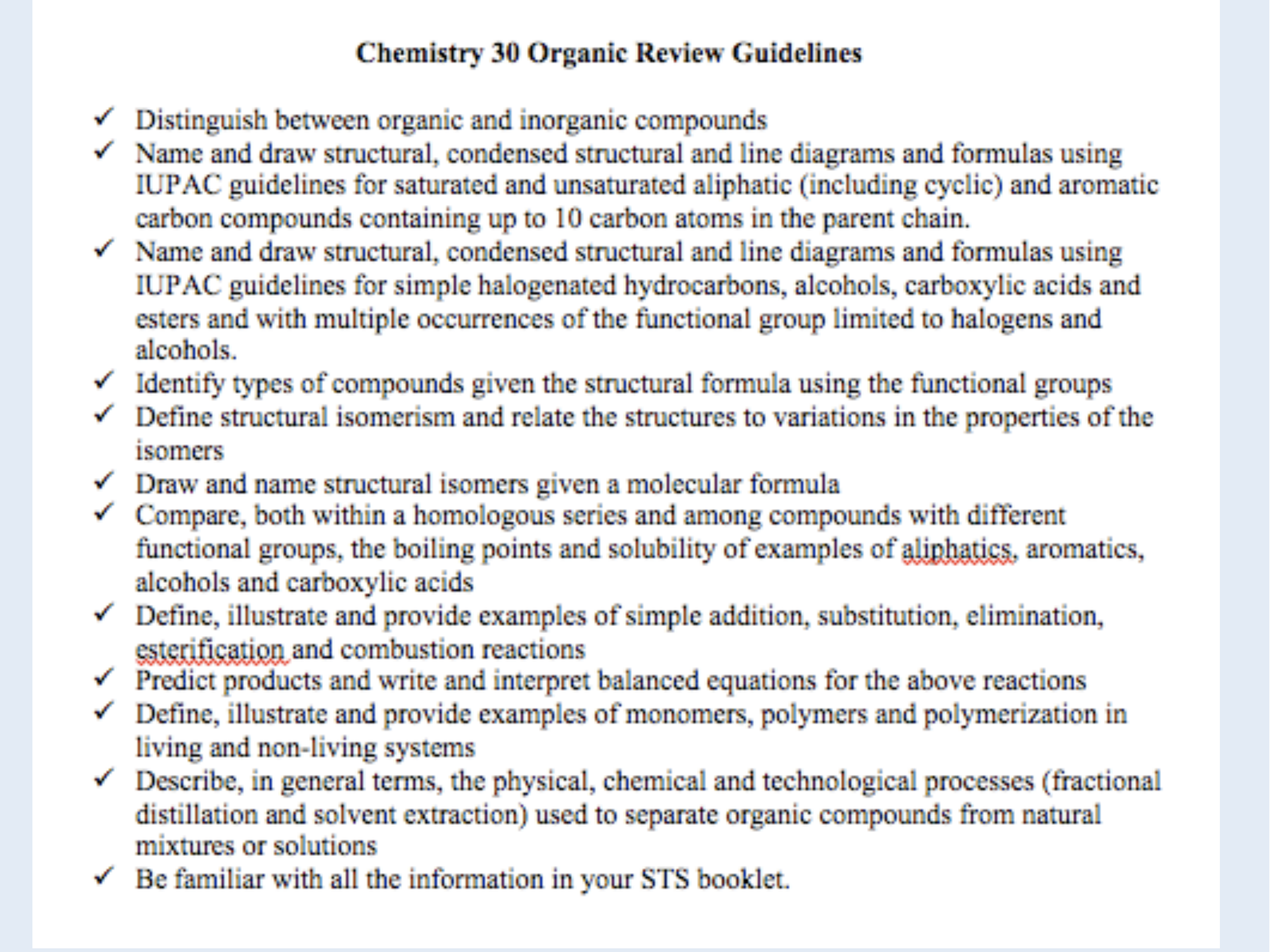
$$\Delta - \Delta + o - o + \Delta - \Delta + o - o \rightarrow -\Delta - \boxed{\Delta o} - \boxed{o\Delta} - \boxed{\Delta o} - o - + \text{water}$$

polyester

Electronic Visual

- A **fractional distillation tower** contains trays positioned at various levels.
- Heated crude oil enters near the **bottom** of the tower.
- The bottom is kept **hot**, and the temperature gradually **decreases** toward the top of the tower.
- As compounds cool to their boiling point, they **condense** in the cooler trays. The streams of **liquid** (called fractions) are withdrawn from the tower at various heights along the tower.





Chemistry 30 Organic Review Guidelines

- ✓ Distinguish between organic and inorganic compounds
- ✓ Name and draw structural, condensed structural and line diagrams and formulas using IUPAC guidelines for saturated and unsaturated aliphatic (including cyclic) and aromatic carbon compounds containing up to 10 carbon atoms in the parent chain.
- ✓ Name and draw structural, condensed structural and line diagrams and formulas using IUPAC guidelines for simple halogenated hydrocarbons, alcohols, carboxylic acids and esters and with multiple occurrences of the functional group limited to halogens and alcohols.
- ✓ Identify types of compounds given the structural formula using the functional groups
- ✓ Define structural isomerism and relate the structures to variations in the properties of the isomers
- ✓ Draw and name structural isomers given a molecular formula
- ✓ Compare, both within a homologous series and among compounds with different functional groups, the boiling points and solubility of examples of aliphatics, aromatics, alcohols and carboxylic acids
- ✓ Define, illustrate and provide examples of simple addition, substitution, elimination, esterification and combustion reactions
- ✓ Predict products and write and interpret balanced equations for the above reactions
- ✓ Define, illustrate and provide examples of monomers, polymers and polymerization in living and non-living systems
- ✓ Describe, in general terms, the physical, chemical and technological processes (fractional distillation and solvent extraction) used to separate organic compounds from natural mixtures or solutions
- ✓ Be familiar with all the information in your STS booklet.

REDOX

Reduction – Oxidation Reactions "REDOX"

- Is a chemical reaction in which electrons are transferred
- Must have both **reduction** and **oxidation** happening for the reaction to occur
  - **REDUCTION** – a process in which electrons are gained by an entity
  - **OXIDATION** – a process in which electrons are lost by an entity
  - How can you remember this?

"LEO the lion says GER"

LEO = Losing Electrons = Oxidation

GER = Gaining Electrons = Reduction

Other memory devices:

OIL RIG (**O**xidation **I**s **L**osing electrons, **R**eduction **I**s **G**aining electrons)

ELMO (**E**lectron **L**oss **M**eans **O**xidation)

Redox Terms

- Review: **"LEO the lion says GER"**
  - Loss of electrons = entity being oxidized
  - Gain of electrons = entity being reduced
  - **BUT….** Chemists don't say *"the reactant being oxidized"* or *"the reactant being reduced"*
  - Rather, they use the terms **OXIDIZING AGENT (OA)** and **REDUCING AGENT (RA)**
    - **OXIDIZING AGENT**: *causes oxidation* by removing (gaining) electrons from another substance in a redox reaction
    - **REDUCING AGENT**: *causes reduction* by donating (losing) electrons to another substance in a redox reaction

What does this mean? Let's revisit our first example when zinc and hydrochloric acid reacted.

Which reactant was reduced? *Which was oxidized?*

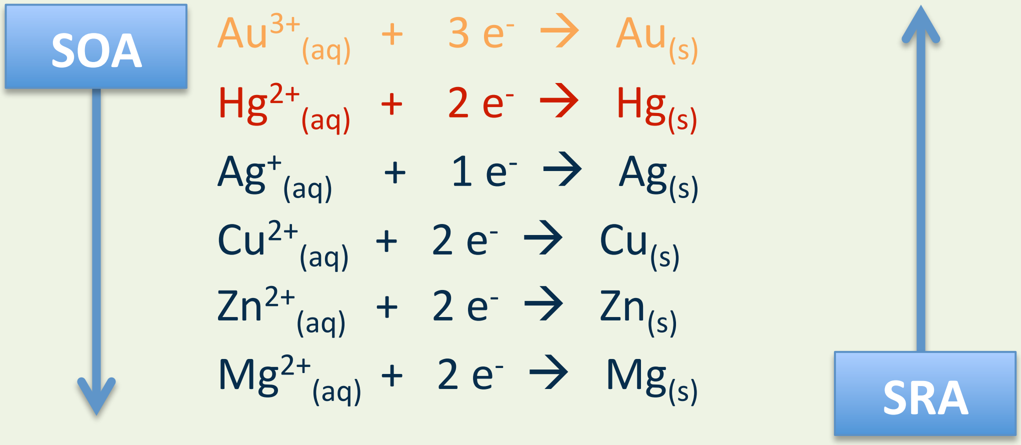
So…. Which is the Oxidizing Agent (OA)? Which is the Reducing Agent (RA)

LEO = Oxidized $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2\ e^-$ **Reducing Agent**

GER = Reduced $2\ H^+_{(aq)} + 2\ e^- \rightarrow H_{2\ (g)}$ **Oxidizing Agent**

Building Redox Tables #1

- Check page 7 of your data booklet. Does our ranking order match up with theirs?



$Au^{3+}_{(aq)} + 3e^- \rightarrow Au_{(s)}$

$Hg^{2+}_{(aq)} + 2e^- \rightarrow Hg_{(s)}$

$Ag^{+}_{(aq)} + 1e^- \rightarrow Ag_{(s)}$

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$

$Mg^{2+}_{(aq)} + 2e^- \rightarrow Mg_{(s)}$

- YES! Because of the **spontaneity rule!**
  - **A reaction will be spontaneous if on a redox table:**

OA above RA = Spontaneous Reaction

RA below OA = Non-spontaneous Reaction

Predicting Redox Reactions

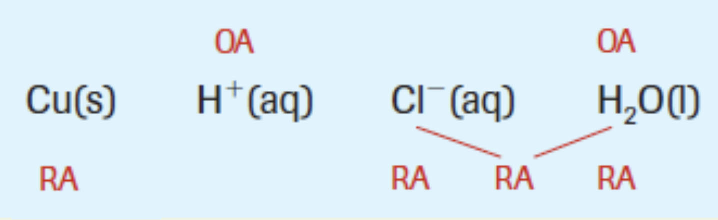
Could copper pipe be used to transport a hydrochloric acid solution?

1. List all entities

$Cu(s) \quad H^+(aq) \quad Cl^-(aq) \quad H_2O(l)$

2. Identify all possible OA's and RA's

3. Identify the SOA and SRA



4. Show ½ reactions and balance

$$2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)$$
$$Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^-$$

5. Predict spontaneity

$$2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)$$
$$Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^-$$
$$2\,H^+(aq) + Cu(s) \xrightarrow{\text{nonspont.}} H_2(g) + Cu^{2+}(aq)$$

Since the reaction is nonspontaneous, it should be possible to use a copper pipe to carry hydrochloric acid

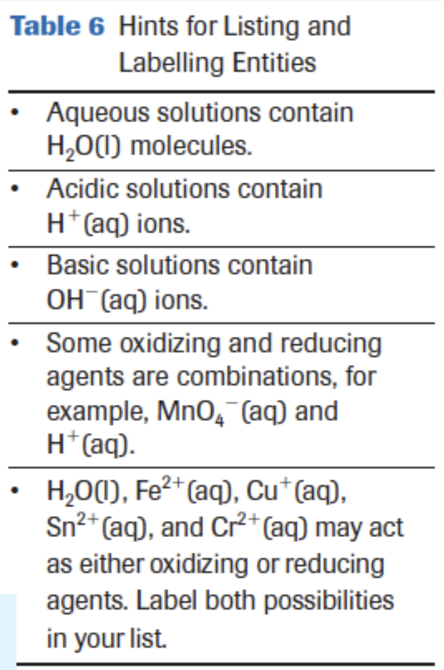
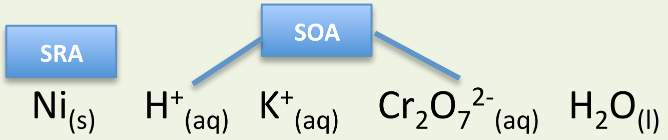


Table 6 Hints for Listing and Labelling Entities

- Aqueous solutions contain $H_2O(l)$ molecules.
- Acidic solutions contain $H^+(aq)$ ions.
- Basic solutions contain $OH^-(aq)$ ions.
- Some oxidizing and reducing agents are combinations, for example, $MnO_4^-(aq)$ and $H^+(aq)$.
- $H_2O(l)$, $Fe^{2+}(aq)$, $Cu^+(aq)$, $Sn^{2+}(aq)$, and $Cr^{2+}(aq)$ may act as either oxidizing or reducing agents. Label both possibilities in your list.

Redox Stoichiometry

- Example #2
  - Nickel metal is oxidized to $Ni^{2+}_{(aq)}$ ions by an acidified potassium dichromate solution. If 2.50g of metal is oxidizes by 50.0 mL of solution, what is the concentration of the $K_2Cr_2O_{7(aq)}$ solution?
  - 
    SRA SOA
    List entities present, identify SOA and SRA: $Ni_{(s)}$ $H^+_{(aq)}$ $K^+_{(aq)}$ $Cr_2O_7{}^{2-}{}_{(aq)}$ $H_2O_{(l)}$
  - Write oxidation and reduction half reactions. Balance the number of electrons gained and lost and add the reactions

$$3\,[Ni_{(s)} \rightarrow Ni^{2+}_{(aq)} + 2e\text{-}\,]$$

$$\underline{Cr_2O_7{}^{2-}{}_{(aq)} + 14\,H^+_{(aq)} + 6\,e^- \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}}$$

$$\mathbf{3Ni_{(s)} + Cr_2O_7{}^{2-}{}_{(aq)} + 14\,H^+_{(aq)} \rightarrow 3Ni^{2+}_{(aq} + 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}}$$

2.50 g 50.0mL

? mol/L

$$\mathbf{2.50\text{ g} \times \frac{\text{mol } Ni_{(s)}}{58.69\text{ g}} \times \frac{1\text{ mol } Cr_2O_7{}^{2-}{}_{(aq)}}{3\text{ mol } Ni_{(s)}} \times \frac{1}{0.0500\text{L}} = 0.284\text{ mol/L } Cr_2O_7{}^{2-}{}_{(aq)}}$$

Practicing Half-Reactions

- Copper metal can be oxidized in a basic solution to form copper(I) oxide. What is the half-reaction for this process? $Cu_{(s)} \rightarrow Cu_2O_{(s)}$

1. Balance all atoms except H and O $2Cu_{(s)} \rightarrow Cu_2O_{(s)}$

2. Balance oxygen by adding water $2Cu_{(s)} + H_2O_{(l)} \rightarrow Cu_2O_{(s)}$

3. Balance hydrogen by adding $H^+_{(aq)}$ $2Cu_{(s)} + H_2O_{(l)} \rightarrow Cu_2O_{(s)} + \mathbf{2H^+_{(aq)}}$

4. Balance charge by adding electrons $2Cu_{(s)} + H_2O_{(l)} \rightarrow Cu_2O_{(s)} + 2H^+_{(aq)} \mathbf{+ 2\, e^-}$

Because the half reaction is occurring in a <u>basic</u> solution,

5. Add $OH^-_{(aq)}$ to both sides to equal the number of $H^+_{(aq)}$ present

$$\mathbf{2OH^-_{(aq)}} + 2Cu_{(s)} + H_2O_{(l)} \rightarrow Cu_2O_{(s)} + 2H^+_{(aq)} + 2\, e^- + \mathbf{2OH^-_{(aq)}}$$

5. Combine $H^+_{(aq)}$ and $OH^-_{(aq)}$ on the same side to form $H_2O_{(l)}$. Cancel equal amounts of $H_2O_{(l)}$ from both sides

$$2OH^-_{(aq)} + 2Cu_{(s)} + \cancel{H_2O_{(l)}} \rightarrow Cu_2O_{(s)} + \mathbf{2\cancel{H_2O_{(l)}}} + 2\, e^-$$

$$\boxed{\mathbf{2OH^-_{(aq)} + 2Cu_{(s)} \rightarrow Cu_2O_{(s)} + H_2O_{(l)} + 2\, e^-}}$$

Oxidation States

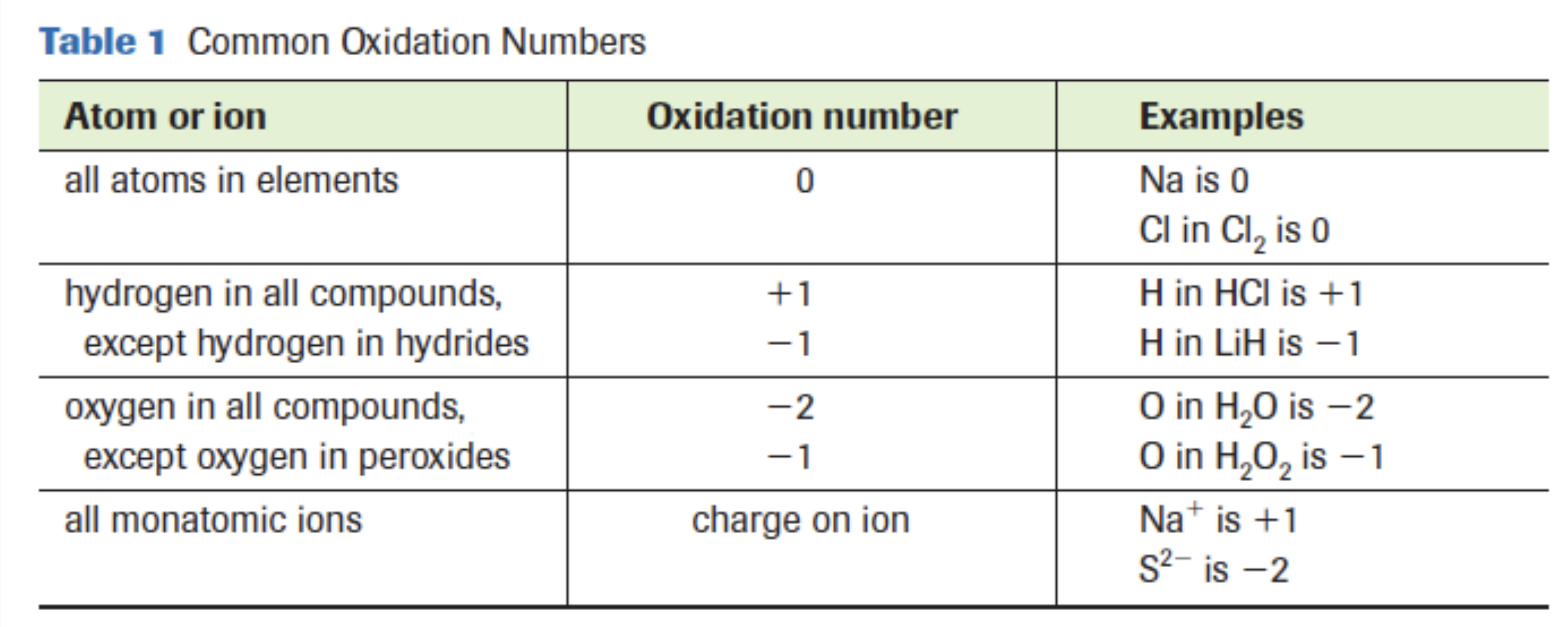


Table 1 Common Oxidation Numbers

Atom or ion	Oxidation number	Examples
all atoms in elements	0	Na is 0 Cl in Cl_2 is 0
hydrogen in all compounds, except hydrogen in hydrides	+1 −1	H in HCl is +1 H in LiH is −1
oxygen in all compounds, except oxygen in peroxides	−2 −1	O in H_2O is −2 O in H_2O_2 is −1
all monatomic ions	charge on ion	Na^+ is +1 S^{2-} is −2

Tip:

- The sum of the oxidation numbers for a neutral compound = 0
- The sum of the oxidation numbers for a polyatomic ion = ion charge

*** This method only works if there is only one unknown after referring to the above table*

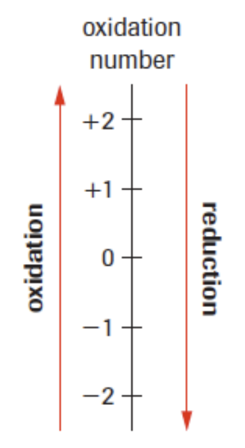
Oxidation Numbers and Redox

- Example: When natural gas burns in a furnace, carbon dioxide and water form. Identify oxidation and reduction in this reaction.
  - First write the chemical equation (as it is not provided)

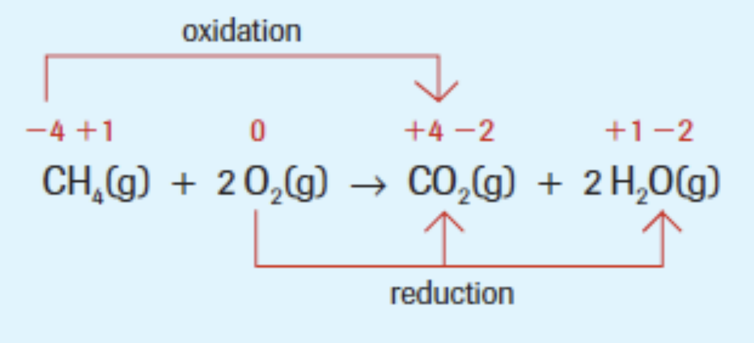
$$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g)$$

  - Determine all of the oxidation numbers

$$\overset{-4\;+1}{CH_4(g)} + 2\,\overset{0}{O_2(g)} \rightarrow \overset{+4\;-2}{CO_2(g)} + 2\,\overset{+1\;-2}{H_2O(g)}$$



  - Now look for the oxidation number of an atom/ion that **increases** as a result of the reaction and label the change as **oxidation.** There must also be an atom/ion whose oxidation number **decreases.** Label this change as **reduction.**



$$\overset{-4\;+1}{CH_4(g)} + 2\,\overset{0}{O_2(g)} \rightarrow \overset{+4\;-2}{CO_2(g)} + 2\,\overset{+1\;-2}{H_2O(g)}$$

Balancing Redox Equations using Oxidation Numbers #2

Example: Chlorate ions and iodine react in an **acidic** solution to produce chloride ions and iodate ions. Balance the equation for this reactions. **$ClO_3^-{}_{(aq)} + I_{2(aq)} \rightarrow Cl^-{}_{(aq)} + IO_3^-{}_{(aq)}$**

1. Assign oxidation numbers to all atoms/ions and look for the numbers that change. Highlight these.
Remember to record the change in the number of electrons per atom and per molecule or polyatomic ion.

$+5\ -2$		0		-1		$+5\ -2$
$ClO_3^-(aq)$	+	$I_2(aq)$	→	$Cl^-(aq)$	+	$IO_3^-(aq)$
$6\ e^-/Cl$		$5\ e^-/I$				
$6\ e^-/ClO_3^-$		$10\ e^-/I_2$				

1. The next step is to determine the simplest whole numbers that will balance the number of electrons transferred for each reactant. The numbers become the coefficients of the reactants. The coefficients for the products can be obtained by balancing the atoms whose oxidation numbers have changed and then any other atoms.

$$5\ ClO_3^-(aq) + 3\ I_2(aq) \rightarrow 5\ Cl^-(aq) + 6\ IO_3^-(aq)$$

2. Although Cl and I atoms are balanced, oxygen is not. Add $H_2O_{(l)}$ molecules to balance the O atoms.

$$3\ H_2O(l) + 5\ ClO_3^-(aq) + 3\ I_2(aq) \rightarrow 5\ Cl^-(aq) + 6\ IO_3^-(aq)$$

3. Add $H^+_{(aq)}$ to balance the hydrogen. The redox equation should now be completely balanced. Check your work by checking the total numbers of each atom/ion on each side and checking the total electric charge, which should also be balanced.

$$3\ H_2O(l) + 5\ ClO_3^-(aq) + 3\ I_2(aq) \rightarrow 5\ Cl^-(aq) + 6\ IO_3^-(aq) + 6\ H^+(aq)$$

Disproportionation

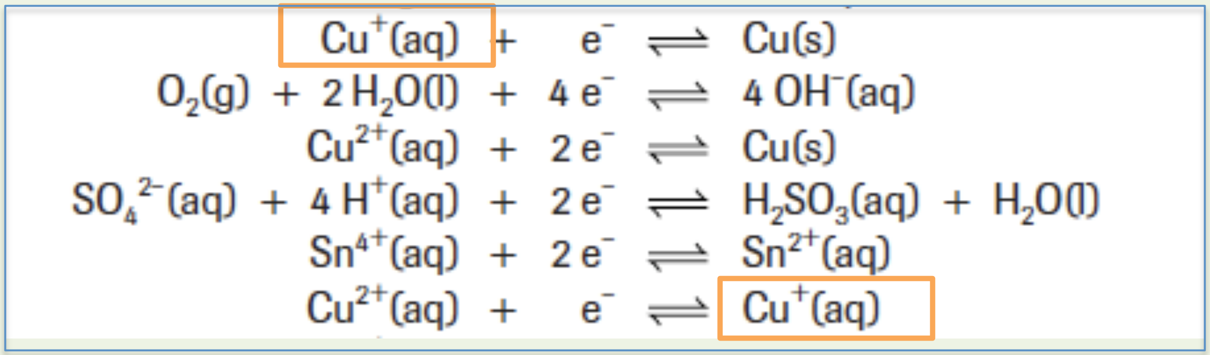
- Example #2: Will a spontaneous reaction occur as a result of an electron transfer from one copper(I) ion to another copper (I) ion?

See pg. 578 Ex.2 for more another example

$$Cu^+_{(aq)} + 1\ e^- \rightarrow Cu_{(s)}$$

$$\underline{Cu^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 1\ e^-}$$

$$2\ Cu^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$$



$$\boxed{Cu^+(aq)} + e^- \rightleftharpoons Cu(s)$$

$$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$$

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$$

$$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O(l)$$

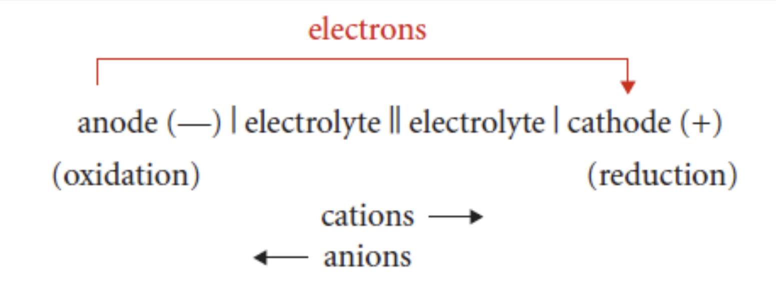
$$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$$

$$Cu^{2+}(aq) + e^- \rightleftharpoons \boxed{Cu^+(aq)}$$

  - YES! Using the redox table and spontaneity rule, we see that copper(I) as an oxidizing agent is above copper(I) as a reducing agent. Therefore, an aqueous solution of copper(I) ions will spontaneously, but slowly, disproportionate into copper(II) ions and copper metal.

Voltaic Cell Summary

- A voltaic cell consists of two-half cells separated by a porous boundary with solid electrodes connected by an external circuit
- SOA undergoes reduction at the cathode (+ electrode) – *cathode increases in mass*
- SRA undergoes oxidation at the anode (- electrode) – *anode decreases in mass*
- Electrons always travel in the external circuit from anode to cathode
- Internally, cations move toward the cathode, anions move toward the anode, keeping the solution neutral



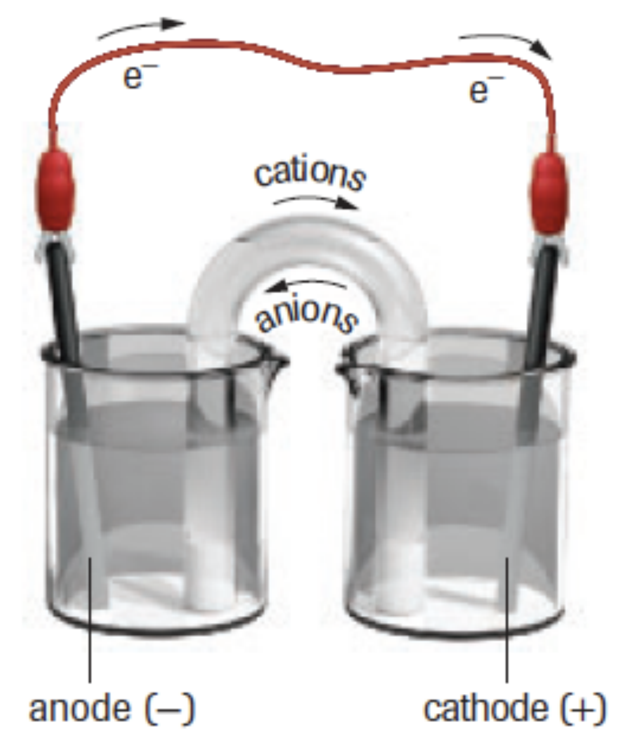


Figure 4
In an operating voltaic cell, the electrical circuit is completed by the electron flow in the external part (wires) of the cell and the ion flow in the internal part (solutions) of the cell.

Standard Cells and Cell Potentials

- A **standard cell** is a voltaic cell where each ½ cell contains all entities necessary at SATP conditions and all aqueous solutions have a concentration of 1.0 mol/L
  - Standardizing makes comparisons and scientific study easier

- **Standard Cell Potential, E^0 cell** = the electric potential difference of the cell (voltage)

$$E^0 \text{ cell} = E^0_r \text{ cathode} - E^0_r \text{ anode}$$

  - Where E^0_r is the standard reduction potential, and is a measure of a standard ½ cell's ability to attract electrons.
  - The higher the E^0_r, the stronger the OA

- All standard reduction potentials are based on the standard hydrogen ½ cell being 0.00V. This means that all standard reduction potentials that are positive are stronger OA's than hydrogen ions and all standard reduction potentials that are negative are weaker.

  - If the E^0 cell is **positive**, the reaction occurring is **spontaneous**.
  - If the E^0 cell is **negative**, the reaction occurring is non-**spontaneous**

Comparing Electrochemical Cells: Voltaic and Electrolytic

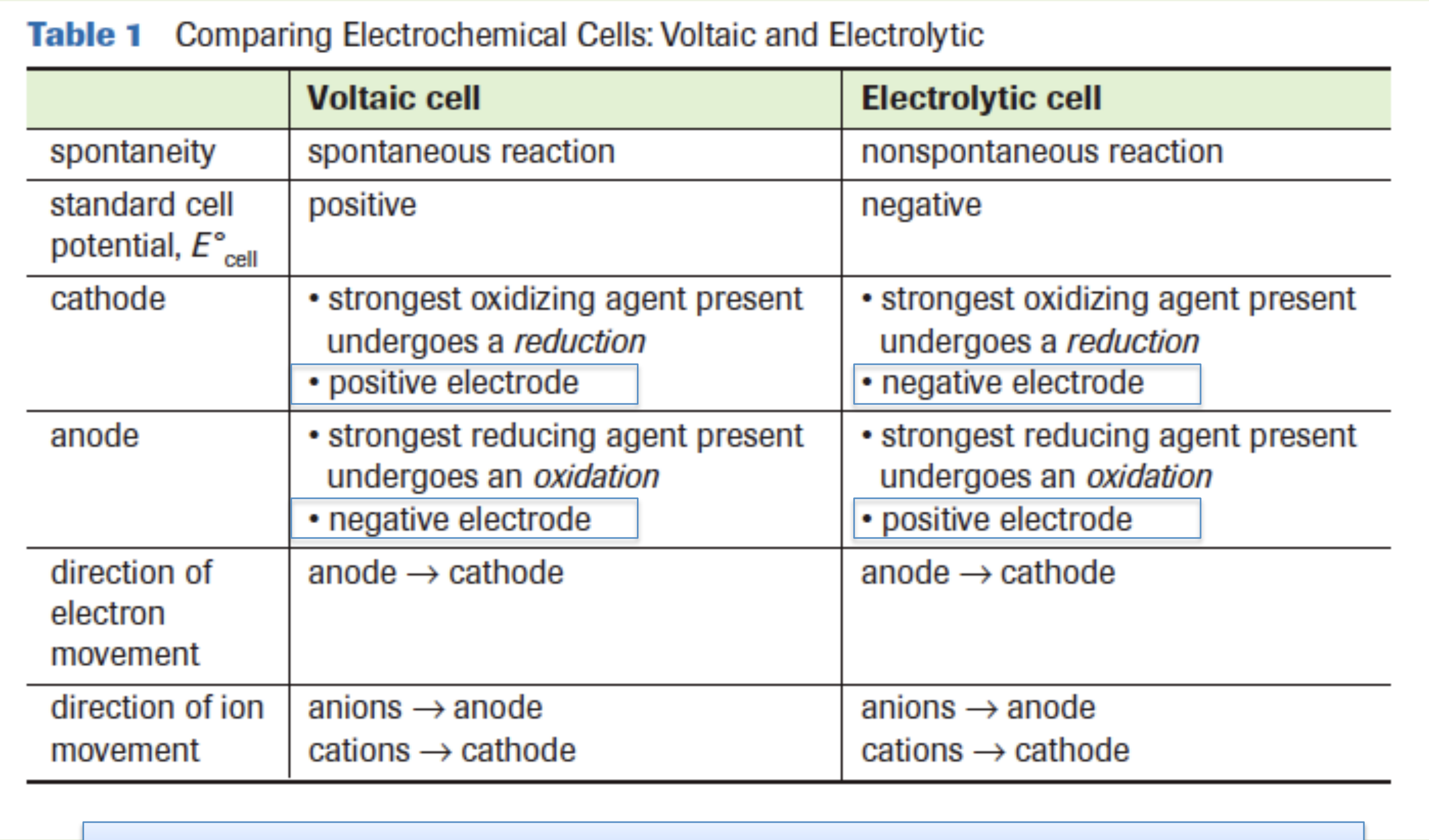


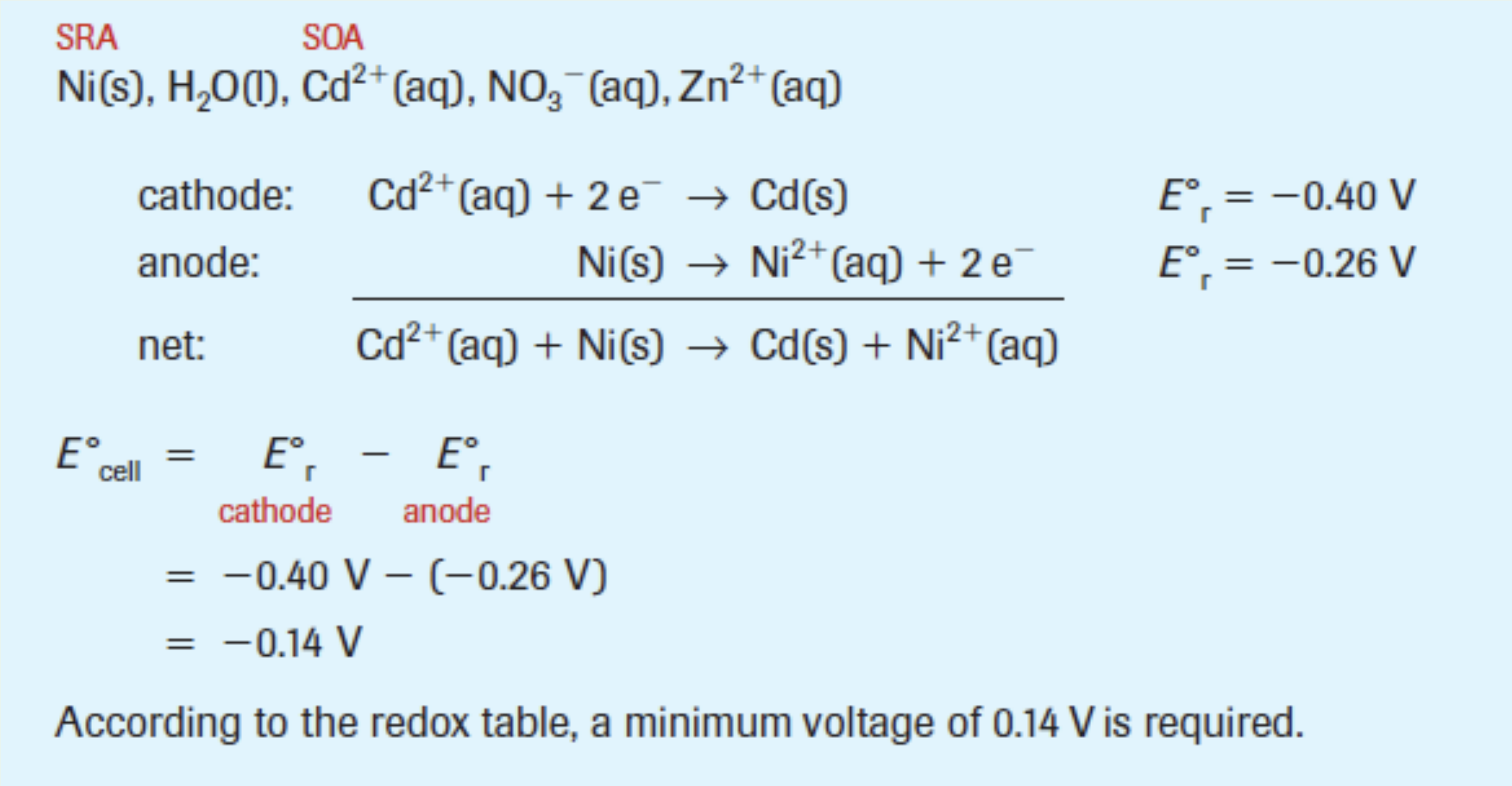
Table 1 Comparing Electrochemical Cells: Voltaic and Electrolytic

	Voltaic cell	**Electrolytic cell**
spontaneity	spontaneous reaction	nonspontaneous reaction
standard cell potential, E°_{cell}	positive	negative
cathode	• strongest oxidizing agent present undergoes a *reduction* • positive electrode	• strongest oxidizing agent present undergoes a *reduction* • negative electrode
anode	• strongest reducing agent present undergoes an *oxidation* • negative electrode	• strongest reducing agent present undergoes an *oxidation* • positive electrode
direction of electron movement	anode → cathode	anode → cathode
direction of ion movement	anions → anode cations → cathode	anions → anode cations → cathode

It is best to think of “positive” and “negative” for electrodes as labels, not charges.

Analyzing Electrolytic Cells #3

- Example: An electrolytic cell is set up with a power supply connected to two nickel electrodes immersed in an aqueous solution containing cadmium nitrate and zinc nitrate.
- Predict the equations for the initial reaction at each electrode and the net cell reaction. Calculate the minimum voltage that must be applied to make the reaction occur.



$$\overset{\text{SRA}}{\text{Ni(s)}}, \text{H}_2\text{O(l)}, \overset{\text{SOA}}{\text{Cd}^{2+}\text{(aq)}}, \text{NO}_3^{\;-}\text{(aq)}, \text{Zn}^{2+}\text{(aq)}$$

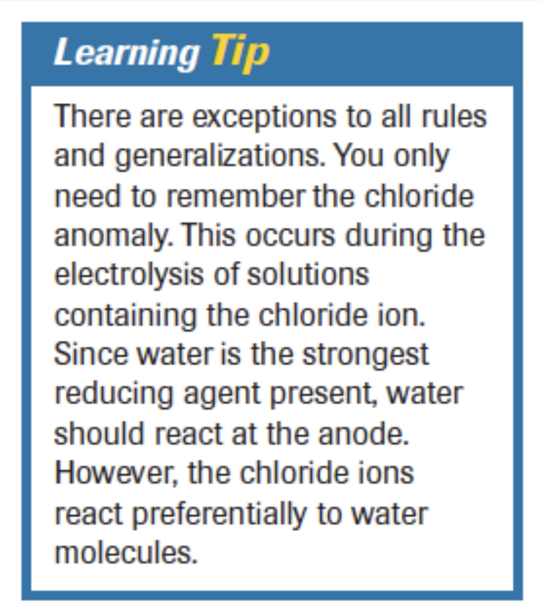
$$\begin{array}{lrcll} \text{cathode:} & \text{Cd}^{2+}\text{(aq)} + 2\,\text{e}^- & \rightarrow & \text{Cd(s)} & E^\circ_r = -0.40\ \text{V} \\ \text{anode:} & \text{Ni(s)} & \rightarrow & \text{Ni}^{2+}\text{(aq)} + 2\,\text{e}^- & E^\circ_r = -0.26\ \text{V} \\ \hline \text{net:} & \text{Cd}^{2+}\text{(aq)} + \text{Ni(s)} & \rightarrow & \text{Cd(s)} + \text{Ni}^{2+}\text{(aq)} & \end{array}$$

$$\begin{aligned} E^\circ_{\text{cell}} &= \underset{\text{cathode}}{E^\circ_r} - \underset{\text{anode}}{E^\circ_r} \\ &= -0.40\ \text{V} - (-0.26\ \text{V}) \\ &= -0.14\ \text{V} \end{aligned}$$

According to the redox table, a minimum voltage of 0.14 V is required.

The Chloride Anomaly (*****Diploma)

- Some redox reactions predicted using the SOA and SRA from a redox table do not always occur in an electrolytic cell.
- The *actual* reduction potential required for a particular half-reaction and the *reported* half-reaction reduction potential may be quite different (depending on the conditions or half-reactions)
  - This difference is known as the half-cell overvoltage
- *"As an empirical rule, you should recognize that chlorine gas is produced instead of oxygen gas in situations where chloride and water are the only reducing agents present."*



Learning Tip

There are exceptions to all rules and generalizations. You only need to remember the chloride anomaly. This occurs during the electrolysis of solutions containing the chloride ion. Since water is the strongest reducing agent present, water should react at the anode. However, the chloride ions react preferentially to water molecules.

Practice: Half-Cell Calculations #1

- What is the mass of copper deposited at the cathode of a copper electrorefining cell operated at 12.0 A for 40.0 min?

$$\begin{array}{lllll}
\mathrm{Cu^{2+}(aq)} & + & 2\,\mathrm{e^-} & \rightarrow & \mathrm{Cu(s)} \\
 & & 40.0\ \mathrm{min} & & m \\
 & & 12.0\ \mathrm{A} & & 63.55\ \mathrm{g/mol} \\
 & & 9.65 \times 10^4\ \mathrm{C/mol} & &
\end{array}$$

  - Yes, we can solve for the number of moles, and then use the mole ratio to convert from a chemical amount of one substance to another.

$$\begin{aligned} n_{\mathrm{e^-}} &= \left(12.0\,\frac{\cancel{\mathrm{C}}}{\mathrm{s}} \times 40.0\ \cancel{\mathrm{min}} \times \frac{60\ \cancel{\mathrm{s}}}{1\ \cancel{\mathrm{min}}}\right) \times \frac{1\ \mathrm{mol}}{9.65 \times 10^4\ \cancel{\mathrm{C}}} \\ &= 0.298\ \mathrm{mol} \end{aligned}$$

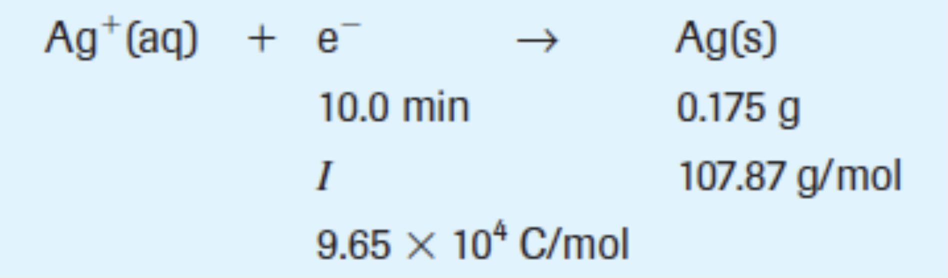
$$\begin{aligned} n_{\mathrm{Cu}} &= 0.298\ \mathrm{mol} \times \frac{1}{2} \\ &= 0.149\ \mathrm{mol} \end{aligned}$$

  - The last step is to convert to the quantity requested in the question, in this case the mass of the copper metal
  - Could we do this as one equation instead

$$\begin{aligned} m_{\mathrm{Cu}} &= 0.149\ \cancel{\mathrm{mol}} \times \frac{63.55\ \mathrm{g}}{\cancel{\mathrm{mol}}} \\ &= 9.48\ \mathrm{g} \end{aligned}$$

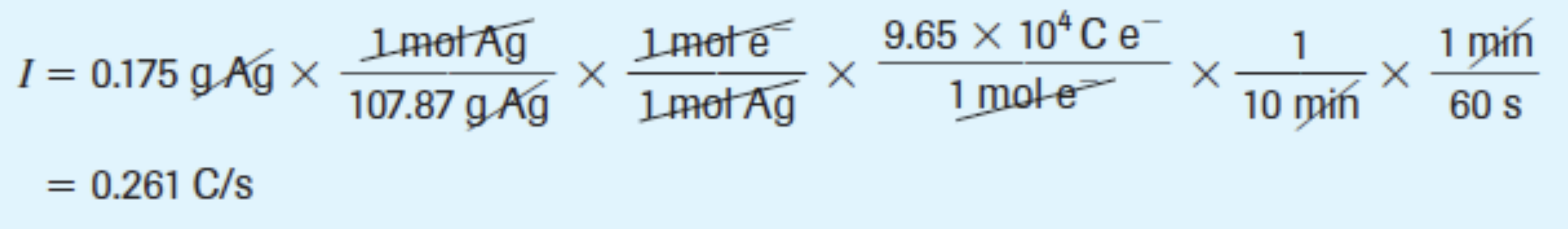
Practice: Half-Cell Calculations #2

- Silver is deposited on objects in a silver electroplating cell. If 0.175 g of silver is to be deposited from a silver cyanide solution in a time of 10.0 min, predict the current required.
- Write the balanced equation for the half-cell reaction, list the measurements and conversion factors.



$Ag^+(aq)$	+	e^-	$\rightarrow$	$Ag(s)$
		10.0 min		0.175 g
		I		107.87 g/mol
		9.65×10^4 C/mol		

- Convert to moles, use the mole ratio, convert to the current (C/s)



$$I = 0.175\ \text{g}\ \cancel{\text{Ag}} \times \frac{\cancel{1\ \text{mol Ag}}}{107.87\ \text{g}\ \cancel{\text{Ag}}} \times \frac{\cancel{1\ \text{mol e}^-}}{\cancel{1\ \text{mol Ag}}} \times \frac{9.65 \times 10^4\ \text{C e}^-}{\cancel{1\ \text{mol e}^-}} \times \frac{1}{10\ \cancel{\text{min}}} \times \frac{1\ \cancel{\text{min}}}{60\ \text{s}}$$

$$= 0.261\ \text{C/s}$$

THERMOCHEMISTRY

Energy from the Sun

- Stored energy in the chemical bonds of hydrocarbons originated from the sun

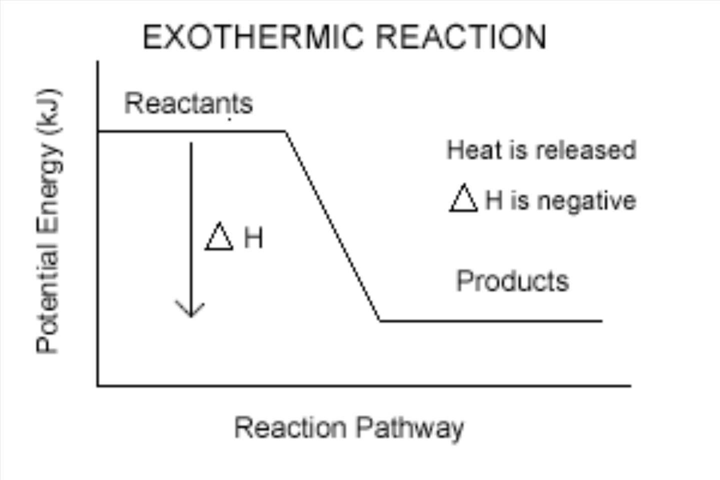
Remember:

- Photosynthesis:
  - **Liquid** H_2O and CO_2 **gas** → glucose and $O_{2(g)}$
- Hydrocarbon combustion:
  - Fuel + $O_{2(g)}$ → water **vapour** and CO_2 **gas**

DO YOU REMEMBER??

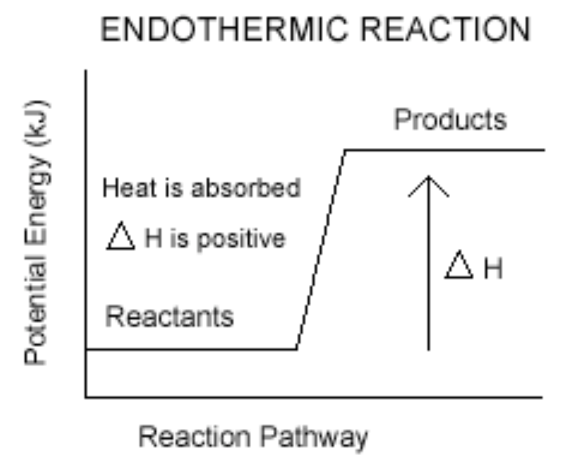
EXOTHERMIC

- A change in a chemical energy where energy/heat EXITS the chemical system
- Results in a decrease in chemical potential energy



ENDOTHERMIC

- A change in chemical energy where energy/heat ENTERS the chemical system
- Results in an increase in chemical potential energy



An Introduction to Energetics

- **Kinetic Energy (E_k)** is related to the motion of an entity
  - Molecular motion can by translational (straight-line), rotational and vibrational
- **Chemical Potential Energy (E_p)** is energy stored in the bonds of a substance and relative intermolecular forces
- **Thermal Energy** is the total kinetic energy of all of the particles of a system. Increases with temperature.
  - Symbol (*Q*), Units (*J*), Formula used (***Q=mcΔT***)
- **Temperature** is a measure of the average kinetic energy of the particles in a system
- **Heat** is a transfer of thermal energy. Heat is not possessed by a system. Heat is energy flowing between systems.

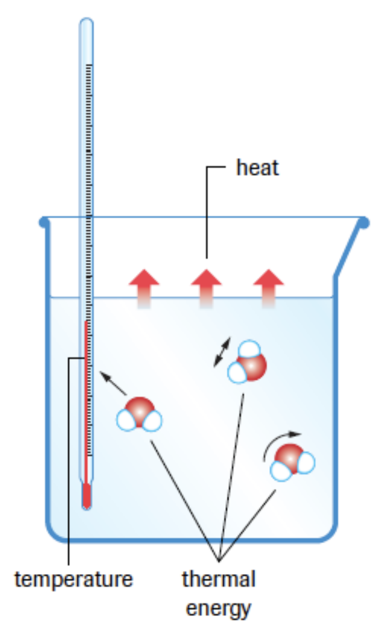
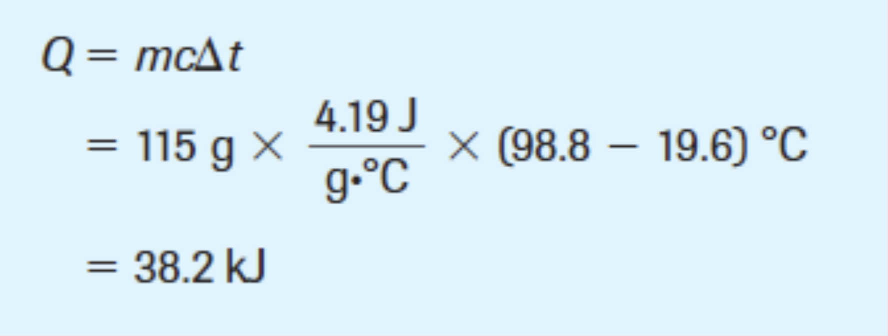


Figure 2
A thermometer (or a temperature probe) measures the average kinetic energy of the molecules in a beaker of water.

Thermal Energy Calculations

- <u>Example:</u> Determine the change in thermal energy when 115 mL of water is heated from 19.6^{o}C to 98.8^{o}C?



$$
\begin{aligned}
Q &= mc\Delta t \\
&= 115\ \mathrm{g} \times \frac{4.19\ \mathrm{J}}{\mathrm{g}\cdot{}^{\circ}\mathrm{C}} \times (98.8 - 19.6)\ {}^{\circ}\mathrm{C} \\
&= 38.2\ \mathrm{kJ}
\end{aligned}
$$

Mass = density x volume

Show how **L = kg** and **mL = g**

The density of a dilute aqueous solution is the same as that of water; that is, 1.00g/mL or 1.00kg/L

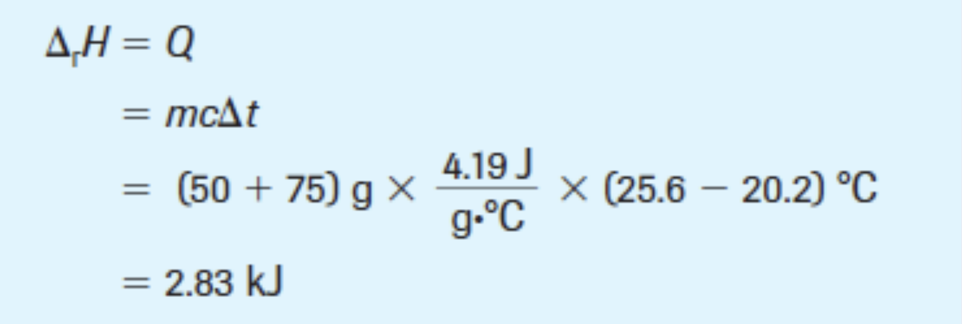
c_{water} = 4.19J/g •°C or 4.19 kJ/kg •°C or 4.19 kJ/L •°C

Comparing Q's

Negative Q value	Positive Q value
– An exothermic change	– An endothermic change
– Heat is lost by the system	– Heat is gained by the system
– The temperature of the surroundings increases and the temperature of the system decreases	– The temperature of the system increases and the temperature of the surroundings decreases
– Example: Hot Pack	– Example: Cold Pack
– Question Tips: *"How much energy is released?"*	– Question Tips: *"What heat is required?"*

ENTHALPY CHANGES

- When 50 mL of 1.0 mol/L hydrochloric acid is neutralized completely by 75 mL of 1.0 mol/L sodium hydroxide in a polystyrene cup calorimeter, the temperature of the total solution changes from 20.2°C to 25.6°C. Determine the enthalpy change that occurs in the chemical system.



$$\begin{aligned}\Delta_r H &= Q \\ &= mc\Delta t \\ &= (50 + 75)\ \text{g} \times \frac{4.19\ \text{J}}{\text{g}\cdot{}^\circ\text{C}} \times (25.6 - 20.2)\ {}^\circ\text{C} \\ &= 2.83\ \text{kJ}\end{aligned}$$

Is this an Endothermic or Exothermic reaction??

- Based upon the evidence available, the enthalpy change for the neutralization of hydrochloric acid in this context is recorded as -2.83 kJ.

MOLAR ENTHALPY AND CALORIMETRY

- Can we measure the molar enthalpy of reaction using calorimetry?
- Yes, but indirectly. We can ***measure*** a change in temperature, we can then ***calculate*** the change in thermal energy (Q=mct). Then, using the law of conservation of energy we can ***infer*** the molar enthalpy.
- In doing so, we must ***assume*** that the change in enthalpy of the chemicals involved in a reaction is equal to the change in thermal energy of the surroundings.

$$\Delta H = Q$$

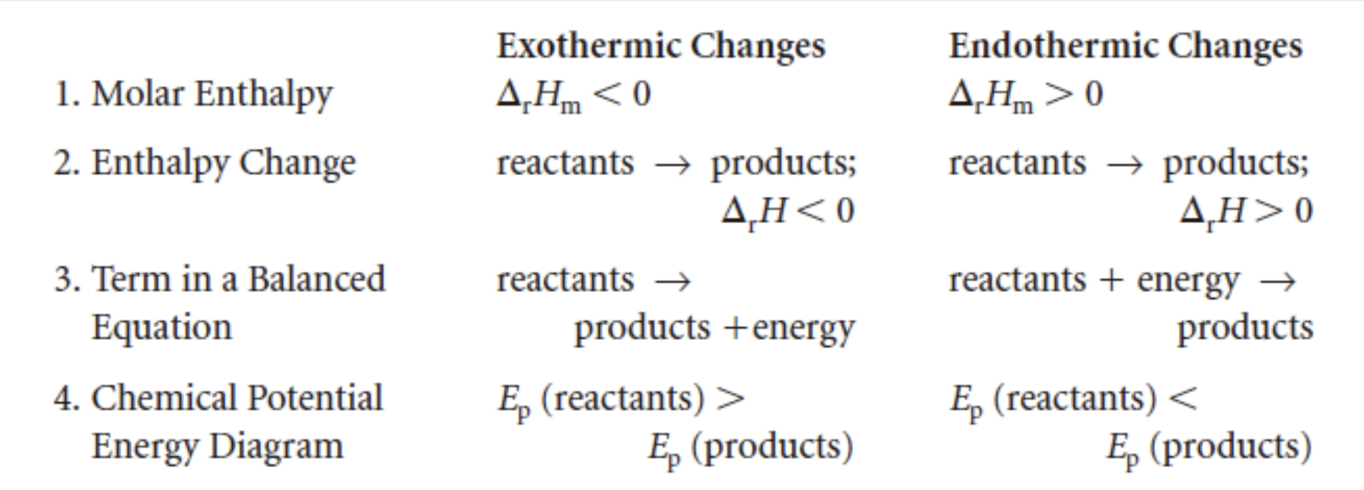
$$n\,\Delta_c H_m = mc\Delta t$$

From this equation, any one of the five variables can be determined as an unknown.

$$\underbrace{n}_{\text{chemical amount of fuel}}\;\underbrace{\Delta_c H_m}_{\text{molar enthalpy of combustion of fuel}} = \underbrace{m}_{\text{mass of water}}\,\underbrace{c}_{\text{specific heat capacity of water}}\,\underbrace{\Delta t}_{\text{temperature change of water}}$$

COMMUNICATING ENTHALPY

- We will be learning how to communicate enthalpy changes in four ways:
  1. By stating the molar enthalpy of a specific **reactant** in a reaction
  2. By stating the enthalpy change for a **balanced reaction equation**
  3. By including an energy value as a **term** in a balanced reaction equation
  4. By drawing a **chemical potential energy diagram**



	Exothermic Changes	**Endothermic Changes**
1. Molar Enthalpy	$\Delta_r H_m < 0$	$\Delta_r H_m > 0$
2. Enthalpy Change	reactants $\rightarrow$ products; $\Delta_r H < 0$	reactants $\rightarrow$ products; $\Delta_r H > 0$
3. Term in a Balanced Equation	reactants $\rightarrow$ products + energy	reactants + energy $\rightarrow$ products
4. Chemical Potential Energy Diagram	E_p (reactants) $>$ E_p (products)	E_p (reactants) $<$ E_p (products)

COMMUNICATING ENTHALPY #3

3. By including an energy value as a term in a balanced reaction equation
   - If a reaction is **endothermic**, it requires additional energy to react, so is listed along with the **reactants**

$$H_2O(l) + 285.8\text{ kJ} \rightarrow H_2(g) + \tfrac{1}{2}O_2(g)$$

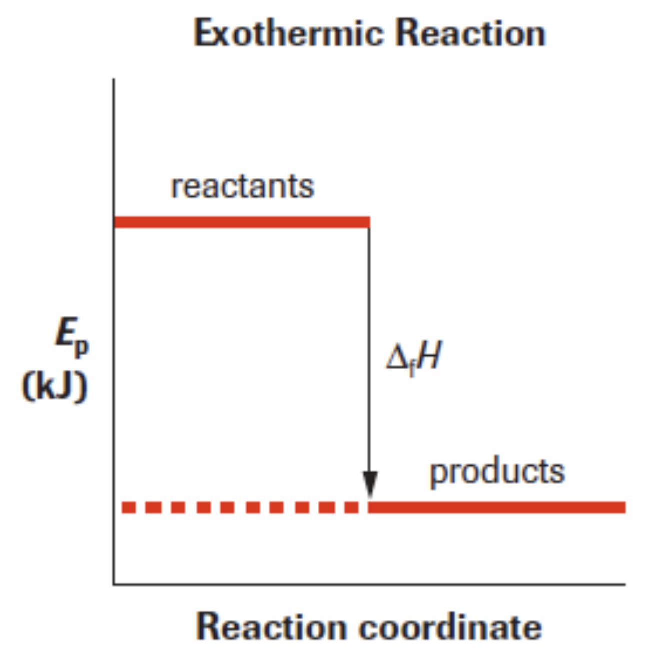
   - If a reaction is **exothermic**, energy is released as the reaction proceeds, and is listed along with the **products**

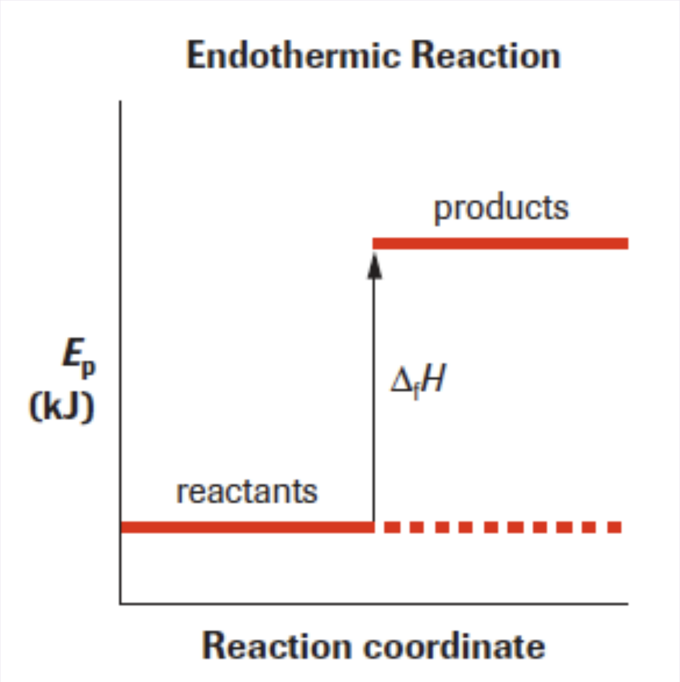
$$Mg(s) + \tfrac{1}{2}O_2(g) \rightarrow MgO(s) + 601.6\text{ kJ}$$

   - In order to specify the initial and final **conditions** for measuring the enthalpy change of the reaction, the temperature and pressure may be specified at the **end of the equation**

$$Mg(s) + \tfrac{1}{2}O_2(g) \rightarrow MgO(s) + 601.6\text{ kJ} \qquad \text{(under standard conditions)}$$

COMMUNICATING ENTHALPY #4





During an exothermic reaction, the enthalpy of the system **decreases** and heat flows into the surroundings. We observe a temperature **increase** in the surroundings.

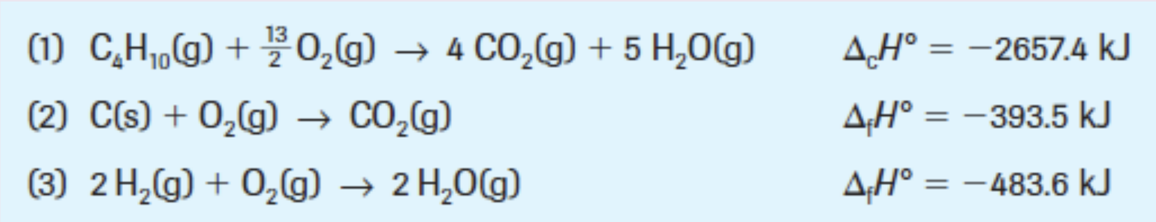
During an endothermic reaction, heat flows from the surroundings **into** the chemical system. We observe a temperature **decrease** in the surroundings.

Hess' Law #4

- <u>Example: What is the **standard enthalpy of formation of butane**?</u> $\Delta_f H_m^{o}$ = ???
- First, we need to be able to write this balanced formation equation.

$$4C_{(s)} + 5H_{2(g)} \rightarrow C_4H_{10(g)}$$

- The following values were determined by calorimetry:

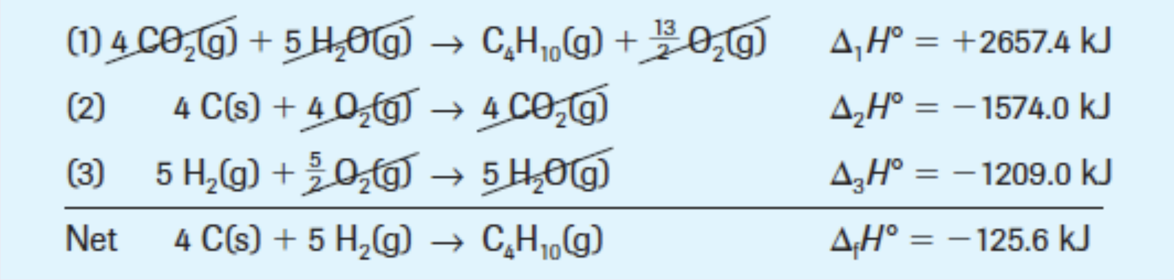


$$(1)\quad C_4H_{10}(g) + \tfrac{13}{2}O_2(g) \rightarrow 4\,CO_2(g) + 5\,H_2O(g) \qquad \Delta_c H^\circ = -2657.4\text{ kJ}$$

$$(2)\quad C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta_f H^\circ = -393.5\text{ kJ}$$

$$(3)\quad 2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g) \qquad \Delta_f H^\circ = -483.6\text{ kJ}$$

- What will we need to do to get our net equation?



$$(1)\quad \cancel{4\,CO_2(g)} + \cancel{5\,H_2O(g)} \rightarrow C_4H_{10}(g) + \cancel{\tfrac{13}{2}O_2(g)} \qquad \Delta_1 H^\circ = +2657.4\text{ kJ}$$

$$(2)\quad 4\,C(s) + \cancel{4\,O_2(g)} \rightarrow \cancel{4\,CO_2(g)} \qquad \Delta_2 H^\circ = -1574.0\text{ kJ}$$

$$(3)\quad 5\,H_2(g) + \cancel{\tfrac{5}{2}O_2(g)} \rightarrow \cancel{5\,H_2O(g)} \qquad \Delta_3 H^\circ = -1209.0\text{ kJ}$$

$$\text{Net}\quad 4\,C(s) + 5\,H_2(g) \rightarrow C_4H_{10}(g) \qquad \Delta_f H^\circ = -125.6\text{ kJ}$$

-Reverse equation (1) and change the ΔH sign

-Multiply equation (2) and its ΔH by 4

-Multiply equation (3) and its ΔH by 5/2

$\Delta_f H_m^{o}$ = -125.6 kJ/1 mol = **-125.6 kJ/mol**

C4H10

MOLAR ENTHALPY OF FORMATION

- Methane is burned in furnaces and in some power plants. What is the standard **molar** enthalpy of combustion of methane? Assume that water vapour is a product.
- Need a balanced chemical equation: $CH_{4(g)} + O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$
- Use the formula and the data booklet to calculate the $\Delta_c H°$

We found all of the $\Delta_f H_m$ for the compounds two slides ago

$$\Delta_r H° = \Sigma n \Delta_{f\,P} H_m° - \Sigma n \Delta_{f\,R} H_m°$$

$$\Delta_c H° = \left(1\ \text{mol CO}_2 \times \frac{-393.5\ \text{kJ}}{1\ \text{mol CO}_2} + 2\ \text{mol H}_2\text{O} \times \frac{-241.8\ \text{kJ}}{1\ \text{mol H}_2\text{O}}\right) - \left(1\ \text{mol CH}_4 \times \frac{-74.6\ \text{kJ}}{1\ \text{mol CH}_4} + 2\ \text{mol O}_2 \times \frac{0\ \text{kJ}}{1\ \text{mol O}_2}\right)$$

$$\Delta_c H° = -877.1\ \text{kJ} - (-74.6\ \text{kJ})$$
$$= -802.5\ \text{kJ}$$

Are we finished with -802.5 kJ?? NO!

$$\underset{CH_4}{\Delta_c H_m°} = \frac{-802.5\ \text{kJ}}{1\ \text{mol}} = -802.5\ \text{kJ/mol}$$

ACTIVATION ENERGY OF A REACTION

Activation Energy – (E_A)

- The minimum collision energy required for effective collision
- Dependant on the kinetic energy of the particles (depend on T)
- Analogy: If the ball does not have enough kinetic energy to make it over the hill – the trip will not happen. Same idea, if molecules collide without enough energy to rearrange their bonds, the reaction will not occur. (*ineffective collision*)

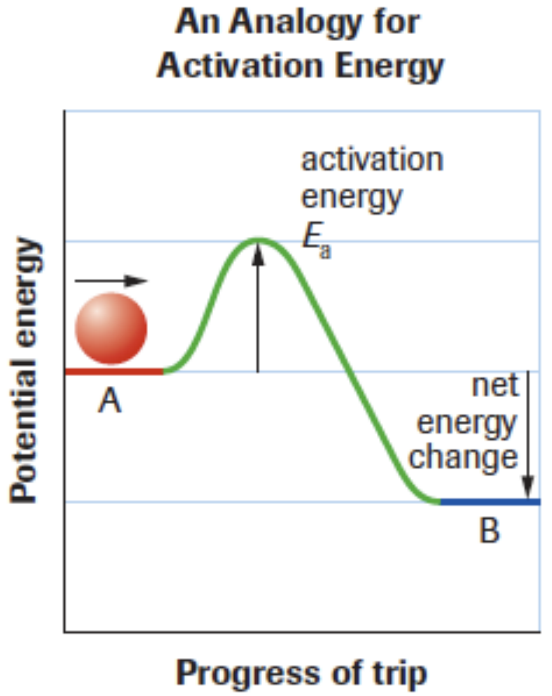
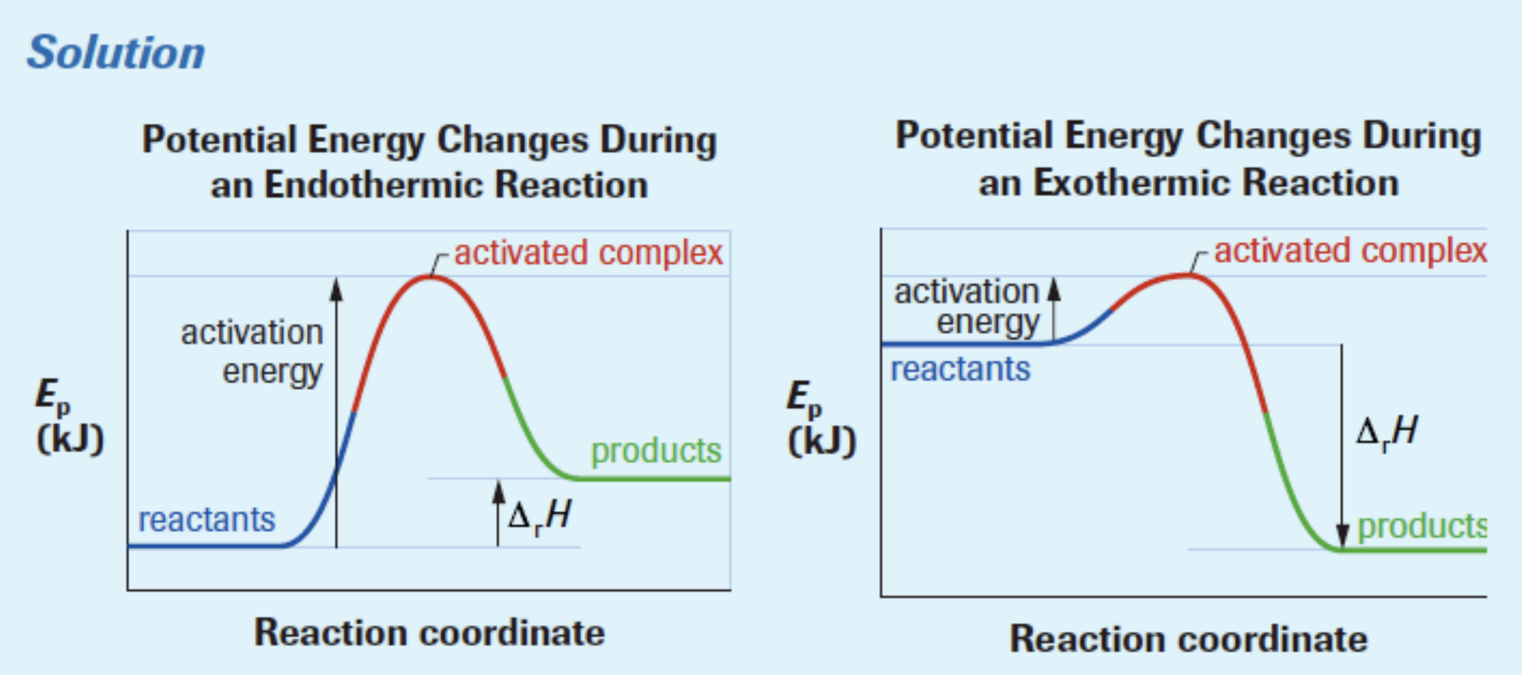


Figure 3
On a trip from A to B, there is a net decrease in potential energy, but there must be an initial increase in potential energy (activation energy) for the trip to be possible.

LET'S SEE IF YOU GET IT

Draw energy pathway diagrams for general endothermic and a general exothermic reaction. Label the reactants, products, enthalpy change, activation energy, and activated complex.



Solution

Potential Energy Changes During an Endothermic Reaction

Potential Energy Changes During an Exothermic Reaction

CATALYSTS AND REACTION RATE

- A **catalyst** is a substance that increases the rate of a chemical reaction without being consumed itself in the overall process.
- A catalyst **reduces** the quantity of energy required to **start** the reaction, and results in a catalyzed reaction producing a **greater yield** in the same period of time than an uncatalyzed reaction.
    - It **does not** alter the net enthalpy change for a chemical reaction

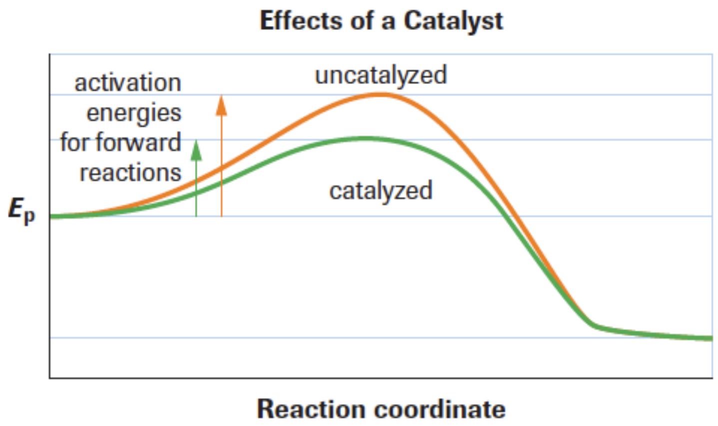


Figure 4
The catalyzed pathway has a lower activation energy, so more collisions lead to a successful reaction.

Catalysts lower the activation energy, so a larger portion of particles have the necessary energy to react = **greater yield**

EQUILIBRIUM

4 Conditions of Dynamic Equilibrium*

1. Can be achieved in all reversible reactions when the rates of the **forward and reverse reaction become equal**

   Represented by $\rightleftarrows$ rather than by $\rightarrow$

2. All observable **properties appear constant** (colour, pH, etc)
3. Can only be achieved in a **closed system** (no exchange of matter and must have a constant temperature)
4. Equilibrium can be approached from **either direction**. This means that the equilibrium concentrations will be the same regardless if you started with all reactants, all products, or a mixture of the two

Describing the Position of Equilibrium

1. **Percent Yield**- the yield of product measured at equilibrium compared with the maximum possible yield of product.

- $$\% \text{ yield} = \frac{[\text{product}]\ \text{eq'm}}{[\text{product}]\ \text{max}} \times 100\ \%$$

- The equilibrium concentration is determined

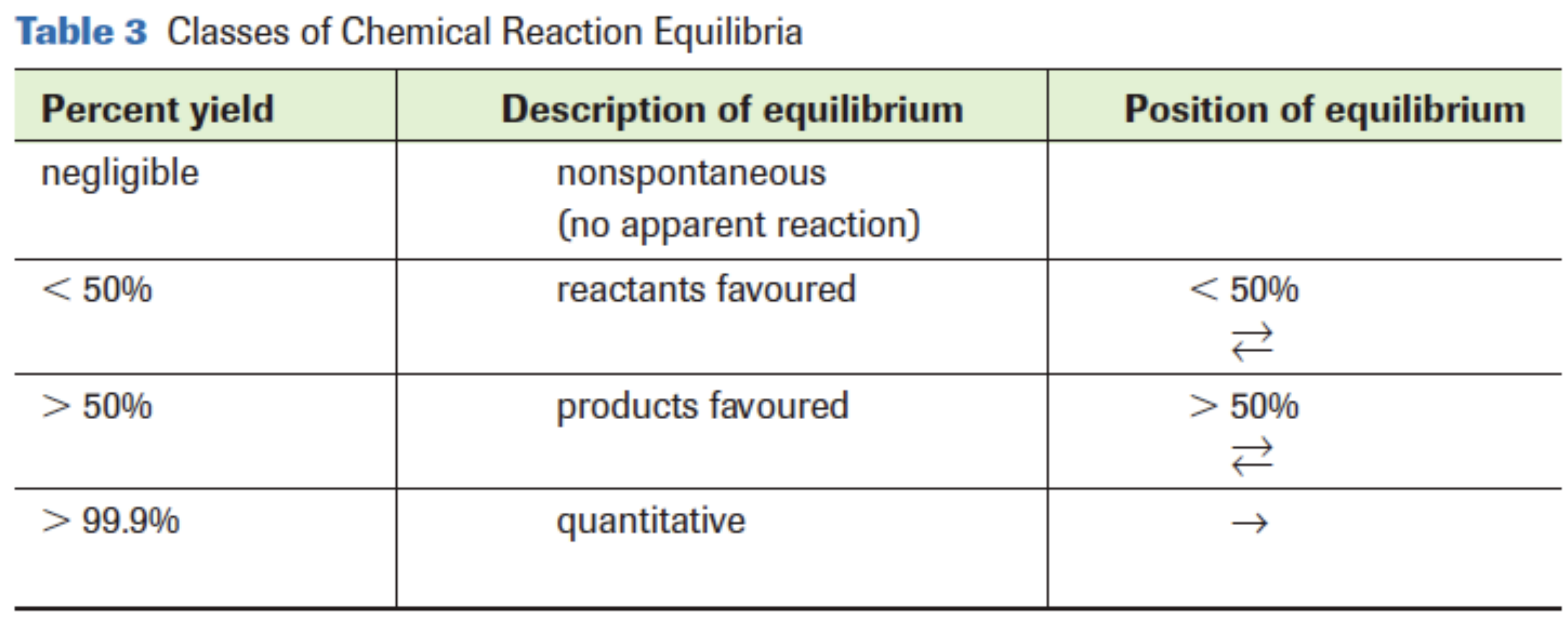
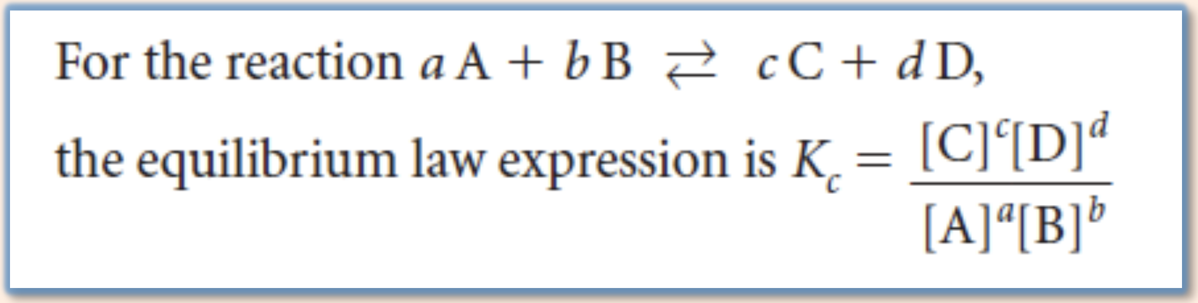


Table 3 Classes of Chemical Reaction Equilibria

Percent yield	Description of equilibrium	Position of equilibrium
negligible	nonspontaneous (no apparent reaction)	
$< 50\%$	reactants favoured	$< 50\%$ $\rightleftarrows$
$> 50\%$	products favoured	$> 50\%$ $\rightleftarrows$
$> 99.9\%$	quantitative	$\rightarrow$

Describing the Position of Equilibrium

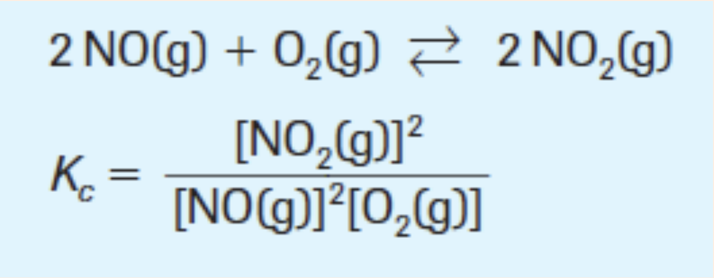
2. Using an Equilibrium Constant, (K_c)



For the reaction $a\,A + b\,B \rightleftarrows c\,C + d\,D$,

the equilibrium law expression is $K_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

- Example #1: Write the equilibrium law expression for the reaction of nitrogen monoxide gas with oxygen gas to form nitrogen dioxide gas.



$$2\,NO(g) + O_2(g) \rightleftarrows 2\,NO_2(g)$$

$$K_c = \frac{[NO_2(g)]^2}{[NO(g)]^2[O_2(g)]}$$

Describing the Position of Equilibrium

2. Using an Equilibrium Constant, (K_c)

- Note: The Kc value describes the extent of the forward reaction.
- $K_{c\ reverse} = \dfrac{1}{K_{c\ forward}}$ = The reciprocal value

- Example #2: The value of K_c for the formation of $HI_{(g)}$ from $H_{2(g)}$ and $I_{2(g)}$ is 40, at a given temperature. What is the value of K_c for the decomposition of $HI_{(g)}$ at the same temperature.

$$K_{c\ reverse} = \frac{1}{K_{c\ forward}} = \frac{1}{40} = 0.025$$

ICE Charts and Equilibrium Calculations

- Example #1: Consider the following equilibrium at 100 °C:

$$N_2O_{4(g)} \leftrightarrow 2\ NO_{2(g)}$$

- **2.0 mol** of $N_2O_{4(g)}$ was introduced into an empty **2.0 L** bulb. After equilibrium was established, only **1.6 mol** of $N_2O_{4(g)}$ remained. What is the value of K_c?

$\frac{2.0\text{ mol}}{2.0\text{L}}$ = 1.0 mol/L **(I)**

$\frac{1.6\text{ mol}}{2.0\text{L}}$ = 0.8 mol/L **(E)**

	$N_2O_{4(g)}$	$2NO_{2(g)}$
I:	1.0 mol/L	0
C:	- x	+ 2x
E:	1.0 – x = 0.80	2x

E: 1.0 – x = 0.80 solve for x x = 0.20 2x = 0.40

Solve for $K_c = \frac{(0.40)^2}{(0.80)} = 0.20$

ICE Charts and Equilibrium Calculations

- Example #3: Using a perfect square
- Given the following reaction:

$N_{2(g)} + O_{2(g)} \leftrightarrow 2NO_{(g)}$ $K_c = 0.00250$

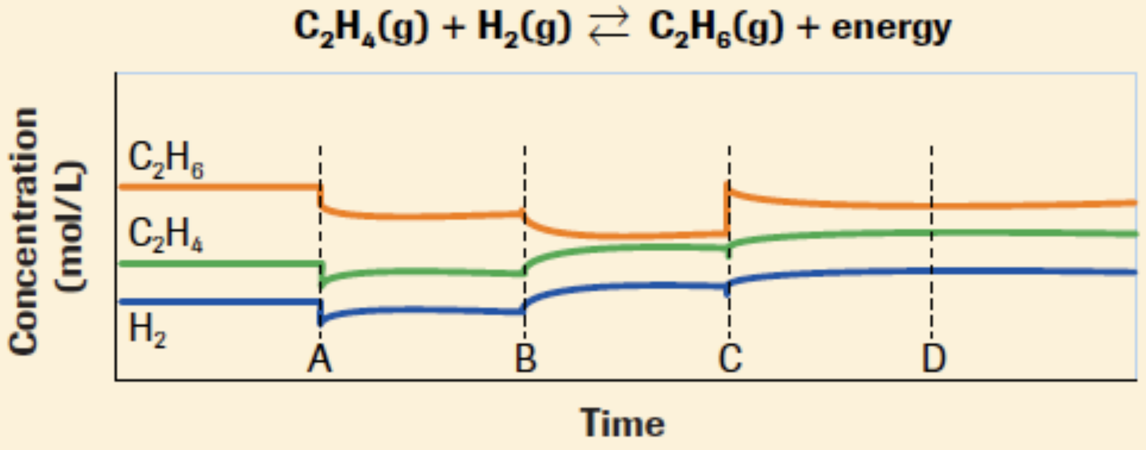
- Determine the equilibrium concentrations for all species present given that the initial concentration of each reactant is 0.200 mol/L.

	$N_{2(g)}$	$O_{2(g)}$	$2NO_{(g)}$
I:	0.200	0.200	0
C:	- x	- x	+ 2x
E:	0.200 - x	0.200 - x	2x
E:	***0.195mol/L***	***0.195mol/L***	***0.00976mol/L***

- **0.00250 =** $\frac{(2x)^2}{(0.200-x)^2}$ square root both sides $0.005 = \frac{2x}{0.200 - x}$ $= 0.01 – 0.05x = 2x$

$= 0.01 = 2.05x$ $= 0.00488$

- Identify the nature of the changes imposed on the following equilibrium system at the four times indicated by coordinates A, B, C and D



$C_2H_4(g) + H_2(g) \rightleftarrows C_2H_6(g) + \text{energy}$

Figure 12
Graph showing four disturbances to an equilibrium system

- At A, the concentration (or pressure) of every chemical in the system is decreased by increasing the container volume. Then the equilibrium shifts to the left (the side with more moles of gas)
- At B, the temperature is increased. Then the equilibrium shifts to left.
- At C, $C_2H_{6(g)}$ is added to the system. Then the equilibrium shifts to the left.
- At D, no shift in equilibrium position is apparent; the change imposed must be addition of a catalyst, or of a substance that is not involved in the equilibrium reaction.

The Water Ionization Constant, K_w

- Since the mathematical relationship is simple, we can easily use K_w to calculate either the hydronium or hydroxide ion concentration, if the other concentration is know.

$$\text{Since } [H_3O^+(aq)][OH^-(aq)] = K_w$$

$$\text{then } [H_3O^+(aq)] = \frac{K_w}{[OH^-(aq)]}$$

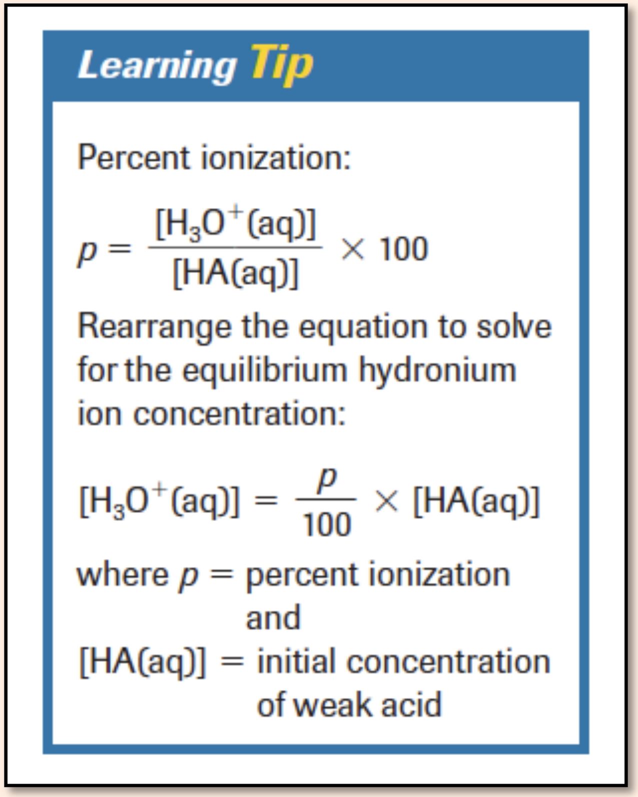
$$\text{and } [OH^-(aq)] = \frac{K_w}{[H_3O^+(aq)]}$$

$$\boxed{K_w = [H_3O^+(aq)][OH^-(aq)] = 1.00 \times 10^{-14} \text{ at SATP}}$$

The presence of substances other than water decreases the certainty of the Kw value to two significant digits; 1.0×10^{-14}

% Ionization

- The pH of 0.10 mol/L methanoic acid solution is 2.38.
  Calculate the percent reaction for ionization of methanoic acid.



Learning Tip

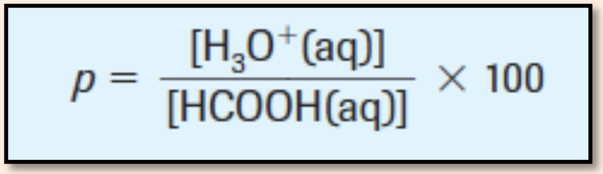
Percent ionization:

$$p = \frac{[H_3O^+(aq)]}{[HA(aq)]} \times 100$$

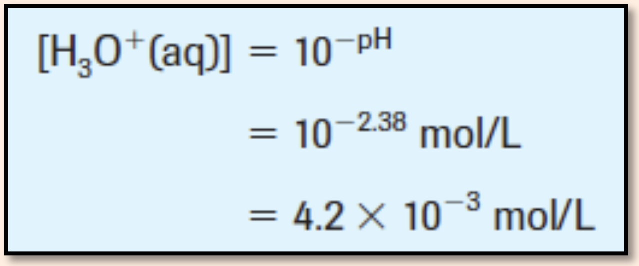
Rearrange the equation to solve for the equilibrium hydronium ion concentration:

$$[H_3O^+(aq)] = \frac{p}{100} \times [HA(aq)]$$

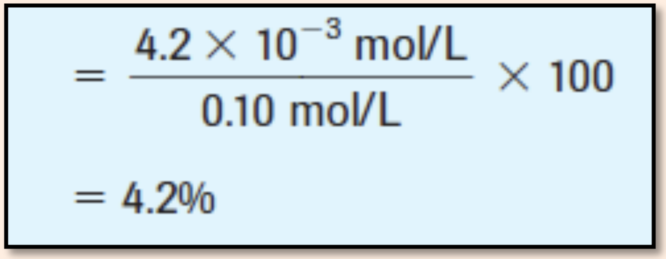
where p = percent ionization
and
$[HA(aq)]$ = initial concentration of weak acid



$$p = \frac{[H_3O^+(aq)]}{[HCOOH(aq)]} \times 100$$



$$\begin{aligned}[H_3O^+(aq)] &= 10^{-pH} \\ &= 10^{-2.38}\ \text{mol/L} \\ &= 4.2 \times 10^{-3}\ \text{mol/L}\end{aligned}$$

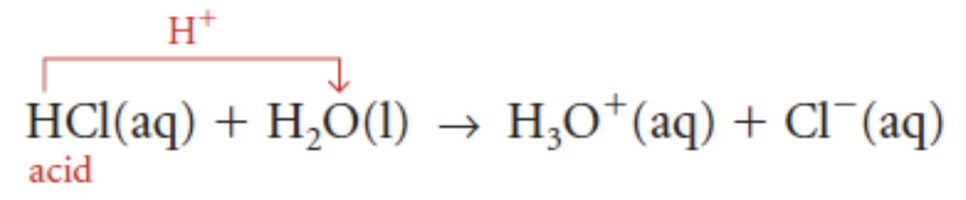


$$= \frac{4.2 \times 10^{-3}\ \text{mol/L}}{0.10\ \text{mol/L}} \times 100$$

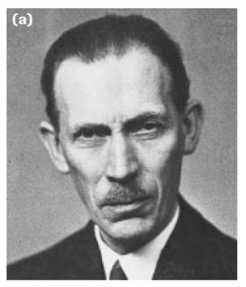
$$= 4.2\%$$

Bronsted-Lowry Acid-Base Concept

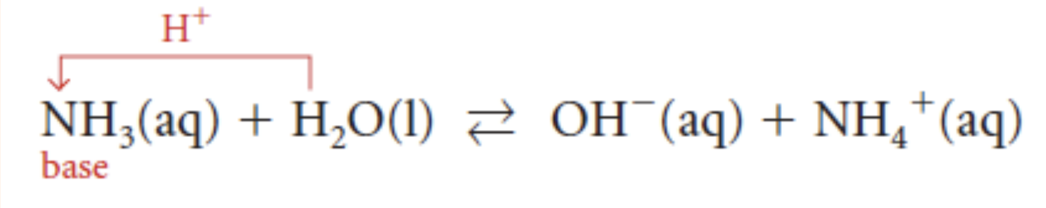
- Focuses on the role of the chemical species *in a reaction* rather than on the acidic or basic properties of their aqueous solutions.
- <u>Bronsted Lowry Definition for an Acid</u>: *proton donor*



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



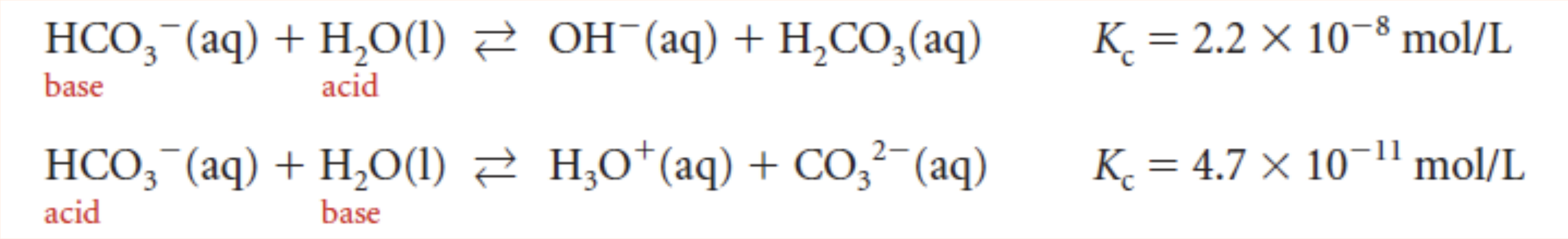
- <u>Bronsted Lowry Definition for an Base</u>: *proton acceptor*



$$NH_3(aq) + H_2O(l) \rightleftarrows OH^-(aq) + NH_4^+(aq)$$

Bronsted-Lowry Acid-Base Concept

- Protons may be gained in a reaction with one entity, but lost in a reaction with another entity.
  - The empirical term, **amphoteric,** refers to a chemical *substance* with the ability to react as either an acid or base.
  - The theoritical term, **amphiprotic**, describes an entity (ion or molecule) having the ability to either accept or donate a proton.



$$\underset{\text{base}}{\mathrm{HCO_3^-(aq)}} + \underset{\text{acid}}{\mathrm{H_2O(l)}} \rightleftarrows \mathrm{OH^-(aq)} + \mathrm{H_2CO_3(aq)} \qquad K_c = 2.2 \times 10^{-8}\ \mathrm{mol/L}$$

$$\underset{\text{acid}}{\mathrm{HCO_3^-(aq)}} + \underset{\text{base}}{\mathrm{H_2O(l)}} \rightleftarrows \mathrm{H_3O^+(aq)} + \mathrm{CO_3^{2-}(aq)} \qquad K_c = 4.7 \times 10^{-11}\ \mathrm{mol/L}$$

Conjugate Acids and Bases

- **RULE**: <u>The stronger the base, the more it attracts a proton (proton acceptor). The stronger the acid, the less it attracts its own proton (proton donor)</u>
- What does this mean about their conjugate pair??
- **The stronger an acid, the weaker is its conjugate base**.
  - If you are good at donating a proton, this means the conjugate base is not good at competing for it (weak attraction for protons)
- **The stronger a base, the weaker is its conjugate acid**.
  - If you are good at accepting a proton, this means the conjugate acid is not good at giving it up (strong attraction for protons).

Predicting Acid-Base Reactions

- **5) Predict the approximate position of equilibrium**
  - **Example**: What will be the predominant reaction if spilled drain cleaner (sodium hydroxide) solution is neutralized by vinegar?

SA

- $Na^+_{(aq)}$ $OH^-_{(aq)}$ $CH_3COOH_{(aq)}$ $H_2O_{(l)}$

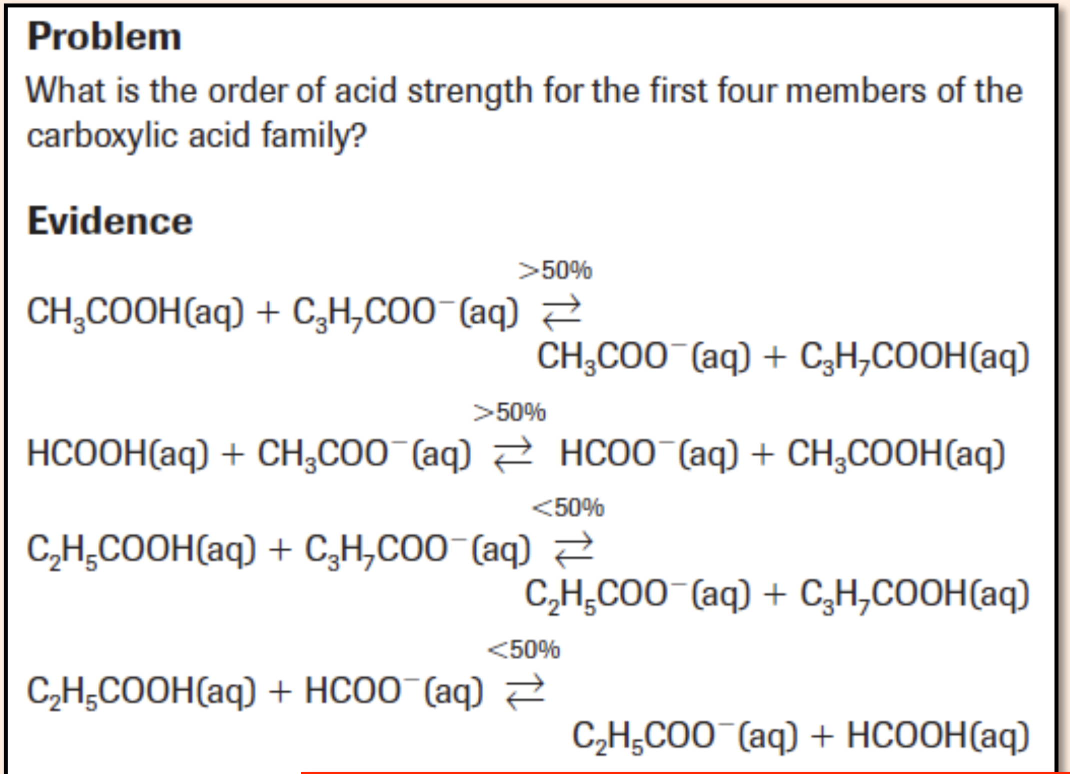
SB

$$CH_3COOH(aq) + OH^-(aq) \overset{>50\%}{\rightleftarrows} CH_3COO^-(aq) + H_2O(l)$$

The reaction of $H_3O^+_{(aq)}$ and $OH^-_{(aq)}$ is always quantitative (100%) so a single arrow is used

Table Building

- Lab Exercise 16.D



Problem

What is the order of acid strength for the first four members of the carboxylic acid family?

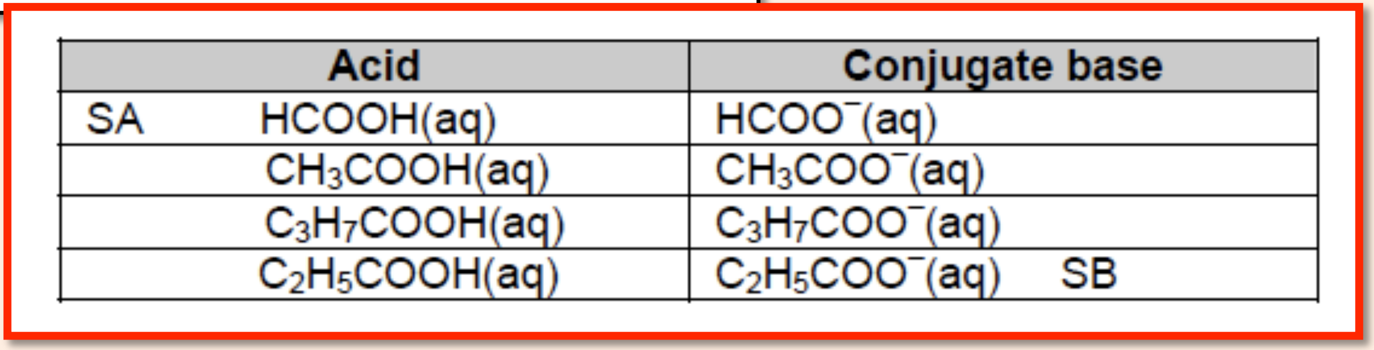
Evidence

$$CH_3COOH(aq) + C_3H_7COO^-(aq) \overset{>50\%}{\rightleftarrows} CH_3COO^-(aq) + C_3H_7COOH(aq)$$

$$HCOOH(aq) + CH_3COO^-(aq) \overset{>50\%}{\rightleftarrows} HCOO^-(aq) + CH_3COOH(aq)$$

$$C_2H_5COOH(aq) + C_3H_7COO^-(aq) \overset{<50\%}{\rightleftarrows} C_2H_5COO^-(aq) + C_3H_7COOH(aq)$$

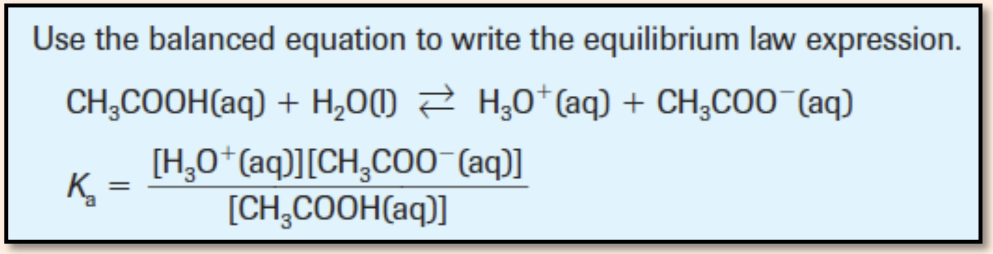
$$C_2H_5COOH(aq) + HCOO^-(aq) \overset{<50\%}{\rightleftarrows} C_2H_5COO^-(aq) + HCOOH(aq)$$



	Acid	Conjugate base	
SA	$HCOOH(aq)$	$HCOO^-(aq)$	
	$CH_3COOH(aq)$	$CH_3COO^-(aq)$	
	$C_3H_7COOH(aq)$	$C_3H_7COO^-(aq)$	
	$C_2H_5COOH(aq)$	$C_2H_5COO^-(aq)$	SB

K_a Calculations

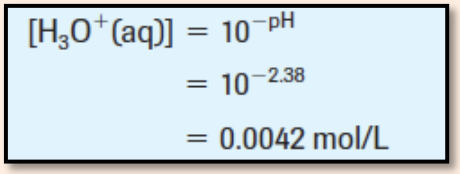
- <u>Example #1:</u> The pH of a 1.00 mol/L solution of acetic acid is carefully measured to be 2.38 at SATP. What is the value of Ka for acetic acid?



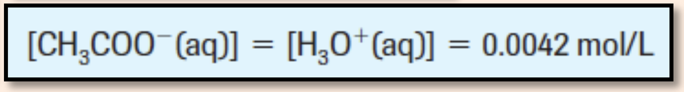
Use the balanced equation to write the equilibrium law expression.

$$CH_3COOH(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + CH_3COO^-(aq)$$

$$K_a = \frac{[H_3O^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]}$$



$$\begin{aligned}[H_3O^+(aq)] &= 10^{-pH}\\ &= 10^{-2.38}\\ &= 0.0042\ \text{mol/L}\end{aligned}$$



$$[CH_3COO^-(aq)] = [H_3O^+(aq)] = 0.0042\ \text{mol/L}$$

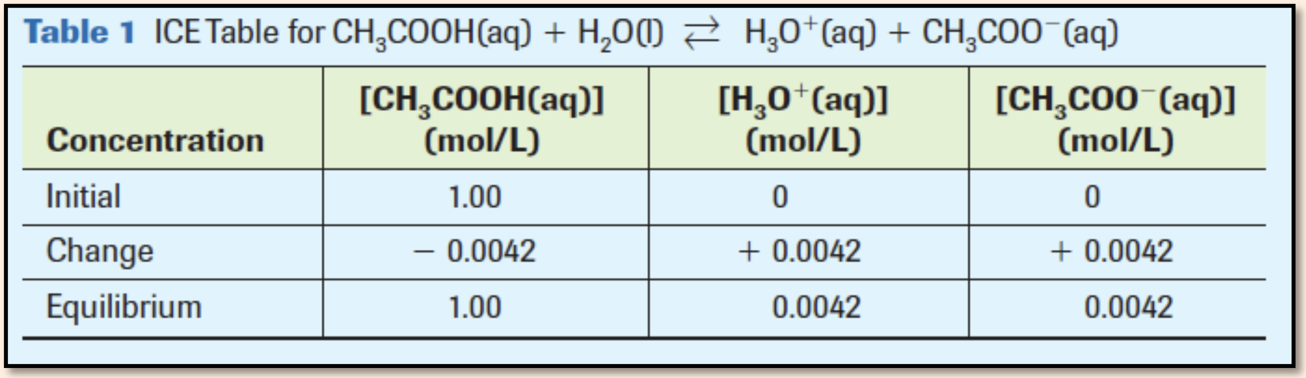
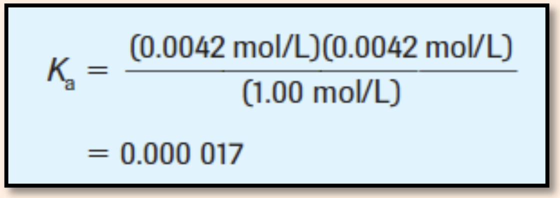


Table 1 ICE Table for $CH_3COOH(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + CH_3COO^-(aq)$

Concentration	$[CH_3COOH(aq)]$ (mol/L)	$[H_3O^+(aq)]$ (mol/L)	$[CH_3COO^-(aq)]$ (mol/L)
Initial	1.00	0	0
Change	− 0.0042	+ 0.0042	+ 0.0042
Equilibrium	1.00	0.0042	0.0042

1.00mol/L – 0.0042 mol/L = 0.9958 (rounds to 1.00 – precision rule)
Change in concentration is negligible in this case – *but not always*

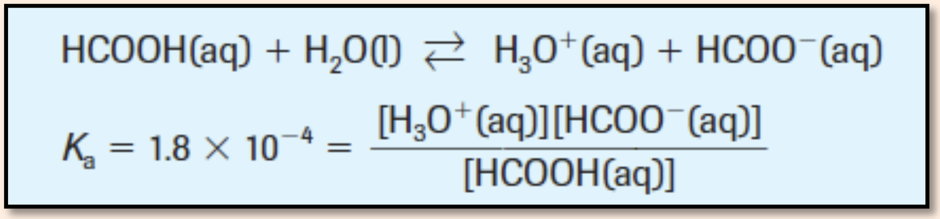


$$\begin{aligned}K_a &= \frac{(0.0042\ \text{mol/L})(0.0042\ \text{mol/L})}{(1.00\ \text{mol/L})}\\ &= 0.000\,017\end{aligned}$$

Regardless of size, Ka values are usually expressed in *scientific notation* = 1.7×10^{-5}

K_a Calculations

- Example #4: Predict the hydronium ion concentration and pH for a 0.200 mol/L aqueous solution of methanoic acid.



$$HCOOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCOO^-(aq)$$

$$K_a = 1.8 \times 10^{-4} = \frac{[H_3O^+(aq)][HCOO^-(aq)]}{[HCOOH(aq)]}$$

Approximation Rule:

$$\frac{0.200}{1.8 \times 10^{-4}} = >1000$$

So (0.200-x) = 0.200

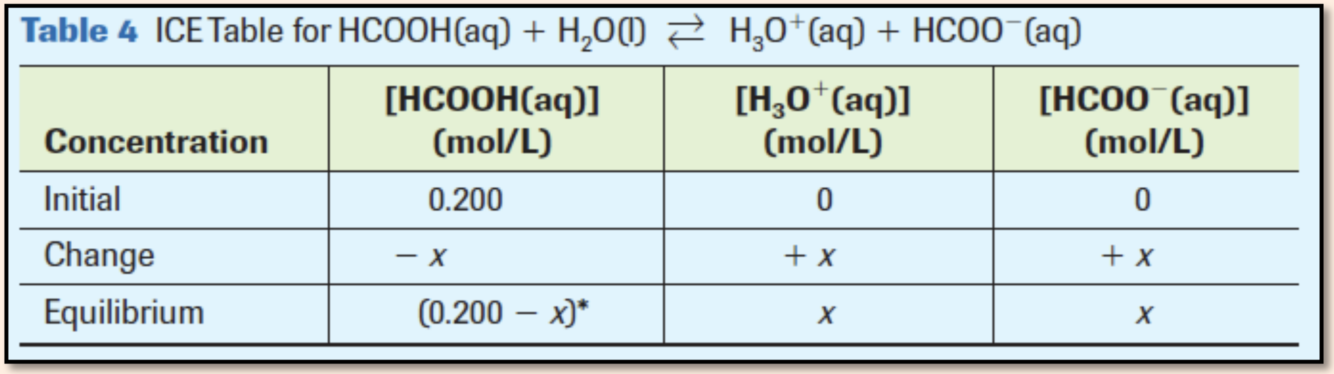
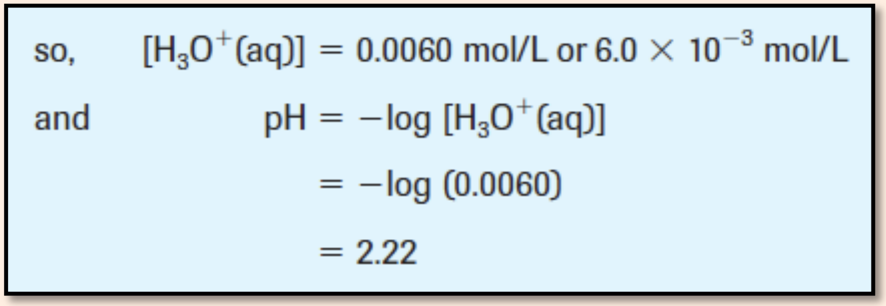


Table 4 ICE Table for $HCOOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCOO^-(aq)$

Concentration	**[HCOOH(aq)] (mol/L)**	**$[H_3O^+(aq)]$ (mol/L)**	**$[HCOO^-(aq)]$ (mol/L)**
Initial	0.200	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$(0.200 - x)$*	x	x

$$1.8 \times 10^{-4} = \frac{x^2}{(0.200)}$$

x = 0.006 = $H_3O^+_{(aq)}$ concentration



so, $[H_3O^+(aq)] = 0.0060$ mol/L or 6.0×10^{-3} mol/L

and $pH = -\log [H_3O^+(aq)]$

$= -\log (0.0060)$

$= 2.22$

K_b Calculations

We will use the same method as Ka calculations, but there is usually one extra step because pH values need to be converted to find hydroxide ion concentrations

- Example #1: A student measures the pH of a 0.250 mol/L solution of aqueous ammonia and finds it to 11.32. Calculate the Kb for ammonia

$$NH_3(aq) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$$

$$K_b = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$$

14 = pH + pOH

pOH = 2.68

$10^{-2.68} = 0.0021 = OH^-_{(aq)}$

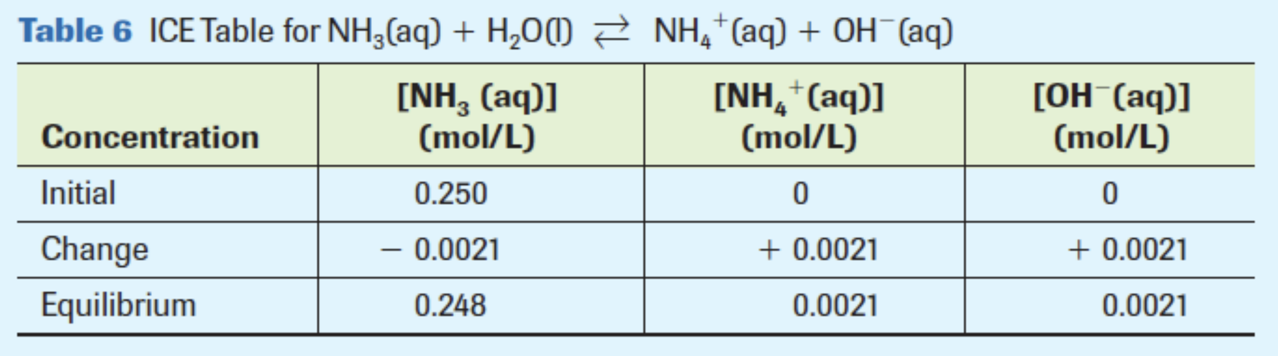


Table 6 ICE Table for $NH_3(aq) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$

Concentration	**$[NH_3(aq)]$ (mol/L)**	**$[NH_4^+(aq)]$ (mol/L)**	**$[OH^-(aq)]$ (mol/L)**
Initial	0.250	0	0
Change	− 0.0021	+ 0.0021	+ 0.0021
Equilibrium	0.248	0.0021	0.0021

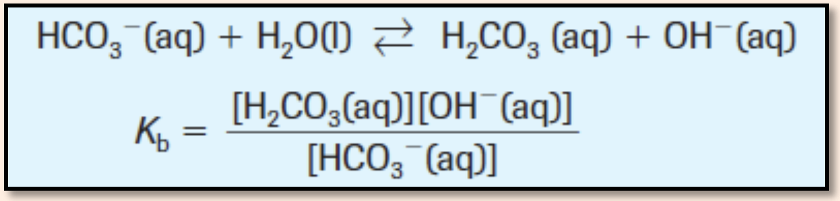
Remember K_b has only 2 sig digs

$$K_b = \frac{[0.0021\ mol/L][0.0021\ mol/L]}{[0.248\ mol/L]} = 0.000\ 018$$

K_b for ammonia is 1.8×10^{-5}

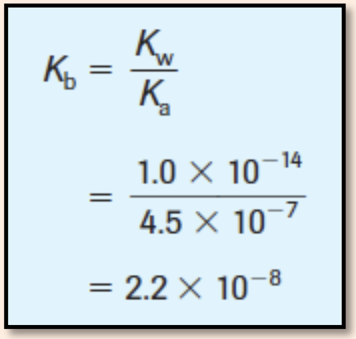
Calculating [OH^-] from K_b

- Example #2: Find the hydroxide ion amount concentration, pOH, pH and the percent reaction (ionization) of a 1.20 mol/L solution of baking soda.
- Baking soda = $NaHCO_{3(s)} \rightarrow Na^+_{(aq)} + HCO_3^-{}_{(aq)}$
- For $HCO_3^-{}_{(aq)}$, the conjugate acid is $H_2CO_{3(aq)}$ whose K_a is = 4.5×10^{-7}



$$HCO_3^-(aq) + H_2O(l) \rightleftarrows H_2CO_3(aq) + OH^-(aq)$$

$$K_b = \frac{[H_2CO_3(aq)][OH^-(aq)]}{[HCO_3^-(aq)]}$$



$$K_b = \frac{K_w}{K_a}$$

$$= \frac{1.0 \times 10^{-14}}{4.5 \times 10^{-7}}$$

$$= 2.2 \times 10^{-8}$$

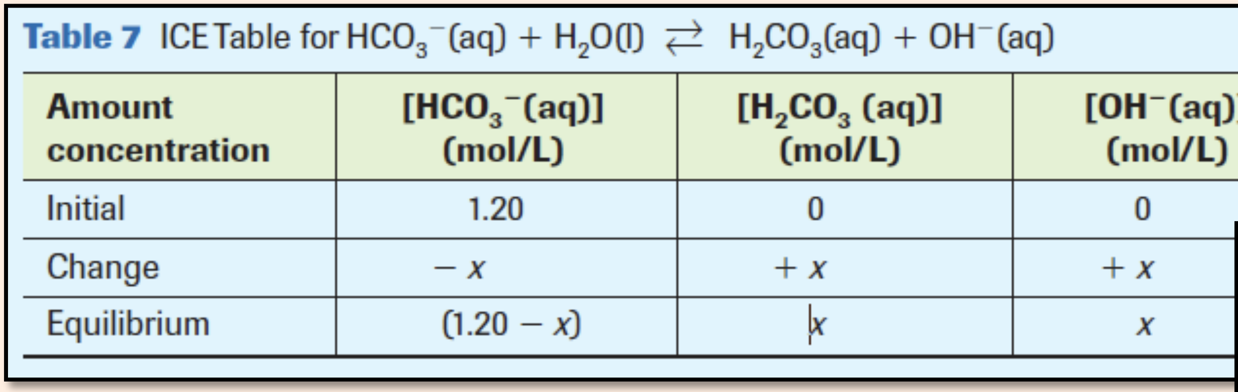


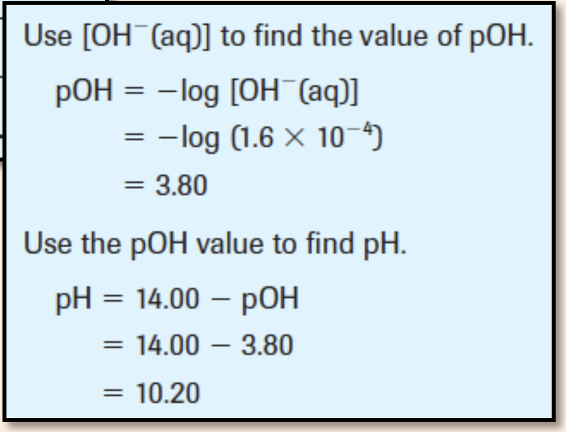
Table 7 ICE Table for $HCO_3^-(aq) + H_2O(l) \rightleftarrows H_2CO_3(aq) + OH^-(aq)$

Amount concentration	**[$HCO_3^-(aq)$] (mol/L)**	**[$H_2CO_3(aq)$] (mol/L)**	**[$OH^-(aq)$] (mol/L)**
Initial	1.20	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$(1.20 - x)$	x	x

Approximation Rule:

$\frac{1.20}{2.2 \times 10^{-8}}$ = >1000

So (1.20-x) = 01.20



Use [$OH^-(aq)$] to find the value of pOH.

$$pOH = -\log [OH^-(aq)]$$
$$= -\log (1.6 \times 10^{-4})$$
$$= 3.80$$

Use the pOH value to find pH.

$$pH = 14.00 - pOH$$
$$= 14.00 - 3.80$$
$$= 10.20$$

$2.2 \times 10^{-8} = \frac{x^2}{2.2 \times 10^{-8}}$ $\quad x = 1.6 \times 10^{-4} = OH^-{}_{(aq)}$

Calculating [OH$^-$] from K$_b$

- Example #2: Find the hydroxide ion amount concentration, pOH, pH and the percent reaction (ionization) of a 1.20 mol/L solution of baking soda.

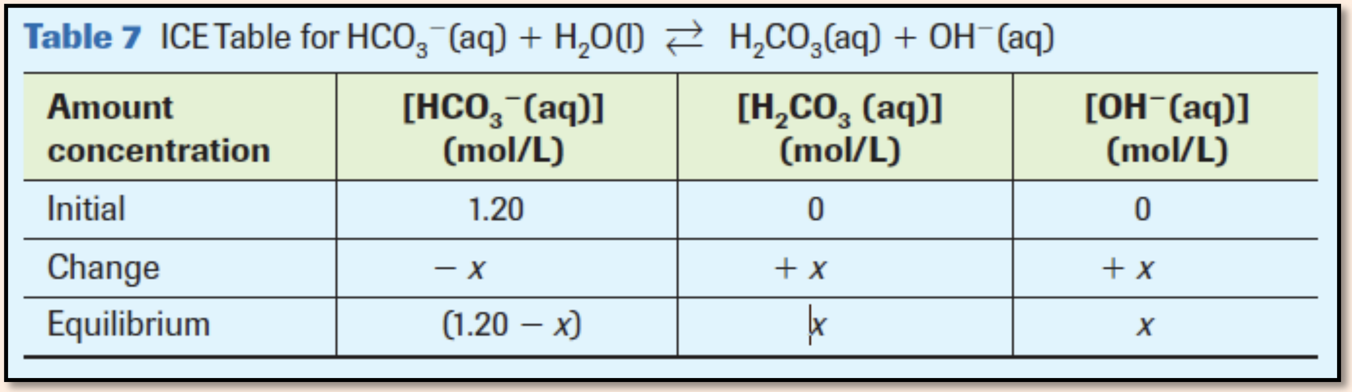
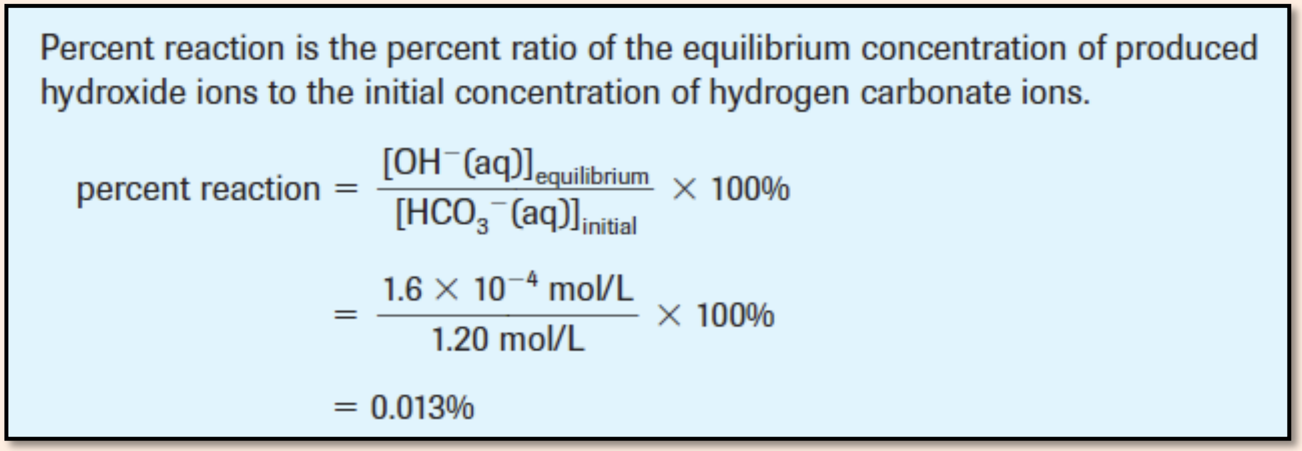


Table 7 ICE Table for $HCO_3^-(aq) + H_2O(l) \rightleftarrows H_2CO_3(aq) + OH^-(aq)$

Amount concentration	**[HCO_3^-(aq)] (mol/L)**	**[H_2CO_3 (aq)] (mol/L)**	**[OH^-(aq)] (mol/L)**
Initial	1.20	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$(1.20 - x)$	x	x

$2.2 \times 10^{-8} = \frac{x^2}{2.2 \times 10^{-8}}$ $\quad x = 1.6 \times 10^{-4} = OH^-_{(aq)}$



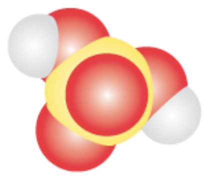
Percent reaction is the percent ratio of the equilibrium concentration of produced hydroxide ions to the initial concentration of hydrogen carbonate ions.

$$\text{percent reaction} = \frac{[OH^-(aq)]_{\text{equilibrium}}}{[HCO_3^-(aq)]_{\text{initial}}} \times 100\%$$

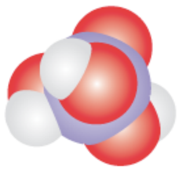
$$= \frac{1.6 \times 10^{-4}\ \text{mol/L}}{1.20\ \text{mol/L}} \times 100\%$$

$$= 0.013\%$$

Polyprotic Entities

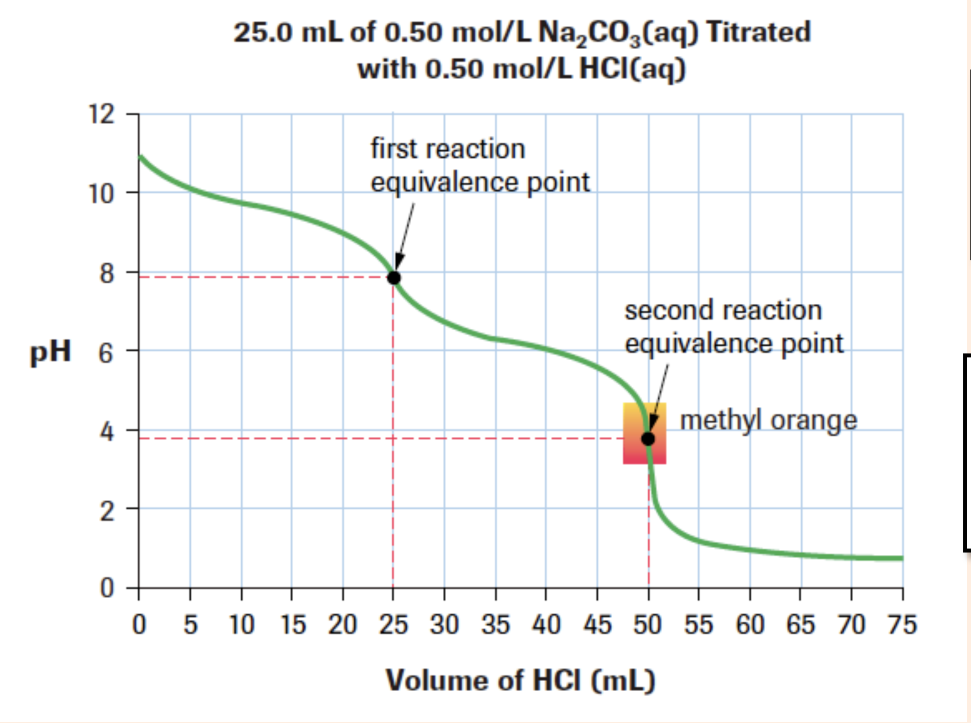


sulfuric acid, $H_2SO_4(aq)$



phosphoric acid, $H_3PO_4(aq)$

- Chem 20 Review:
  - **Polyprotic acids** – can lose more than one proton
  - **Polyprotic bases** – can gain more than one proton
  - If more than one proton transfer occurs in a titration, chemists believe the process occurs as a series of single-proton transfer reactions.
    - On a graph, this means there will be more than one equivalence point



25.0 mL of 0.50 mol/L $Na_2CO_3(aq)$ Titrated with 0.50 mol/L HCl(aq)

First proton transfer = 100%

$$\overset{SA}{H_3O^+(aq)}, Cl^-(aq), Na^+(aq), \underset{SB}{CO_3^{2-}(aq)}, \overset{A}{\underset{B}{H_2O(l)}}$$

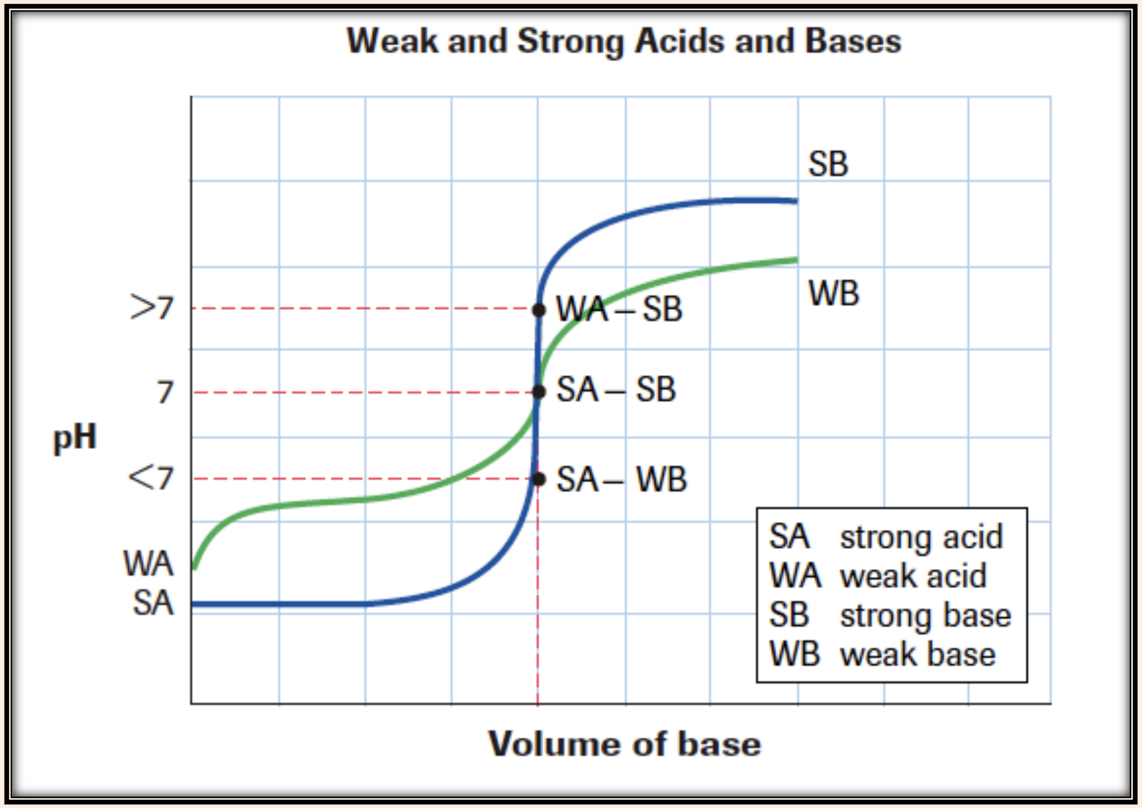
$$H_3O^+(aq) + CO_3^{2-}(aq) \rightarrow H_2O(l) + HCO_3^-(aq)$$

Second proton transfer = 100%

$$\overset{SA}{H_3O^+(aq)}, Cl^-(aq), Na^+(aq), \overset{A}{\underset{B}{H_2O(l)}}, \overset{A}{\underset{SB}{HCO_3^-(aq)}}$$

$$H_3O^+(aq) + HCO_3^-(aq) \rightarrow H_2O(l) + H_2CO_3(aq)$$

Carbonate ion is a diprotic base

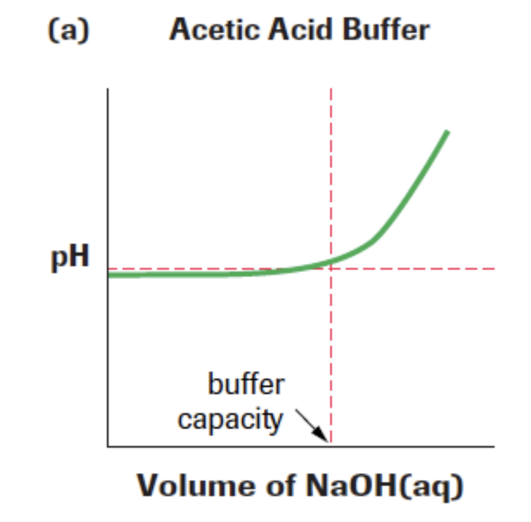


SUMMARY Titration Generalizations

- Strong acid–strong base reactions are quantitative (100%) and have an equivalence point pH = 7.
- Strong acid–weak base quantitative reaction equivalence points have a pH <7.
- Weak acid–strong base quantitative reaction equivalence points have a pH >7.
- Polyprotic entity samples produce sequential reactions in titrations, each of which may or may not be quantitative.

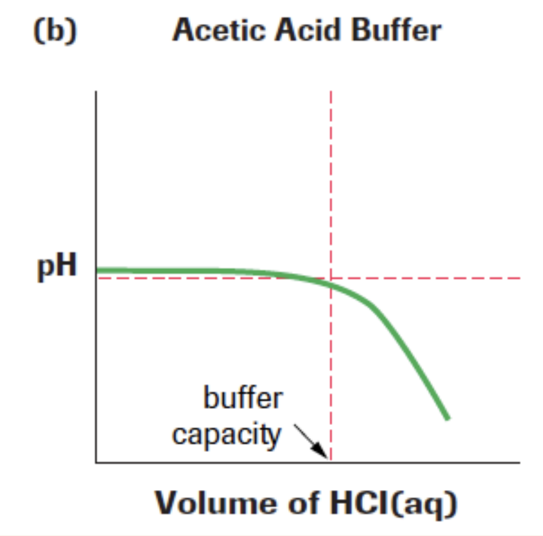
Buffering Capacity

- The limit of the ability of a buffer to maintain a pH level.
- When one of the entities of the conjugate acid-base pair reacts with an added reagent and is completely consumed, the buffering fails and the pH changes dramatically.



$OH^-(aq) + CH_3COOH(aq) \rightarrow H_2O(l) + CH_3COO^-(aq)$

All of the $CH_3COOH_{(aq)}$ is used up, OH^- additions will now cause the pH to drastically increase



$H_3O^+(aq) + CH_3COO^-(aq) \rightarrow H_2O(l) + CH_3COOH(aq)$

All of the $CH_3COO^-_{(aq)}$ is used up, H_3O^+ additions will now cause the pH to drastically decrease