Chemistry Notes

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Lecture 1: The Atom

- Earth's Crust's composition:
    - 46% Oxygen
    - 28% Silicon
    - 8.3% Aluminium
    - 5.6% Iron
    - 4.2% Calcium
    - 2.5% Sodium
    - 2.4% Magnesium
    - 2.0% Potassium
    - 0.61% Titanium
- Atoms have diameters around $10^{-10}m$
- We can detect particles up to around $10^{-15}m$

History of the Atom

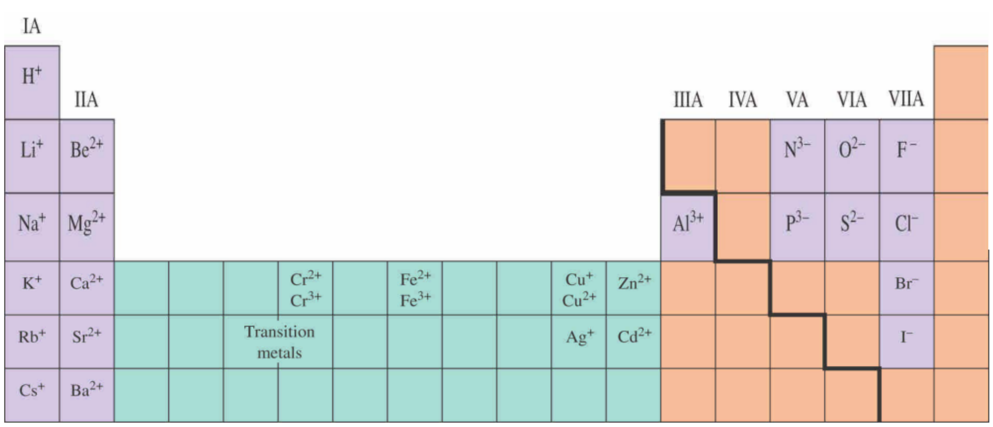
- Democritus first theorized the atom. Atomos: "not to be cut." Matter has limits to how much they can be broken down.
- Antonie Lavoisier wrote the first extensive list of elements and reformed the chemical nomenclature in 1787.
    - "Although matter may change its form or shape, its mass always remains the same".
    - "The mass of the products of a chemical reaction is exactly equal to that of reactants" – Mass conservation law (1785)
    - He discovered the importance of oxygen in combustion.
- John Dalton claimed:
    - Matter is made of atoms. They cannot be separated, created, or destroyed.
    - Atoms of an element cannot turn into those of another: in a chemical reaction, the original substances get separated into atoms that recombine to form different substances.
    - The atoms of an element show identical mass and properties and are different from any other element.
    - The compounds are formed by chemical combinations of different atoms.
- Law of simple multiple proportions (Dalton)
    - "If A and B react to form two or more compounds (e.g. AB and AB2), the two different masses of B that get combined with the same mass of A are multiples of a small prime number"
- Johnstone Stoney (1891) discovered electrolysis, and therefore realized that electricity exists in discrete units: electrons.
- Joseph John Thomson discovered that passing current through a gas can produce light – cathode rays.

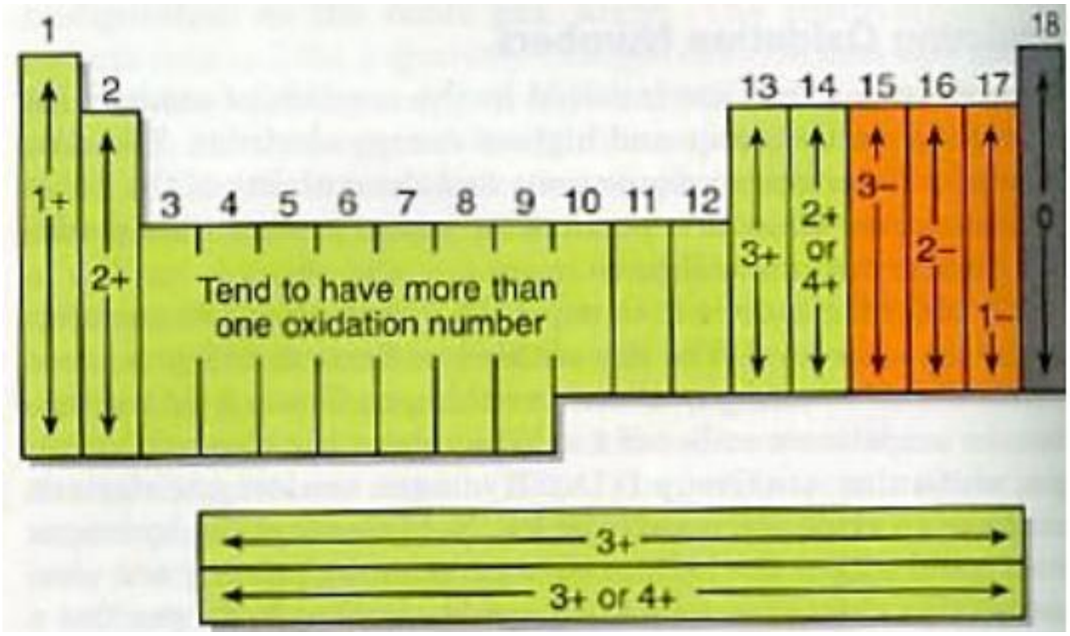
    - Jean Perrin (1895) proved that these cathode rays are electrons, given its deflection in a magnetic field.
- Joseph John Thomson then discovered that electrons' mass-to-charge ratio is $1.76 \times 10^{11} CKg^{-1}$
- Robert Millikan then discovered the actual charge: $1.6022 \times 10^{-19} C$. Leading to its mass being $9.1094 \times 10^{-31} Kg$
- Rutherford then studied deflection of radiation in magnetic fields.

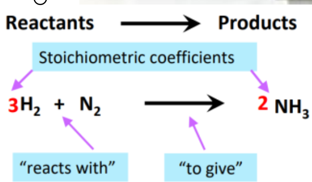
Models of the Atom

- Thomson's plum pudding model
    - Electrons in a positive mass
- Rutherford's Nuclear Model
    - Nucleus which has most of the mass of the atom
    - Nucleus is positively charged
    - Electrons have minimal mass
    - Electrons surround the nucleus in empty space
    - He did it by shooting alpha particles through gold atoms
- Rutherford proposed the presence of neutrons
- $12amu$ = mass of 1 $^{12}_{6}C$ atom
    - Proton: $1.6726 \times 10^{-27} Kg = 1.007\ amu$
    - Neutron: $1.6749 \times 10^{-27} Kg = 1.008\ amu$
    - Electron: $9.1094 \times 10^{-31} Kg = 0.00055\ amu$
- Isotopes usually have very similar properties
    - In hydrogen, the great mass differences can significantly affect things like melting point, boiling point, density etc.
- Cations are positive, while anions are negative

Lecture 2

- A compound is an electronically neutral substance composed of two or more elements with their atoms present in definite ratios. Can be:
  - Organic
  - Inorganic
  - Molecular (Covalent structures)
  - Ionic
- A molecule is a discrete group of atoms bonded in a specific arrangement
- An ion is a charged atom or molecule.
- A chemical formula represents its composition in terms of chemical symbols
  - Molecular formula
  - Structural formula
  - Condensed structural formula
  - Perspective drawing
  - Line structure
- Models of molecule:
  - Ball-and-stick model
  - Space-filling model
  - Density isosurface model
  - Electrostatic potential surface
- Proton number: Z
- Nucleon number: A
- Molecular weight: The total mass of a substance.
- $1mol = 6.0221\ particles$
  - $12g\ of\ {}^{12}_{6}C\ is\ 1\ mol$
- $N_A = 6.0221\ mol^{-1}$
- Molar mass (M) is the mass per mole of substance
  - Equal to the mass number of the element/compound
- Empirical formula is a chemical formula in its most simplified ratio.
- Mass percentage composition is the percentage of mass (Kg) of each element in a compound.
- 

- Anions are attracted towards anodes and cations towards cathodes
- The oxidation number of an element (O.N.) is the charge after becoming an ion.
    - 



- • Mass must be balanced
  • Charge must be balanced

  $\rightleftharpoons$ Indicates a reversible reaction

  $\xrightarrow{\Delta}$ Shows that heat is supplied to the reaction

- $\xrightarrow{Pt}$ Shows that a catalyst is used or supplied to the reaction
- Redox reactions vs non-redox:
    - Redox reaction: A reaction that involves transfer of electrons from one particle/atom/ion which gets oxidised to another which gets reduced.
        - Consequently, oxidation states change.
        - Acid-base reactions (which are redox) are called salifications.
    - Non-redox reaction: A reaction where oxidation states do not change.
- Rules for oxidation states
    - Oxidation states for an uncombined element is zero
    - Large carbon and silicon structures also have oxidation states of zero
    - The sum of oxidation states in a neutral compound is zero.
    - The sum of oxidation states in an ion is equal to the charge of the ion.
    - The more electronegative element in a substance is assigned a negative oxidation state, while the least electronegative element is assigned a positive oxidation state
        - Electronegativity is greatest in top right of periodic table and lowest on bottom left.

Rules For Oxidation States

- Group 1 metals: always +1
- Group 2 metals: always +2
- Oxygen: usually -2
    - Except peroxides (-1 since hydrogen peroxide is neutral), superoxides ($-\frac{1}{2}$ – this is an average, meaning that 1 oxygen is -1 and the other is 0) and F_2O (+2 since F is more electronegative than oxygen)
- Hydrogen: usually +1
    - Except in metal hydrides (-1)
- Fluorine: always -1
- Chlorine: usually -1
    - Except compounds with O or F (varies)

- Sulfate ion: SO_4^{2-}

Practice Lesson 1

- Different nomenclatures:
  - Classic (-ous -ic)
  - Stock system (oxidation states are indicated in brackets in roman numerals
  - IUPAC: di, tri, tetra etc are used to name compounds

Naming cations:

- Same name of the atom + "ion"
  - Eg. Sodium ion, calcium ion, etc.
- If there are multiple charges on the ions, happens with transition metals, stock/classical system is used, for example:
  - Fe^{2+} is ferrous ion or Iron (II) ion
  - Fe^{3+} is ferric ion or Iron (III) ion

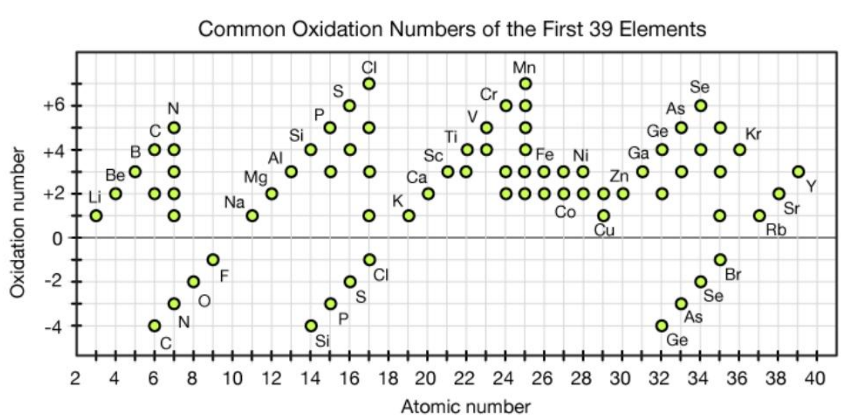
Naming anions

- Root of parent atom with "-ide"
  - Nitride
  - Oxide
  - Chloride

Diatomic Molecules

Molecules that occur in pairs:

- Nitrogen
- Oxygen
- Fluorine
- Chloride
- Bromine
- Iodine



Acids, bases and salts

- Elements (both metals and non-metals) can react with oxygen and hydrogen to form binary compounds: acids and bases
  - Metals:
    - +hydrogen: metal hydroxide
    - +oxygen: basic oxides
  - Non-metals:
    - +hydrogen: covalent hydrides/hydracids
    - +oxygen: acid oxides/anhydrides
- They combine to make salts
- Adding water to binary compounds can change them.
  - Basic oxides + water = hydroxides
  - Acid oxides (anhydrides) + water = oxoacids

Binary ionic compounds – metal + non-metal

- In name, metal is first. General rules:
  - Cation is metal, anion is non-metal
  - Cation is named first
  - Cation takes the name of the metallic element
  - Simple anion takes the root of the element followed by "-ide"
- If the metal can have different oxidation states, classic or stock systems can be used, eg:
  - Ferrous chloride / iron(II) chloride ⇒ $FeCl_2$
  - Ferric chloride / iron(III) chloride ⇒ $FeCl_3$

Binary covalent compounds

- For binary compounds containing two non-metals, a Greek/Latin prefix is added to indicate the number.
  - 1: mono
  - 2: di
  - 3: tri
  - 4: tetra
  - Etc.
- Occasionally also used with metals are present
- Naming:
  - The element that occurs first in the series is written and named first, then the second (which retains the "-ide" suffix)
  - Attach the number prefix to the second element (ALWAYS)
  - Attach the number prefix to the first element if it contains more than one atom.

Stock system

- The stock system works differently.
- An example is carbon(II) oxide is CO, while carbon(IV) oxide is CO_2.

- So, the number of atoms is not represented, but the oxidation state of the first element is.

Acid oxides (binary covalent)

- Nonmetal + oxygen
- Classic nomenclature:
  - Root of non-oxygen element + suffix + anhydride
  - If two oxidation numbers:
    - Lower gets "-ous"
    - Higher gets "-ic"
  - If 4 oxidation numbers hypo- and per- prefixes are added

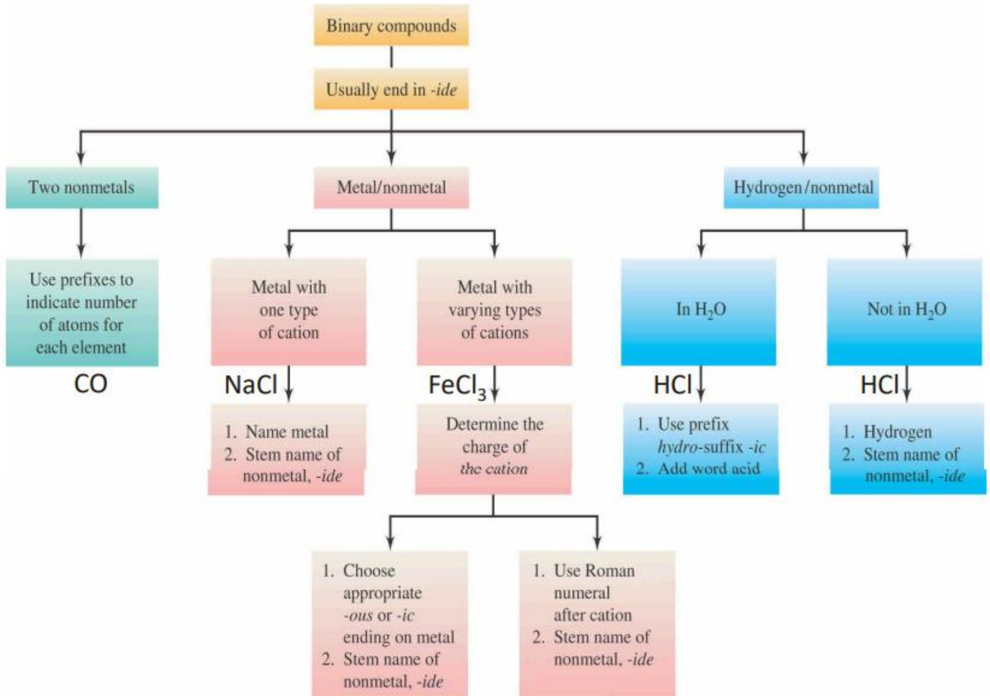
Covalent hydrides

- Group V elements when bonded to H using their negative O.N. (-3):
  - NH_3 – ammonia
  - PH_3 – phosphine (IUPAC = phosphane)
  - AsH_3 – arsine (IUPAC = arsane)
- Compounds containing hydrogen and nonmetals have 2 different nomenclatures depending on if it is in water or not:
  - Gas phase: hydrogen + root of element + "ide"
    - Hydrogen chloride = $HCl(g)$
    - Hydrogen sulfide = $(H_2S(g)$
  - In water: root of element + "ic acid"
    - Hydrochloric acid = $HCl(aq)$
    - Hydrosulfuric acid = $H_2S(aq)$

Peroxides and superoxides

- Peroxide is a compound with R -O-O- R bond
  - Element + peroxide
    - Eg. Sodium peroxide = Na_2O_2
- Superoxide is a compound with the superoxide ion (O_2^-)
  - Element + superoxide
    - Eg. Potassium superoxide = KO_2

Flow chart for binary compounds



Polyatomic compounds

Hydroxides

- Metal ion + hydroxide ion (OH-)
- Naming: name of metal + "hydroxide"
  - $NaOH$ = sodium hydroxide
  - $Ba(OH)_2$ = barium hydroxide
- Classic/IUPAC suffix for different ON apply

Ternary acids

- Water + acid oxide
  - $CO + H_2O \rightarrow H_2CO_3$ (carbonic acid)
- Prefix (-ous/-ic) + root f non-oxygen element + suffix + acid
  - $HClO$ = hypochlorous acid
  - $HClO_2$ = chlorous acid
  - $HClO_3$ = chloric acid
  - $HClO_4$ = perchloric acid
- Nitrogen acids only from III and IV ON
- Carbon acids only from IV ON
- Phosphorus, boron, arsenic, silicon acids can combine with more than 1 water molecule, adding prefixes:
  - Even ON: meta- and ortho- with 1/2 water molecules

    - Odd ON: meta-, pyro-, ortho with1/2/3 water molecules
    - $P_2O_5 + H_2O \rightarrow 2HPO_3$ = metaphosphoric acid
- When oxyacids react, they release hydrogen atoms and leave behind polyatomic anions
    - $HNO_3 \rightarrow H^+ + NO_3^-$
    - $H_2SO_4 \rightarrow 2H^2 + SO_4^{-2}$
-

ate anions	Carbonate	Nitrate	Sulfate	Phosphate	Chlorate	Bromate	Iodate
per ... ate					ClO_4^-	BrO_4^-	IO_4^-
... ate	CO_3^{-2}	NO_3^-	SO_4^{-2}	PO_4^{-3}	ClO_3^-	BrO_3^-	IO_3^-
... ite		NO_2^-	SO_3^{-2}	* HPO_3^{-2}	ClO_2^-	BrO_2^-	IO_2^-
hypo ... ite				** $H_2PO_2^-$	ClO^-	BrO^-	IO^-

* H_3PO_3 only has 2 acidic H's, so phosphite is HPO_3^{-2}

** H_3PO_2 only has 1 acidic H, so hypophosphite is $H_2PO_2^-$

Important polyatomic ions

- CN^- = cyanide ion
- OH^- = hydroxide ion
- NH_4^+ = ammonium ion
- SO_4^{2-} = sulfate ion

Salts of oxygen acids

- Contain metal and non-metal parts
- Brackets are placed around the polyatomic ions
    - $NaCl$
    - $CaCl_2$
    - $Al(SO_4)_3$
- Examples of IUPAC nomenclature:
    -

Formula	Name
$Ca_3(PO_4)_2$	tricalcium bis(phosphate)
$Ca_2P_2O_7$	dicalcium diphosphate

Acid salts

- Acids with only 1 H atom are called monoprotic
- Acids with more H^+ ions are called polyprotic acids because they can release more than 1 proton
-

$H_2CO_3 \rightarrow H^+ + HCO_3^-$	bicarbonate or monohydrogen carbonate
$HCO_3^- \rightarrow H^+ + CO_3^{-2}$	carbonate
$H_2SO_4 \rightarrow H^+ + HSO_4^-$	bisulfate or monohydrogen sulfate
$HSO_4^- \rightarrow H^+ + SO_4^{-2}$	sulfate
$H_2SO_3 \rightarrow H^+ + HSO_3^-$	bisulfite or monohydrogen sulfite
$HSO_3^- \rightarrow H^+ + SO_3^{-2}$	sulfite
$H_3PO_4 \rightarrow H^+ + H_2PO_4^-$	dihydrogen phosphate
$H_2PO_4^- \rightarrow H^+ + HPO_4^{-2}$	monohydrogen phosphate
$HPO_4^{-2} \rightarrow H^+ + PO_4^{-3}$	phosphate

- When polyvalent cations like Ca^{+2}, Al^{+3}, etc are combined with partially ionized acids, the convention is to state how many hydrogens there are, eg:
    - Calcium dihydrogen phosphate
    - Calcium monohydrogen phosphate

Hydrated ionic compounds

- When a specific number of water molecules are associated to the formula, the compound is hydrated. A “[prefix]hydrate” is added to the end:
    - Eg: $CuSO_4 \cdot H_2O$ = copper sulfate monohydrate
    - $BaI_2 \cdot 2H_2O$ = barium iodide dihydrate

Lecture 3

- Quantum mechanics explains how electrons exist and behave within atoms.
- $c = 3.00 \times 10^8 ms^{-1}$
- Photoelectric effect:
  - $E = \nu h$ where ν = frequency
  - $E_k = h\nu - \phi$
- Emission spectra are caused by different energy levels of electron energies which are quantized.
- Electrons can behave like waves
  - Diffraction happens with electron waves
- $\lambda = \frac{h}{mv}$
- $m\Delta v * \Delta x \geq \frac{h}{4\pi}$
- Schrodinger Equation:
  - $\hat{H}(\psi) = E\psi$

Orbitals

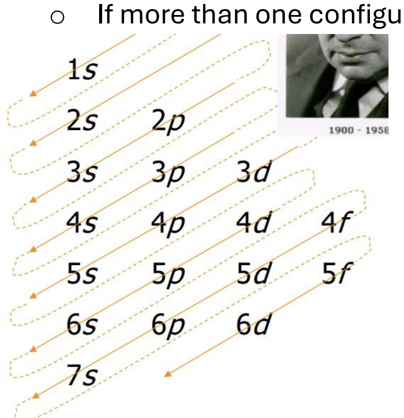
- Orbital numbers are n, l, m.
- $n \in \mathbb{Z}^+$ is the principal quantum number
  - Relates to Bohr's energy levels
  - Higher n means higher energy
  - For higher n values, the difference between energy levels decreases
- $l \in \mathbb{Z} \cap [0, n-1]$ is the angular momentum quantum number
  - Determines the shape of the orbital
  - Different values have different letters assigned:
    - $l = 0$: s orbital – sphere
    - $l = 1$: p orbital – 2 balloons pointing towards each other, tied at the knot
    - $l = 2$: d orbital – mainly 4 balloons pointing towards each other, tied at the knot
    - $l = 3$: f orbital – mainly 8 balloons pointing towards each other, tied at the knot
- $m \in \mathbb{Z} \cap [-l, l]$ is the magnetic momentum number
  - Determines the orientation of the orbital
- A node is a distance from the origin where the probability of an electron being there is negligible
- S orbitals
  - Number of nodes is n-1
  - $l = 0$
  - Each principal energy state has 1 s orbital
- P orbitals
  - $m \in \{-1, 0, 1\}$
  - Different directions, represented by p_x, p_y, p_z
  - Number of nodes is n

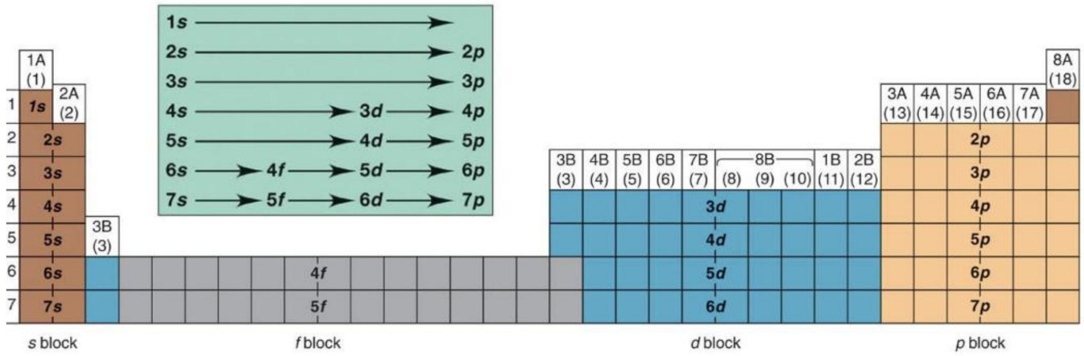
    - Mainly 2 lobed
    - Each principal energy state has 3 p orbitals for $n \geq 2$
- D orbitals
    - $d_{yz}, d_{xy}, d_{z^2}, d_{xz}, d_{x^2-y^2}$ represent directions
    - Each principal energy state has 5 d orbitals for $n \geq 3$
    - Mainly 4 lobed
- F orbitals
    - Mainly 8 lobed
    - 7 f orbitals for $n \geq 4$

Electrons in Orbitals

- Electrons can have spin
    - $m_s \in \left\{-\frac{1}{2}, \frac{1}{2}\right\}$
    - Spin up/spin down
    - Spins must be paired in an orbital
- Max number of electrons in an energy level n is $2n^2$
    - $n = 1 \rightarrow 2$
    - $n = 2 \rightarrow 4$
    - $n = 3 \rightarrow 16$
    - $n = 4 \rightarrow 32$
- Orbitals with the same energy are called degenerate
    - Sublevels in each energy level in hydrogen are degenerate
    - Sublevels in each energy level are not degenerate

Filling orbitals

- AUFBAU method
    - The orbitals with lower energy get occupied first
- Pauli Principle
    - A maximum of two electrons with opposite spin can be hosted in each orbital
- Hund Rule
    - If more than one configuration is possible, the one giving the highest spin is favoured
- 

- The periodic table can be subdivided depending on the group of valence electron
    - 

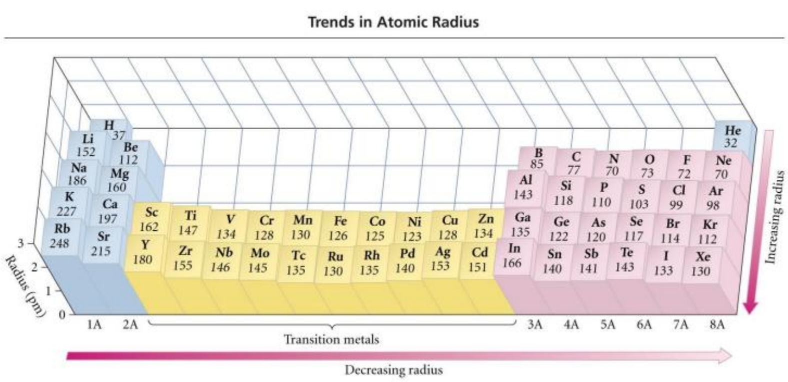
Practice Lesson 2

- Atomic mass is the mass in amu of an atom, weighted average by isotope frequency
- Molecular weight is the same but for molecules
- Molar mass is the mass in grams per mole of substance. It is the same value as the atomic mass/molecular weight.
- $Mass\ percentage\ of\ an\ element = \frac{Mass\ of\ an\ element\ in\ the\ sample}{Total\ mass\ of\ the\ sample} \times 100\%$
  - Measurements in grams

Lecture 4

- Periodic law (1869, Mendeleev & Meyer)
    - "If the elements are ordered by increasing atomic mass, some properties are changing periodically."

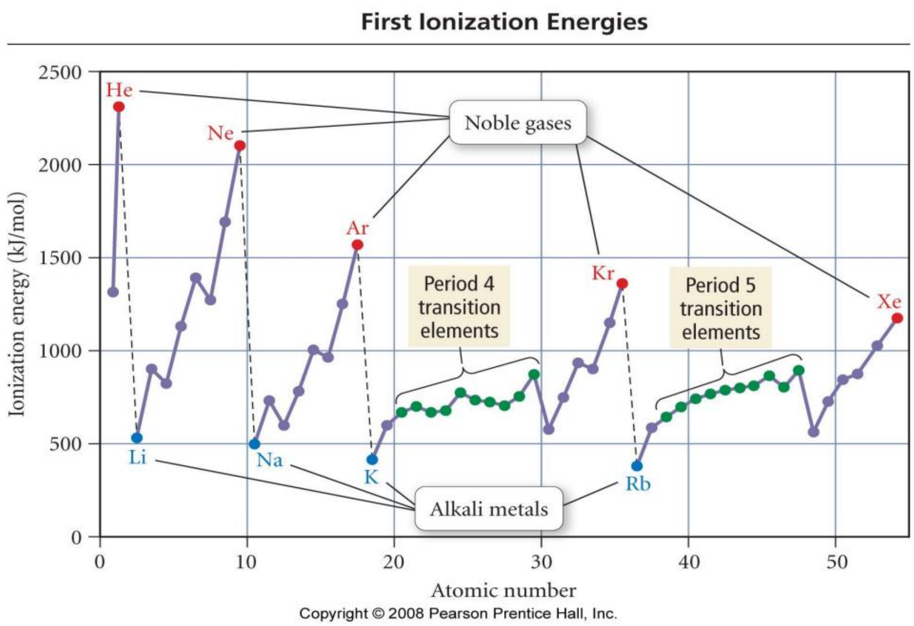
Measuring the atomic radius

- Measured in ångströms ($1\text{Å} = 100pm = 0.1nm = 10^{-12}m$)
- Van der Waals radius
    - Non-bonding
- Covalent radius
    - Binding radius
- Effective Nuclear Charge
    - $Z_{EFF} = Z - S$
    - Z is the atomic number
    - S is a shield constant
- Electrons are attracted to the nucleus but repel each other.
    - Atomic radius decreases across periods (more electrons in valence shell)
    - Atomic radius increases along a group (more shells, but similar EFF)
    - EXCEPTION with transition metals
        - Radius increases along group
        - Size remains roughly the same across periods (across the d block)
    - 

- Ionic radius is the radius of an ion
    - Cations are smaller than their parent atoms.
        - 1 less shell and repulsions decrease.
        - Larger positive charge = smaller cation
    - Anions are larger than their parent atoms.
        - Electrons are added and repulsions are increased.
        - Larger negative charge = larger anion

Ionization energy

- Minimum energy needed to remove an electron from an atom in gas state.
    - Endothermic process

    - Valence electrons are easiest to remove.
    - 1^{st} IE: energy needed to remove an electron from atom.
    - 2^{nd} IE: Energy needed to remove an electron from +1 ion.
    - Etc.
- Trends in 1^{st} ionization energy
    - The larger the effective nuclear charge on the electron, the greater the energy required.
    - The further the electron is from the nucleus, the easier it is to remove.
    - 1^{st} IE decreases along group.
        - Valence electron further away
    - 1^{st} IE generally increases along period.
        - Effective nuclear charge increases
        - Except from group 2A to 3A, or from group 5A to 6A
            - This is because breaking a full sublevel costs extra energy, while getting a full sublevel costs less energy
    - 

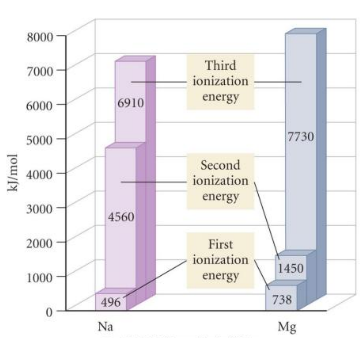
- Trends in successive ionization energies
    - Removal of each successive electron costs more energy.
    - Regular increase in energy for each successive valence electron
    - Large increase in energy when removing core electrons.
    - 

Table 8.5 Successive Ionization Energies of the Elements Lithium Through Sodium

Z	Element	Number of Valence Electrons	Ionization Energy (MJ/mol)*									
			IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7	IE_8	IE_9	IE_{10}
3	Li	1	0.52	7.30	11.81							
4	Be	2	0.90	1.76	14.85	21.01			CORE ELECTRONS			
5	B	3	0.80	2.43	3.66	25.02	32.82					
6	C	4	1.09	2.35	4.62	6.22	37.83	47.28				
7	N	5	1.40	2.86	4.58	7.48	9.44	53.27	64.36			
8	O	6	1.31	3.39	5.30	7.47	10.98	13.33	71.33	84.08		
9	F	7	1.68	3.37	6.05	8.41	11.02	15.16	17.87	92.04	106.43	
10	Ne	8	2.08	3.95	6.12	9.37	12.18	15.24	20.00	23.07	115.38	131.43
11	Na	1	0.50	4.56	6.91	9.54	13.35	16.61	20.11	25.49	28.93	141.37

*MJ/mol, or megajoules per mole = 10^3 kJ/mol.

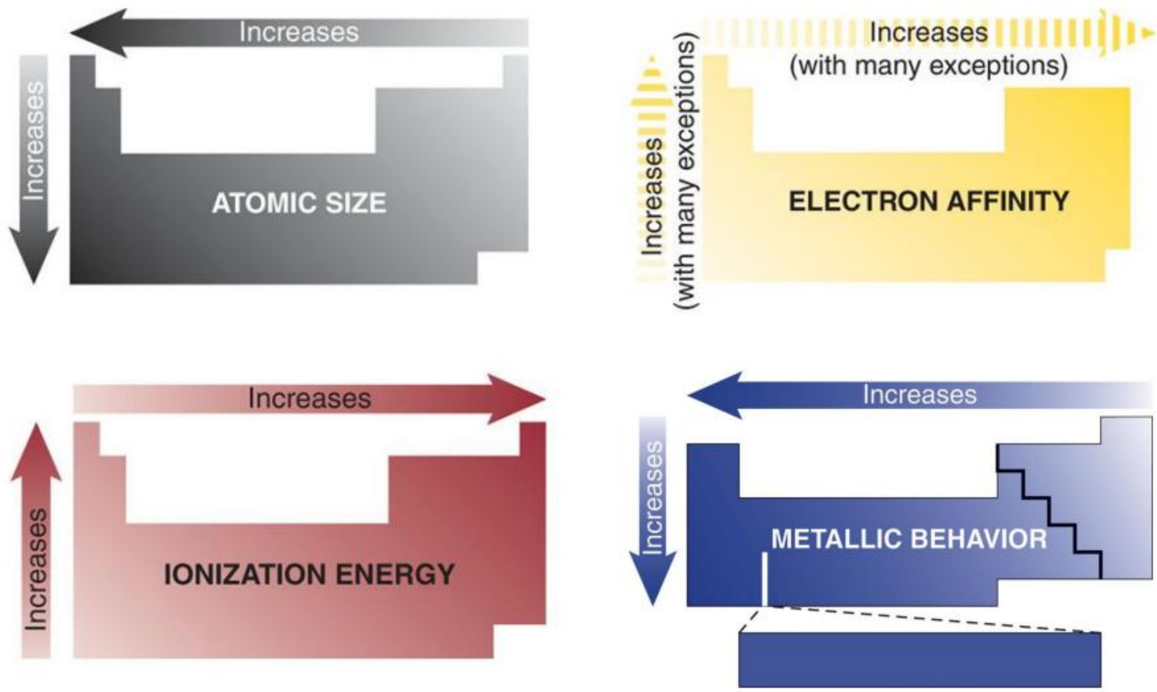
Electron Affinity

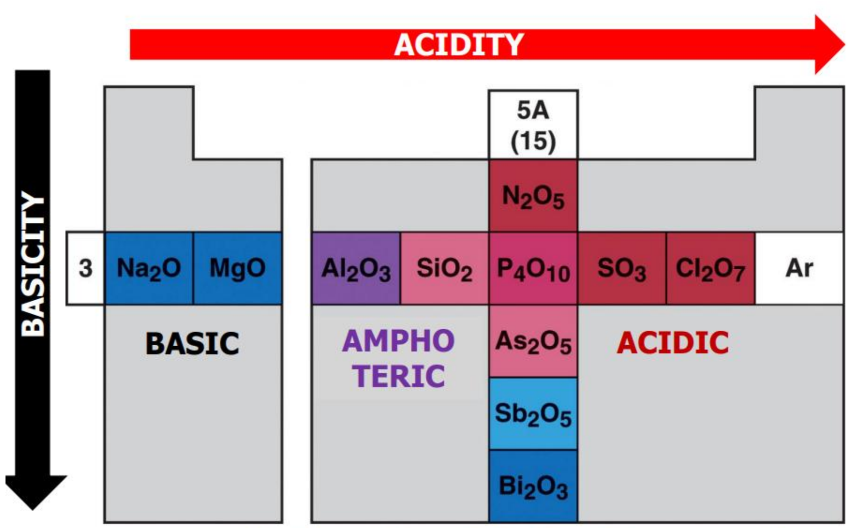
- Energy released when a neutral atom gains an electron in the gas state.
  - Exothermic
  - Generally increases across a period.
  - Becomes more negative from left to right.
  - Highest value of EA in a period = halogen
  - Lowest value of EA in a period = alkali earth metal or noble gas
  - Exceptions
    - Between groups 1A and 2A
      - Added electron must go into the p orbital rather than s in group 2 metals. So electron is further from the nucleus and feels a repulsion from the s electrons
    - Between groups 4A and 5A
      - Added electron must go int an occupied orbital in group 5, creating repulsion

Metallic character

- Metals
  - Malleable & ductile
  - Shiny
  - Conduct heat and electricity.
  - Most oxides are basic and ionic
  - Form cations in solutions
  - Lost electrons in reactions
    - Oxidized
- Non-metals
  - Brittle in solid state
  - Typically dull
  - Thermal and electrical insulators
  - Most oxides are acidic and molecular
  - Form anions and polyatomic anions
  - Gain electrons in reactions
    - Reduced

- Metalloids
    - Some characteristics of metals and some of non-metals
    - Silicon in shiny, brittle and is a poor conductor
- Metallic character trends
    - Decreases from left to right
    - Increases within a group



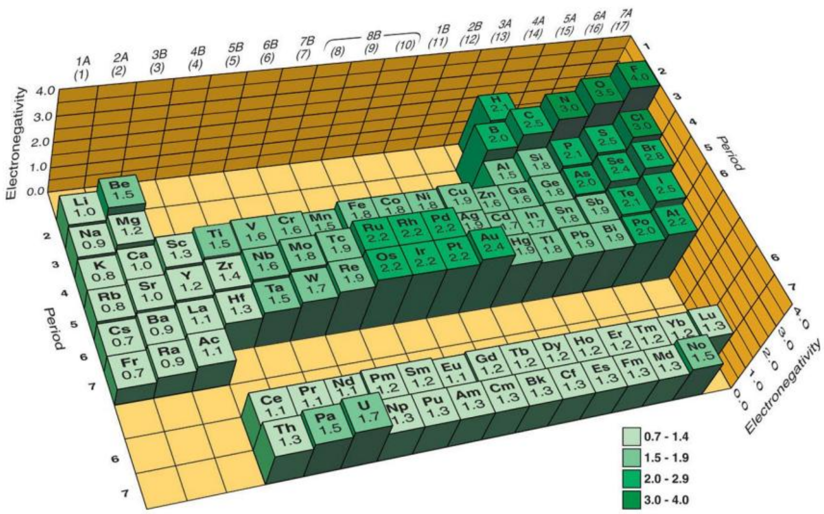


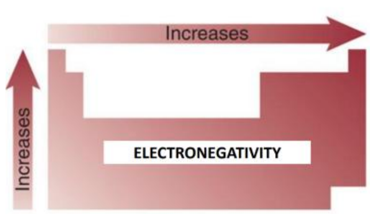
The trend in the acid-base behavior of element oxides

- Amphoteric means that it can react with both acids and bases.

Electronegativity

- Electronegativity (EN) is the property of **an atom in a molecule** to attract electrons of another atom it binds to
    - Mulliken definition:
        - $EN \propto \frac{1}{2}(IE + EA)$
        - IE = ionization energy
        - EA = electron affinity
    - Pauling definition
        - $(X_x - X_Y)^2 = c\left(BE_{XY} - (BE_{XX} \times BE_{YY})^{\frac{1}{2}}\right)$
        - BE_{mn} is the bond energy when m and n bond.
    - Two definitions give similar results.

- 

- 

Hydrogen

- 1 proton and 1 electron
- Most abundant element in the universe
- Diatomic gas H_2
- H_2 is odourless and colourless.
- Low melting and boiling points
- Abundant in combination with oxygen (H_2O)
- Tritium and deuterium are the 2 important isotopes

- Can be produced by hydrocarbons reforming
    - Or when metals react with hydracids
- Outer shell configuration of ns^1
- Mostly a +1 oxidation state
- Comparison to alkali metals (1A)
    - Shares electron with nonmetals rather than transferring an electron to them
    - Due to small size it has a higher ionization energy than alkali metals
- Comparison to halogens (7A)
    - Exists in diatomic molecule and needs 1 electron to fill valence shell.
    - Unlike halogens, it has much lower electron affinity than any halogen as H lacks the three valence electron pairs that halogens have, hence halide ions are common and stable, but hydride ions (H^-) are rare and reactive.

Alkali Metals (1A)

- Largest in each period
- Electron config of ns^1
- Usually soft for metals
    - Easily cut with a knife
- Low melting point
- Low density

Alkaline Earth Metals (2A)

- Form basic solutions
- Melt at extremely high temperatures
- Higher ionization energies than alkali metals
    - Higher effective nuclear charge and smaller size
- Strong reducing agents

Boron Family (3A)

- Z_{EFF} increases for the larger elements due to poor shielding constant by d and f electrons
- Larger elements have smaller atomic raii and larger ionization energies and electronegativities than expected
- Larger elements exhibit multiple oxidation states.
    - Lose either np electron or both ns and np
- Lower oxidation state becomes increasingly prominent down the group
    - ns^2 electrons form an inert pair
- Oxides of the element in the lower oxidation state are more basic than oxides in the higher oxidation state

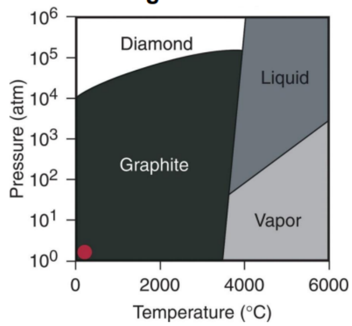
Carbon Family (4A)

- Carbon forms predominantly covalent bonds
    - Larger members can form ionic bonds

- Multiple oxidation states
    - Lower oxidation states become more prominent down the group
- Pb and Sn show more metallic character in their lower oxidation states

Allotropes

- Different crystalline or molecular forms of the same element
- One allotrope of a particular element is usually more stable than another at a particular temperature and pressure
    - Carbon has several, including graphite, diamond, fullerenes
    - Tin has two: white β-tin and grey α-tin.
    - **Phase diagram of carbon.**



The Nitrogen Family (5A)

- N gains 3 electrons to form the anion N^{3-} but only in compounds with active metals
- The heavier elements in the group are metallic and lose electrons to form cations
- Oxides change from acidic to amphoteric to basic as you move down the group
    - Amphoteric means able to react with both acids and bases
- Form gaseous hydrides with formula EH_3
    - All except for nitrogen hydride are extremely reactive and toxic

The Oxygen Family (6A)

- Two allotropes
    - O_2 which is essential to life
    - O_3 which is poisonous
- Sulphur has more than 10 different forms, due to its ability to catenate
    - S–S bonds lengths and bond angles may vary greatly
- Selenium has several allotropes, some consisting of crown shaped Se_8 molecules

The Halogens (7A)

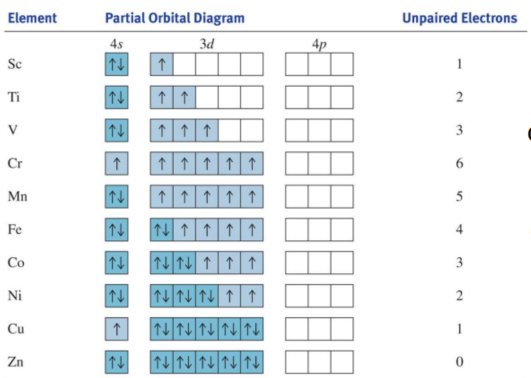
- Very reactive
    - Only 1 electron for a full outer shell
- Wide range of electronegativities, but all are electronegative enough to behave as non-metals
- Will either:

    - Gain one electron to form a halide ion
    - Share an electron pair with a non-metal atom
- Reactivity decreases down the group, reflecting decrease in electronegativity

The Noble Gases (8A)

- Full valence shell
- Smallest elements in the periods, with highest ionization energies
- Atomic size increases down group and IE decreases
- Noble gases have low melting and boiling points

Transition Metals

- Similarities within a given period and within a group
    - Last electrons added are inner electrons (d & f).
    - Inner d and f electrons cannot participate as easily in bonding as can the valence s and p electrons
- Period 4 Orbital Occupancy
    - For the first-row transition metals 3d orbitals begin to fill after the 4s orbital is complete.
    - 

Chromium configuration occurs because the energies of the 3d and 4s orbital are very similar for the first row transition elements.

Cu: [Ar]$4s^2 3d^9$ (expected) but the actual is [Ar]$4s^1 3d^{10}$.

- General decrease in size going left to right for each of the series
    - However4d and 5d metals are similar in size
        - Result of lanthanide contraction
        - IN the lanthanide series, electrons are filling the 4f orbitals. The 4f orbitals are buried in the interior of these atoms and have low shielding effect on the nucleus, so that the increasing nuclear charge causes the radii of the lanthanide elements to decrease significantly going left to right.
- Can form a variety of ions by losing one or more electrons
    - For the first five metals the max possible oxidation state corresponds to the loss of all the 4s and 3d electrons
    - Towards the right end of the period, the max oxidation state is not observed, in fact 2+ ions are the most common because 3d orbitals become lower in energy as the nuclear charge increases, and the electrons become increasingly difficult to remove
- Electron configurations that result in unpaired electrons mean that the atom or ion will have a net magnetic field

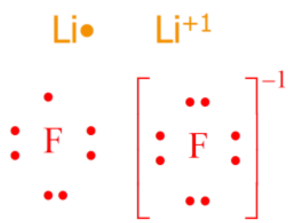
    - Called paramagnetism
- Electron configurations that result in all paired electrons mean that the atom or ion will have no magnetic field
    - Called diamagnetism
- Both Zn atoms and Zn^{2+} ions are diamagnetic, showing that the two 4s electrons are lost before the 3d

Practice Lesson 3

- Redox reactions
  - Reducing agents contains the element that gets reduced (loses electrons)
  - Oxidizing agent contains the element that gets oxidized (gains electrons)
- Redox also happens when oxygen or hydrogen is transferred
  - Oxidizing agents lose oxygen
  - Reducing agents lose hydrogen

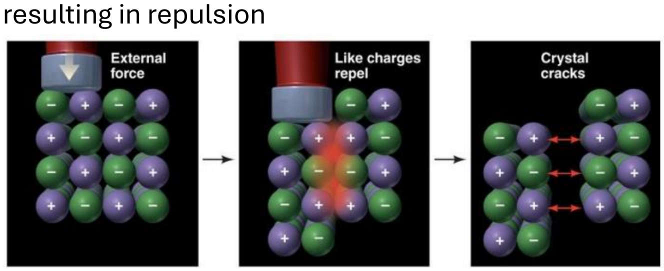
Lecture 5

- Lewis Theory: explains binding using Lewis structures (electron dot structures), by showing valence electrons.
  - 

  - 

  - Ions are shown with charge and structure in square brackets
- Processes are spontaneous if they result with lower potential energy
  - Potential energy is directly proportional to the product of charges
  - Potential energy between charged particles is inversely proportional to their distances

Ionic Bonds

- Electrostatic
  - Electron is transferred from electro-positive atom to electro-negative, creating a neutral structure.
- Lattice structure
- Bond strength depends on forces of attraction between neighbouring ions.
- Attraction between + and – ions is maximized
- Lattice energy is directly proportional to magnitude of charges and inversely to distances between ions.
  - Energy released when the solid crystals form from separate ions in gas state.
  - Always exothermic
- Ionic compounds are hard and brittle solids.
  - Brittle because a small change in the structure means that charges are misaligned, resulting in repulsion
  - 

- Conductive in liquid state
  - Solid does not

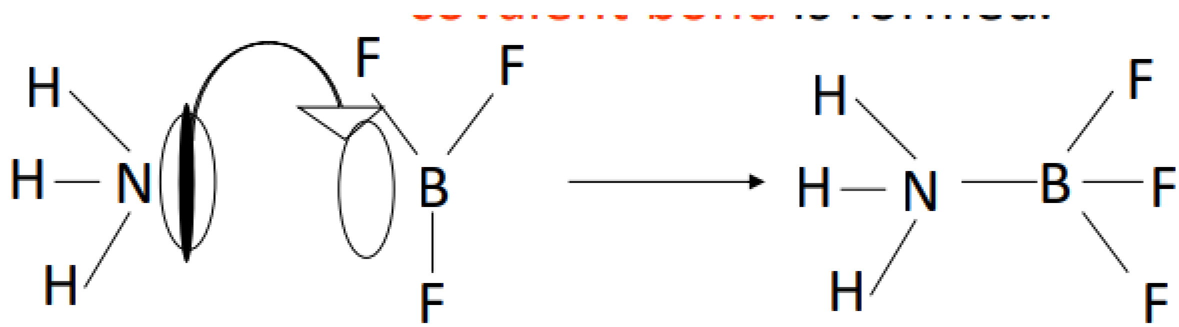
- Many are soluble in water
    - Solution is very conductive
- Melting points are generally >300 degrees C
    - Stronger the attraction, the higher the melting point

Covalent Bonding

- Atoms sharing electrons to achieve 8 valence electrons
    - Bonding pairs are electrons that are shared
    - Lone pairs are electrons that are not shared and are owned by a particular atom
- One atom can have a single, double or triple bond
    - Single = 2 electrons shared
    - Double = 4
    - Triple = 6
- $Formal\ Charge = Valence\ e^{-}\ count - Lone\ Pair\ Count - \frac{Bonding\ Electron\ Count}{2}$
    - Sum in a molecule is 0
    - Sum for an ion is equal to the charge
- When there are more structures for 1 molecule, differing only in position of electrons, these are called resonance structures
    - Eg But-1-ene, but-2-ene and but-3-ene
- An actual molecule is a combination of the resonance forms
    - Resonance hybrid
    - Electrons are delocalized
        - They are shared between multiple atoms
    - Low energy structures contribute more than high energy ones

Exceptions to the Octet Rule

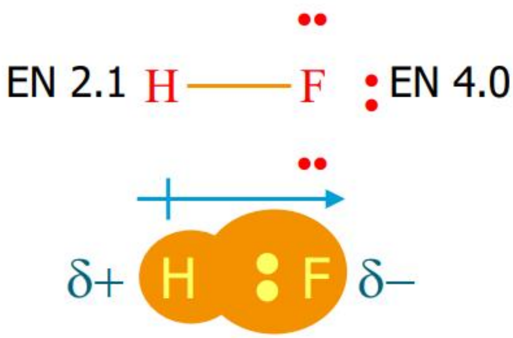
- Expanded Octets
    - Elements with empty d orbitals can have more than 8 electrons
    - Odd number electron species
        - Eg. NO, NO_2
        - 1 unpaired electron
        - Very reactive
        - Free-radical
- Incomplete octets
    - B, Al
- A compound containing an atom with more atoms attached to it than it is permitted by the octet law is called hypervalent compound
- Elements from groups 2 and 3 can have less valence electrons
    - Be: 4
    - Bo, Al: 6
    - H: 2
- When a couple of electrons from ONE atoms get shared with another atom, it is called a coordinate covalent bond

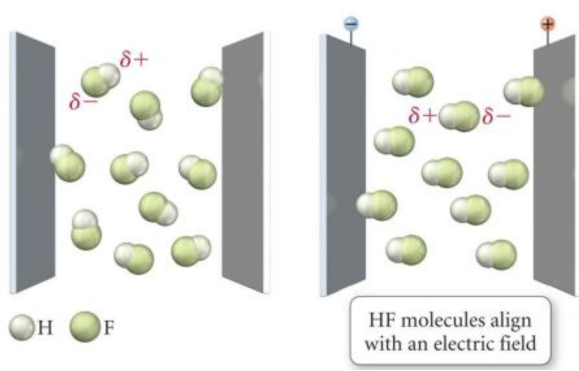
- 

- Radicals are compounds where not all valence shells are saturated
  - These substances are paramagnetic
  - Highly reactive and unstable
    - E.g. nitrogen monoxide

Bond Polarity

- Covalent bonds between unlike atoms result in unequal sharing of electrons.
  - One atom pulls electrons in the bond closer to its side
  - This means that charge is distributed unevenly, creating a difference in electron density
  - This creates bond polarity
  - The end with the greater electron density gets a partial negative charge





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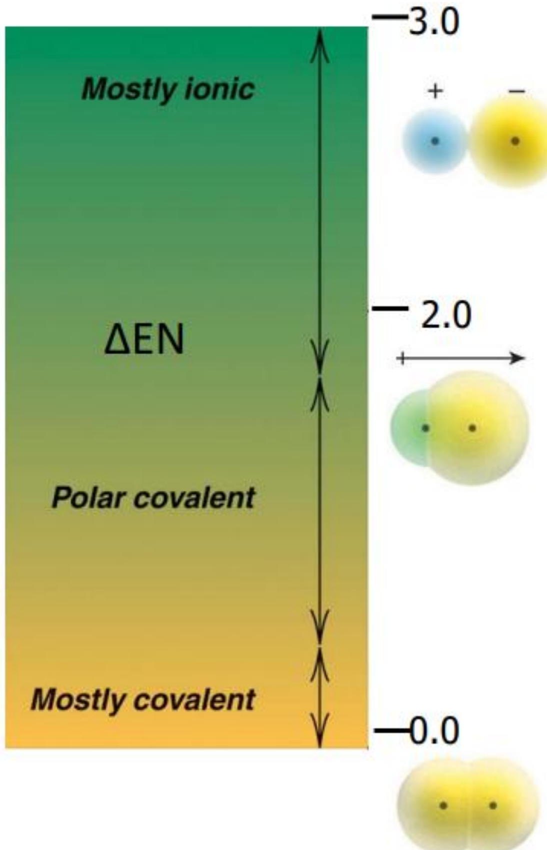
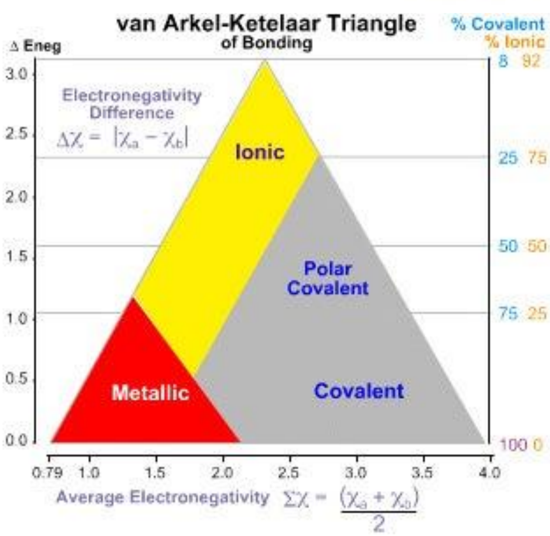
- The greater the difference in electronegativity, the greater the polarity
  - The element with the greatest electronegativity gets the partial negative charge
  - $\Delta EN = 0$
    - Pure covalent bond
  - $0.1 \leq \Delta EN \leq 0.4$

    - Nonpolar covalent
  - $0.5 \leq \Delta EN \leq 1.9$
    - Polar covalent bond
  - $\Delta EN \geq 2.0$
    - Ionic bond
  - 

  - 

  -
- Dipole moment (m) is a measure of bond polarity measured in Debyes (D)
  - $m = q \times r$
  - q is the magnitude of partial charges

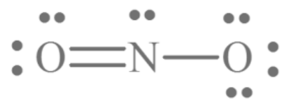
- r is the distance
- The percent ionic character is the percentage of a bond's measured dipole moment to what it would be if full ions

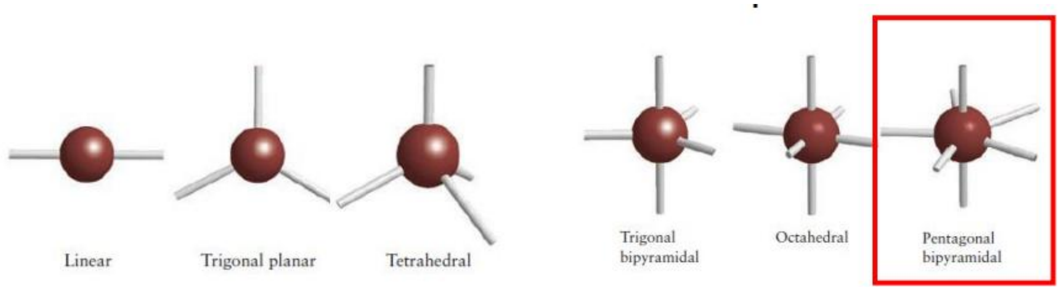
- More shared electrons mean more energy in the bond
- More shared electrons also mean lower bond length
  - The stronger the bond, the shorter its length

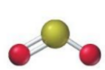
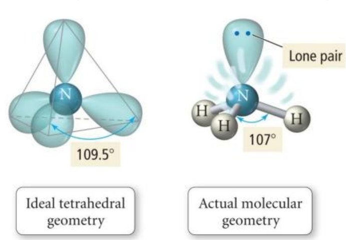
Metallic Bonds

- Low ionization energy
  - Easy to lose electrons
  - Electrons are shared between all atoms in the metal
  - Metal cations are formed in a sea of free (delocalized) electrons
    - Ions are attracted to this sea, creating the bonds
- Strength of bonds increases as group number increases
- High melting point (usually)
- Attractions of metal cations for free electrons is strong and hard to overcome
- Melting point generally increases across a period since the charge of the cation increases
- Melting point generally decrease down a column
  - Cation gets larger, resulting in greater distance between nucleus and electrons
- Conductive
  - Free electrons are mobile
- Increase in temperature decreases conductivity since vibrating ions make it harder for electrons to move through
- Malleable and ductile since the free electrons are mobile
  - Cation islands can move around

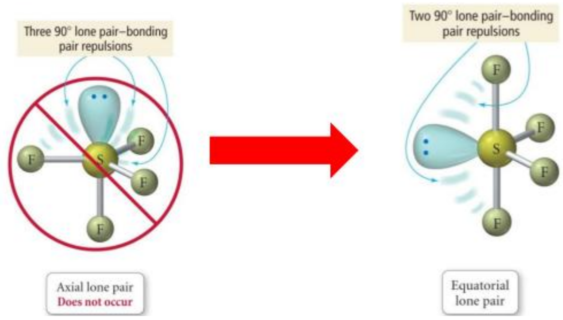
Lecture 6

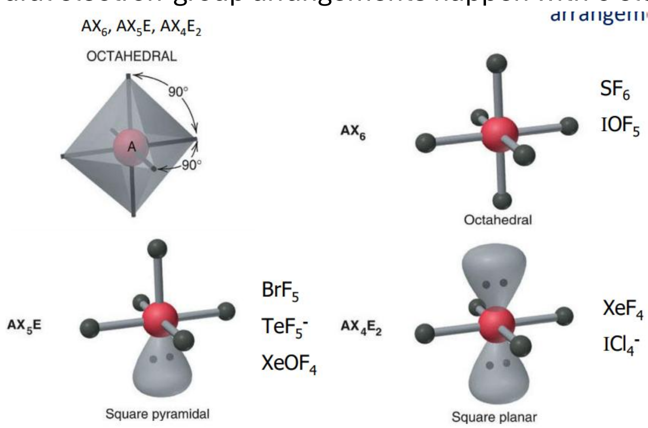
- Each lone pair and bond make an electron group
    - 

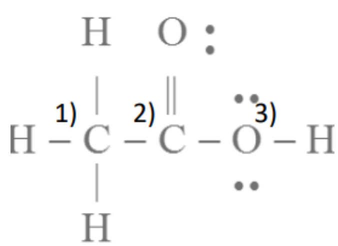
      There are 3 electron groups on N:
      1 lone pair
      1 single bond
      1 double bond
- There are several arrangements/shapes of electron groups around a central atom
    - Maximum of 6 groups
    - Exceptions for very large atoms
    - 

- Valence Shell Electron Pair Repulsion (VSEPR)
    - Electrons repel each other, causing distance between bonds and lone pairs to maximize
- VSEPR formula
    - AX_nE_m
    - A is the central atom
    - X is the attached atom
    - E is the lone pair
    - Molecules with same VSEPR formula have same electron arrangement and same shape
- Relative sizes of repulsive forces are:
    - Lone-lone > Lone-bonding>Bonding-Bonding
- When there is one lone pair among 3 electron groups, the molecule is trigonal planar-bent shape
    - Bond angle $< 120°$
    - 
    - Lone pairs distort the shape, reducing the bond angles
    - 

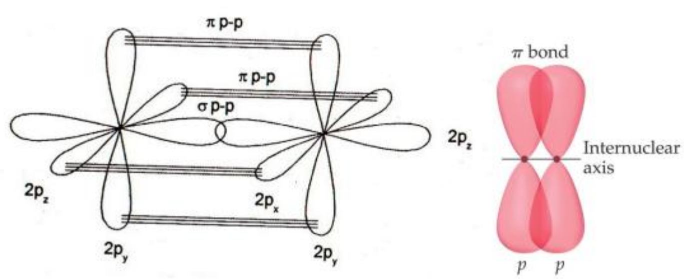
- Trigonal bipyramid occurs with 4 bonds and a lone pair

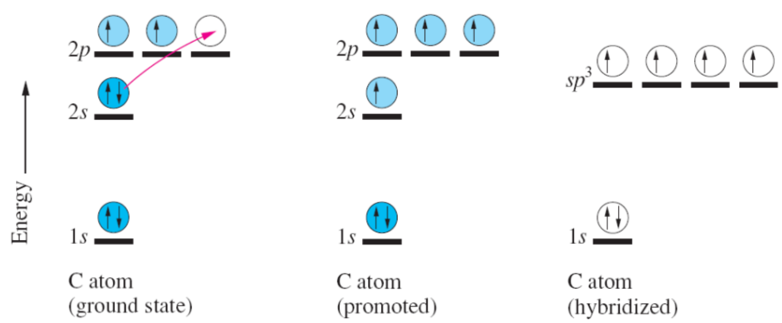
- Example is SF_4
- Lone pair is equatorial since it minimizes energy
- 

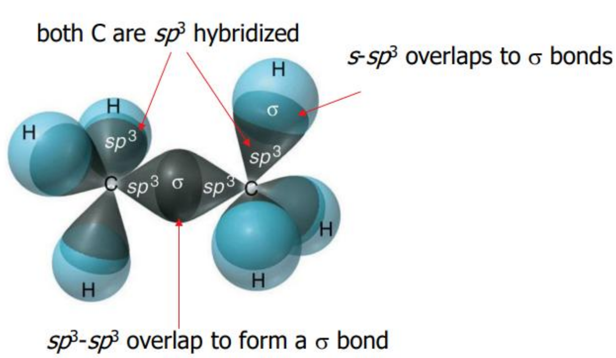
- Octahedral electron-group arrangements happen with 6 electron groups
  - 

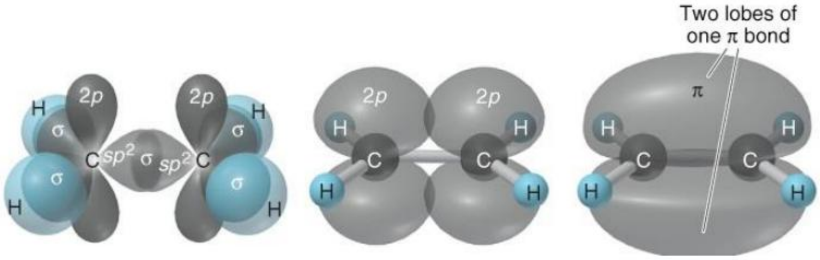
- Molecules with larger structures can have multiple central atoms
  - In this case, we describe the shapes in sequence
- For example, in acetic acid:
  - 

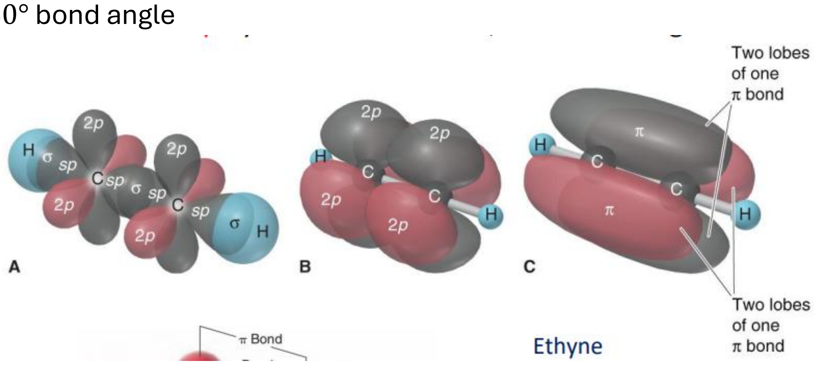
    1. Tetrahedral
    2. Trigonal planar
    3. Tetrahedral bent
- A polar molecule either has polar bonds or it has an asymmetrical shape
  - Polarity affects intermolecular forces of attraction
    - Boiling points
    - Solubility
- A polyatomic molecule can be nonpolar even if the bonds are polar
  - CO_2 has 2 polar bonds, but the linear shape makes the molecule nonpolar
  - H_2O is polar because of the trigonal bent shape and polar bonds
- Since water is polar, other polar molecules dissolve well in it since they are attracted to it
  - Oil is non-polar

- Some molecules have polar and nonpolar parts
- Valence bond theory explains the Lewis model in terms of quantum mechanics
    - Maximum overlap between atomic orbitals generates a covalent bond
    - Overlapped orbitals host max 2 electrons
    - Double and triple bonds are made of a single σ bond
        - Bond along an axis
        - s-s, s-p, p-p overlappings
        - Cylindrical symmetry
    - Second and third bonds are π bonds
        - In N_2, only 1 bond can be sigma, the rest need to be pi bonds
        - 

- Carbon has hybrid bonds
    - 2s and 2p orbitals merge to the same energy level, forming the sp orbital
        - The energy is higher than 2s and lower than 2p
    - 

    - Tetrahedron with angle of 109.5°
    - $2s + 2p = 4 \times sp^3$
    - In sp^3 orbitals, one lobe is longer than the other, allowing for greater overlaps and therefore stronger bonds
- Ethane has hybrid sp^3 orbital group (single bond)
    - 

- Ethene has a hybrid sp^2 orbital group (double bond)
    - $120°$ bond angle
    - 

- Ethyne has a hybrid sp orbital group (triple bond)
    - $180°$ bond angle
    - 

- Multiple carbon-carbon bonds are weaker than sum of single bonds because of the pi bonds creating less overlap
- In molecular orbital theory, electrons occupy molecular orbitals, spread throughout the entire molecule
    - Related to wavefunction
    - Number of molecular orbitals is equal to the number of atomic orbitals
    - The new wavefunction is the sum of all atomic orbital wavefunctions
- The molecular orbital has lower energy than all the original atomic orbitals when wavefunctions interact constructively (bonding) and higher if constructive interference occurs (antibonding)
- $Bond\ Order\ (B.O) = \frac{1}{2}(Electrons\ in\ bonding\ molecular\ orbitals) - Electrons\ in\ antibonding\ molecular\ orbitals$
    - BO>0: Molecule is more stable compared to single atoms
    - BO=0: Molecule is not formed
    - The higher BO, the stronger the bond
- For two orbitals to combine:
    - Their energies must be similar
    - Overlapping between orbitals should be high
    - Same symmetry with respect to AB axis

Band Theory of Metals and Semiconductors

- Other than electron-sea model of metals, there is the band theory
    - Atomic orbitals for every atom combines to look like very large molecular orbitals

    - Highest energy state when no excitation occurred is called the Fermi Level
    - Each band is named from the orbital that created it
- A metal is conductive if the valence band is not full
    - That is the conduction band
- In group 2, the valence band is full, but the 2s and 2p bands overlap, so it is easy for electrons to move between them, and therefore conduct electricity
- $k_B T$ is a measure of the average thermal energy of particles in a sample
    - $k_B = 1.38065 \times 10^{-23} JK^{-1}$ (Boltzmann constant)
    - T is temperature in Kelvin
    - If the band gap is much larger than $k_B T$: insulator
    - If the band gap is smaller than (or close to) $k_B T$: conductor
    - If the band gap is about 10 times larger than $k_B T$: semiconductor
- Band gaps can be measured by absorption spectrum
- Two types of semiconductors
    - Intrinsic semiconductors
        - A small fraction of electrons can be excited into the conduction band, and the valence band can conduct since gaps are left from these electrons
    - Extrinsic semiconductors
        - Need impurities (process is called doping) to conduct
        - These provide extra electrons or extra holes
            - With extra electrons it is called n-type (negative)
            - With extra holes it is called p-type (positive)

Lecture 8

- A gas is a collection of particles moving with Brownian (random) motion in a primarily empty space
  - High energy
  - Low density
- Pressure is force per area
  - $1atm = 14.7psi = 760mmHg = 101\ 325Pa$
  - $1Pa = 1kgm^{-1}s^2$
  - $1bar = 10^5Pa$
- Gas temperature is a measure of average kinetic energy
- Ideal gas is a simplified real gas
  - $pV = nRT$
  - $R = 8.20574 \times 10^{-2}L\ atmK^{-1}mol^{-1} = 8.31446JK^{-1}mol^{-1}$
- Boyle's Law
  - $V \propto \frac{1}{p}$
- Charles' Law
  - $V \propto T$
- Avogadro's Law
  - $V \propto n$
- Gay-Lussac's Law
  - $p \propto T$
- Standard volumes of gases are often compared at standard temperature and pressure ($0°C$ and 1atm)
- $\frac{P_iV_i}{n_iT_i} = \frac{P_fV_f}{n_fT_f}$
- Can be used to determine molar mass and density
  - $n = m/M_M$
  - $\therefore M_M = \frac{mRT}{PV}$
  - $\rho = \frac{m}{V} = \frac{M_MP}{RT}$

Reacting Gases

- Ideal gas law can be used to calculate amount of gas produced or used in a reaction
- Dalton's Law of Partial Pressures
  - $P = \sum_{i=1}^{n} P_i$
  - Sum of partial pressures is equal to the total pressure
- Amagat's law of partial volumes
  - $V = \sum_{i=1}^{n} V_i$
  - Sum of partial volumes is equal to the total volume
- $mole\ fraction = x_i = \frac{n_i}{n_{tot}}$
- $\%weight_i = \frac{weight_i}{weitht_{tot}} \times 100\%$

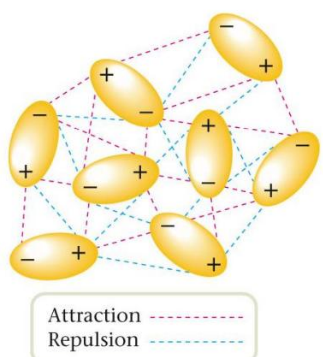
- $\%volume_i = \frac{volume_i}{volume_{tot}} \times 100\%$
- Compression factor Z indicates ratio of actual molar volume of a gas to the ideal one
    - $Z = \frac{V_m}{V_m^{ideal}}$
- Van der Waals equation of real gases:
    - $\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$
    - a represents the role of attractions
    - b represents the role of repulsions
    - $\therefore Z = \frac{1}{1-\frac{nb}{V}} - \frac{an}{RTV}$
    - a and b depend on the composition of the gas
- Critical pressure (P_c) represents the limit for a substance to still become vapor in the presence of its liquid
    - Pressure required to turn a gas into a liquid at its critical temperature
- Critical temperature (T_c) is the temperature above which a substance cannot exist as a liquid at any temperature.

Lecture 8 Bis – Liquids Part 1

Ion-dipole Interactions

- Ion-dipole are forces between polar molecules and ionic molecules.
  - For example, when sodium ions are dissolved in water.
- The dipole aligns to minimize energy
  - $E_p \propto -\frac{|q|\mu}{r^2}$
  - $q = Total\ charge$
  - $\mu = \delta r = Dipole\ moment$
  - $\delta = Partial\ charges$
  - $r = distance$
- The dipole dictates orientation since ions are not directional.
- Hydration is the process of dissolving ionic compounds with water
  - Ion-dipole interaction

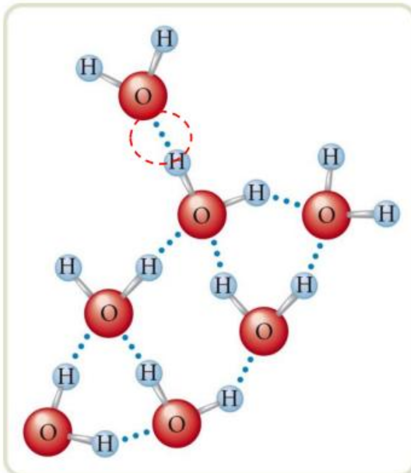
Dipole-Dipole Interactions

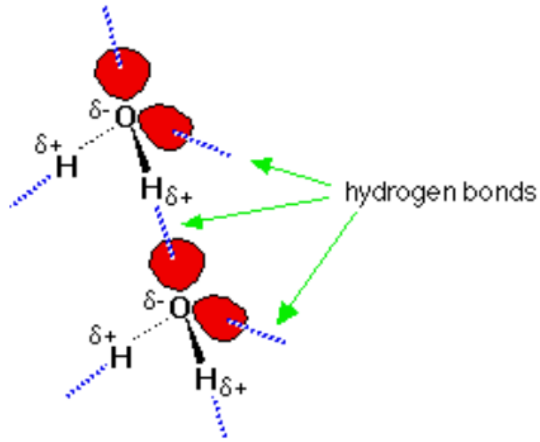
- Dipole-dipole interactions are weak forces that arise from permanent or induced dipoles
- Oppositely charged ends attract and like charged repel.
- Particles align to maximize attractions and minimize repulsions
  - 

- In gases particles spin, and the spin favors positions that maximize attractions, therefore there is a weak attraction
  - $E_p \propto -\frac{\mu_1^2 \mu_2^2}{r^6}$

Hydrogen Bonds

- Hydrogen bonds are strong dipole-dipole forces
- Results from hydrogen covalently bonding with a very electronegative element, which is attracted by another very electronegative element with lone pairs, such as O, N, F.
- Because of the partial positive charge of hydrogen atoms, in water, they can get very close to other water molecules' oxygen atoms with lone pairs, creating hydrogen bonds.

    - 



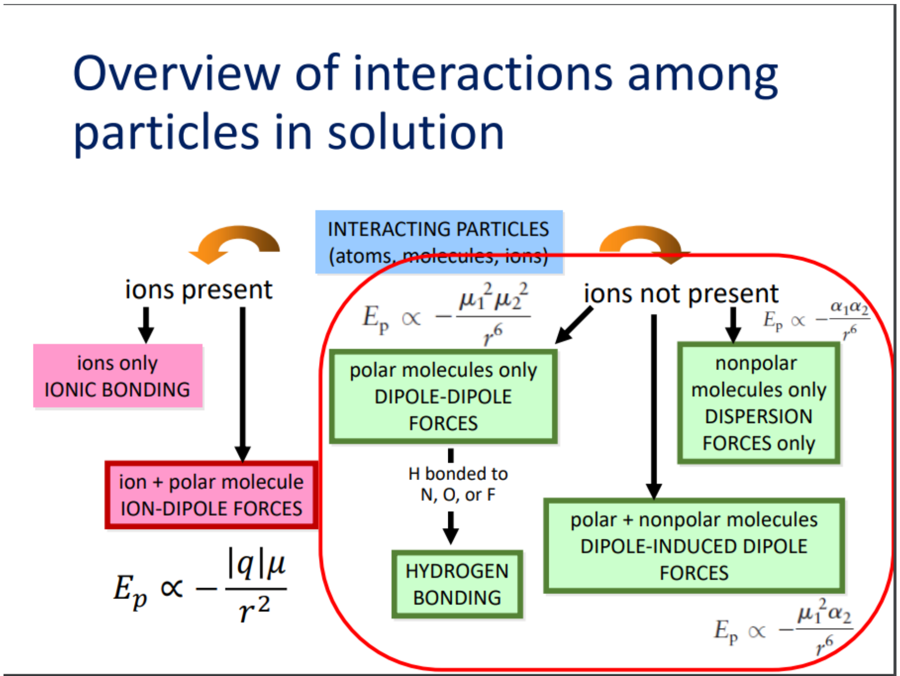
- Hydrogen bonds cause higher boiling points
- Larger atoms cause hydrogen bonds to be weaker

London Dispersion Forces

- When particles are non-polar, electron clouds can be in such position to induce polarity for a moment, causing instantaneous dipoles
    - This induces dipoles in neighboring atoms
- Strength of London forces depends on the polarizability α of the atoms/molecules
    - Polarizability is how easily they can be polarized and have electrons displaced
    - More electrons in a molecule means higher polarizability
        - Because inner electrons shield positive charge from nucleus
    - Polarizability increases down group and across left to right in a period
- $E_p \propto -\frac{\alpha_1\alpha_2}{r^6}$

Dipole-Induced-Dipole Interactions

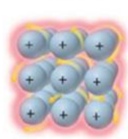
- Non-polar substance dissolved in polar substance
- $E_p \propto -\frac{\mu_1^2\alpha_2}{r^6}$
- Polar molecules induce polarity on non-polar molecules
    - Eg. Water to oxygen molecules



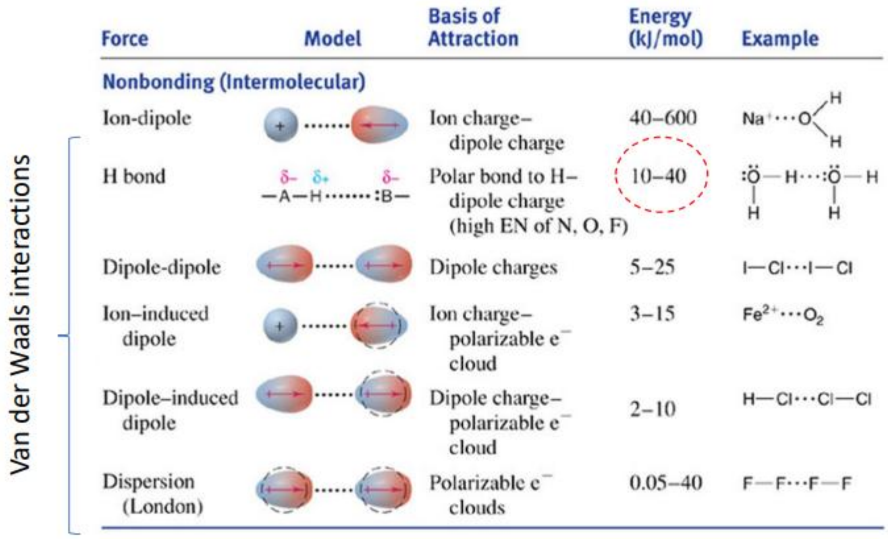
Van Der Waals Interactions

- Forces dependent on the distance to the sixth power (circled in red above) are called the Van Der Waals interactions.
- $E_p \propto -\frac{C}{r^6}$

Overview of bonding forces

Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Bonding				
Ionic		Cation–anion	400–4000	NaCl
Covalent		Nuclei–shared e^- pair	150–1100	H—H
Metallic		Cations–delocalized electrons	75–1000	Fe

Overview of non-bonding forces

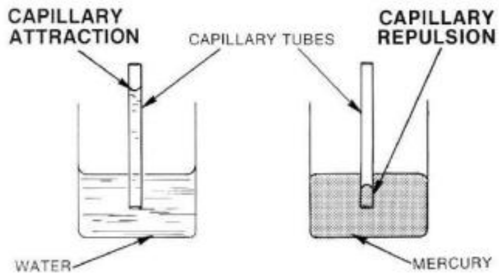


Van der Waals interactions

Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Nonbonding (Intermolecular)				
Ion-dipole		Ion charge–dipole charge	40–600	$Na^+ \cdots OH_2$
H bond	$\delta-$ $\delta+$ $\delta-$ —A—H·······:B—	Polar bond to H–dipole charge (high EN of N, O, F)	10–40	:Ö—H···:Ö—H (each O bonded to H)
Dipole-dipole		Dipole charges	5–25	I—Cl···I—Cl
Ion–induced dipole		Ion charge–polarizable e^- cloud	3–15	$Fe^{2+} \cdots O_2$
Dipole–induced dipole		Dipole charge–polarizable e^- cloud	2–10	H—Cl···Cl—Cl
Dispersion (London)		Polarizable e^- clouds	0.05–40	F—F···F—F

The Liquid State

- Viscosity is the resistance to change shape
    - Unit is the Poise
        - $P = Pa \cdot s^{-1} = N \cdot s\, m^{-2}$
    - As temperature increases, viscosity increases since the average intermolecular forces decrease
- Surface tension is the energy required to increase surface area of a liquid due to intermolecular forces
    - Intermolecular forces tend to pull the liquid inward, meaning that a smooth film is created
    - Liquids with strong intermolecular forces have greater surface tensions
    - Surface tension decreases as temperature increases since the forces are overcome by the higher kinetic energy
- Capillary action is the rise of liquids in narrow tubes
    - Forces between liquid and the surface of the container
    - Forces of adhesion bind the liquid to a surface
    - Forces of cohesion hold the liquid to itself
    - The relation between the two forces causes the shape of the meniscus
        - Meniscus is a curve on the liquid’s surface in a small tube
    - Capillary action occurs when adhesive forces are stronger than cohesive forces
    - Capillary repulsion is the opposite, which causes the liquid to curve into itself

- 

- The vapor pressure of a liquid is the pressure of the vapor when in equilibrium with the liquid
    - Depends on temperature, but is independent of the amount of liquid
    - High vapor pressure = weak intermolecular forces in the liquid
    - Liquids with high vapor pressure at room temperature are said to be volatile
    - Clausius–Clapeyron equation gives a relation between two temperatures and two vapor pressures
        - $\ln\left(\frac{P_1}{P_2}\right) = -\frac{\Delta H^\circ vap}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$
    - When vapor pressure is equal to atmospheric pressure, boiling starts
        - Vaporization occurs in all the liquid rather than just on the surface
        - Endothermic
    - Increase in intramolecular forces causes boiling point to be higher
- Most solids melt at higher temperatures at higher pressures
- Water has lowest density at $4°C$ due to larger hydrogen bonds forming at lower temperatures and higher kinetic energy at higher temperatures
    - Bottom of large water bodies is always 4 degrees in temperature

Lecture 8 Tris

- A solution is a homogeneous mixture of atoms, molecules or ions distributed in the whole space
  - The component with higher moles or mass is called the solvent, while the others are called solutes
  - Three types of solutions:
    - Gas mixtures
    - Liquid solutions
    - Solid solutions

Liquid Solutions

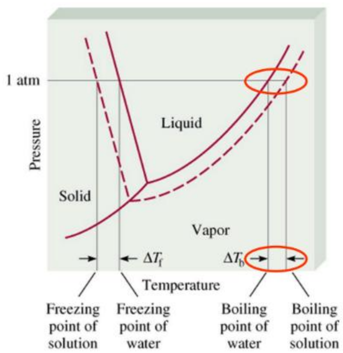
- How ionic solutions are made:
  - Solvent surrounds atoms on ionic solid's surface
  - Enthalpy changes with process
    - Solute separates from other ions
    - Solvent separates from other solute molecules
    - Solute binds with solvent
    - Can be endothermic or exothermic
- If the solvent is water, the ions are hydrated
- When the undissolved solute is in equilibrium with the dissolved solute, the solution is saturated
- Molar solubility is the molar concentration in a saturated solution
- A supersaturated solution has more solute than should normally be possible
  - Unstable
  - Can form crystals by adding a seed crystal or by scratching the side of the flask
- Generally, increasing temperature increases solubility, with exceptions
  - There are exceptions such as lithium carbonate and cesium sulfate
    - Sodium sulfate's solubility increases up to 32 degrees, and then decreases beyond that temperature
- Dissolution is revertible by evaporating the solvent
- Polar substances tend to dissolve well in polar solvents and vice-versa
  - Solutes with mostly hydrogen bonds tend to dissolve well in solutes with hydrogen bonds
- Soap has hydrophilic head and hydrophobic (non-polar) tail, making it good at cleaning hydrophobic substances, such as grease

Gases in solutions

- Solubility of gases is represented by S_g
- In general, solubility of gases in water increases with increasing mass
  - Larger molecules have stronger dispersion forces
- Solubility of gases is proportional to pressure, while for liquids it is not
- Henry's law links outside partial pressure of a gas to the solubility

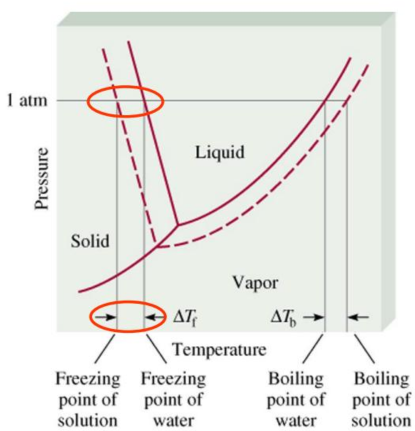
- $S_g = kP_g$
  - k is Henry's law constant for the gas in the solute
  - P_g is the partial pressure of the gas above the liquid
- An increase in temperature reduces solubility of gases
  - It drives gases out of the solution
- Ways of expressing concentration:
  - Mass percent
    - g of solute in $100g$ of solution
  - Volume percent
    - ml of solute in $100ml$ of solution
  - Molarity (M)
    - Solute moles in $1l$ solution
  - Molality (m)
    - Solute moles in $1000g$ solvent
  - Mole fraction (χ_s)
    - $\chi_s = \frac{n}{n+N}$
    - $n =$ Solute moles
    - $N =$ Solvent moles
- Some properties of solutions depend on quantity of solution and solvent and are independent of the type of solute. The most important ones are:
  - Vapor pressure lowering
  - Boiling point elevation
  - Freezing point depression
  - Osmotic pressure
- Ideal solution (Raoult's Law):
  - Solution is diluted
  - Vapor pressure of the solute is negligible compared to that of the solvent
  - The solute does not bind to the solute and does not dissociate
  - Solvent and solute do not react
- A solution that does not abide by these is a non-ideal solution
- Real solutions are approximately idea below 0.1M for non-electrolyte solutions and below 0.01M for electrolyte solutions
- Solutions that contain non-volatile solutes have a lower vapor pressure than the pure solvent
  - The solute interacts with the solvent, so less of the solvent can escape the liquid
- Vapor pressure of a solvent is proportional to its mole fraction in the solution
  - For ideal solutions
  - $\frac{p^\circ - P}{p^\circ} = \frac{n}{n+N}$
    - $P =$ Total vapor pressure
    - $p^\circ =$ Solvent vapor pressure
    - $n =$ Moles of solute
    - $N =$ Moles of solvent
- Ina binary solution, we can calculate the vapor pressure of the mixture

- $p_{tot} = \chi_a(l) * p_{vap,a\ pure} + \chi_b(l) * p_{vap,b\ pure}$
- $$\chi_a\,(vap) = \frac{p_a}{p} = \frac{p_a}{p_a + p_b} \quad partial\ pressure$$
- $$p_a = \chi_a\,(l) * p_{vap,a\ pure} \quad Raoult \qquad \chi_a\,(g) = \frac{\chi_a\,(l)\cdot p_{vap,a\ pure}}{\chi_a\,(l)\cdot p_{vap,a\ pure} + \chi_b\,(l)\cdot p_{vap,b\ pure}}$$

* Boiling point elevation means that the boiling point of a solution will be higher than that of the pure solvent
    - 

$\Delta T_b = T_b - T_b^0$
T_b^0 is the boiling point of the pure solvent
T_b is the **boiling** point of the solution
$T_b^0 < T_b$
$\Delta T_b < 0$

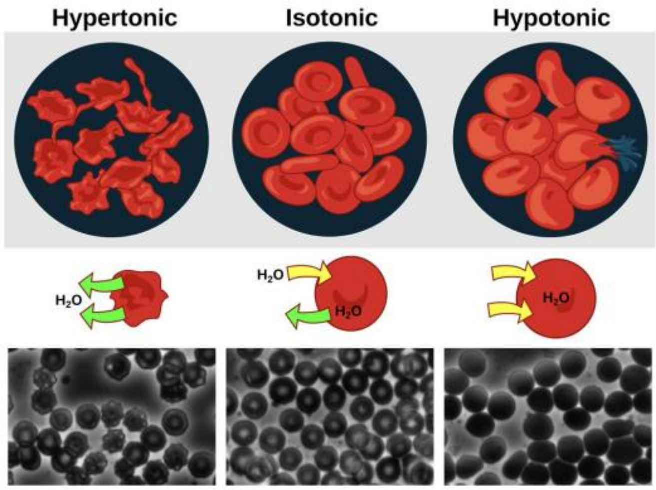
$\Delta T_b = K_b \cdot m$
m is the molality of the solution
K_b is the molal boiling-point elevation constant ($^0C/m$)

* Freezing point depression means that the freezing point of a solution is less than that of the solvent
    - 

$\Delta T_f = T_f^0 - T_f$
T_f^0 is the freezing point of the pure solvent
T_f is the freezing point of the solution
$T_f^0 > T_f$
$\Delta T_f > 0$

$\Delta T_f = K_f \cdot m$
m is the molality of the solution
K_f is the molal freezing-point depression constant ($^0C/m$)

* Osmosis is the diffusion of water through a semi-permeable membrane
    - $\pi =$ MRT
    - $\pi =$ Osmotic pressure
    - $M =$ Molarity of solution
    - $R =$ Ideal gas constant
    - $T =$ Temperature
    - Osmotic pressure is the pressure required to stop osmosis
* A hypertonic solution has a solute concentration higher than another
* Isotonic solution is equal

- Hypotonic solution is lower
    - 

Electrolytes

- Electrolytes are substances that when dissociate in a solution will separate into positive and negative molecules, therefore conducting electricity
- Strong electrolytes completely ionize when dissolved, therefore creating no neutral molecules
- Nonelectrolytes do not ionize at all
- Electrolytes will conduct more if they ionize and dissociate more
- The amount of the dissocation is measured by the dissociation degree α:
  Dissociation degree: $\alpha = N_{diss}/N$
  Dissociated moles: $N_{diss} = \alpha \cdot N$
  Undissociated moles: $N_{undiss} = N - \alpha \cdot N$
  z = number of ions (e.g. 2 for NaCl)
  Produced ions in total $z \cdot \alpha \cdot N$
- Some substances (salts, bases, acids) dissociate in solutions, producing ions

Lecture 9

- Internal energy U is the energy within a closed system
  - This can be exchanged with the surroundings by doing work (w) or by releasing/absorbing heat (q)
    - Work implies physical displacement
    - Heat transfer implies temperature change
- In a system with a piston compressing/expanding a gas in a container, work can be defined as:
  - $w = Fd = P_{ext}\Delta V$
    - P_{ext} is the pressure of the surrounding
    - ΔV is the difference in volume inside the container due to the piston moving
- Energy is the capacity for something to do work
- $1cal = 4.184J =$ Energy required to increase $1g$ of water by $1°C$
- $q = C\Delta T = mC_S\Delta T = nC_m\Delta T$
  - C_S is the specific heat capacity
  - C_m is the molar heat capacity
- Adiabatic walls do not allow heat transfer
- Diathermic walls allow heat transfer
- First law of thermodynamics:
  - $\Delta U = q + w$
- Internal energy is a state function
  - The result depends on the current state of the system, and is independent of how it got there
- Work and heat transfer are not state functions
- At constant volume, $\Delta U = q$ since no mechanical work can occur
- Enthalpy keeps track of energy changes at constant pressure
  - $H = U + PV$
  - $\Delta H = \Delta U + P\Delta V$
  - H, P, V are state functions
- With constant pressure,
  - $\Delta H = q$
- Enthalpy in vapor state is greater than at liquid state ceteris paribus
  - $\Delta H_{vap} > 0$ being enthalpy of vaporization
  - $\Delta H_{vap} = H_{m(v)} - H_{m(l)}$
- $\Delta H_{vap}°$ means standard enthalpy
  - 1 bar (100kPa) with a pure substance
  - Standard property X is denoted by $X°$
    - If relevant, at $25°C = 298.15K$
    - If solute in liquid, at concentration of $1mol \cdot L^{-1}$
- $\Delta H_{fus} = H_m(liquid) - H_m(solid) > 0$
  - Enthalpy of fusion
- $\Delta H_{sub} = H_m(vapor) - H_m(solid) = \Delta H_{fus} + \Delta H_{vap}$

- Enthalpy of sublimation

- On heating curves, the steeper the curve, the lower the heat capacity
- Superheating occurs when a liquid is heated to above boiling point, and after state change, the temperature decreases down to boiling point
  - Similarly to freezing
    - Supercooling
- Enthalpy changes during reactions are hard to predict.
  - State affects it
  - Number of bonds does not affect the ΔH linearly
- Standard enthalpy of combustion is $\Delta H_c°$

$$C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(g)\ \Delta H = -2044\text{ kJ}$$

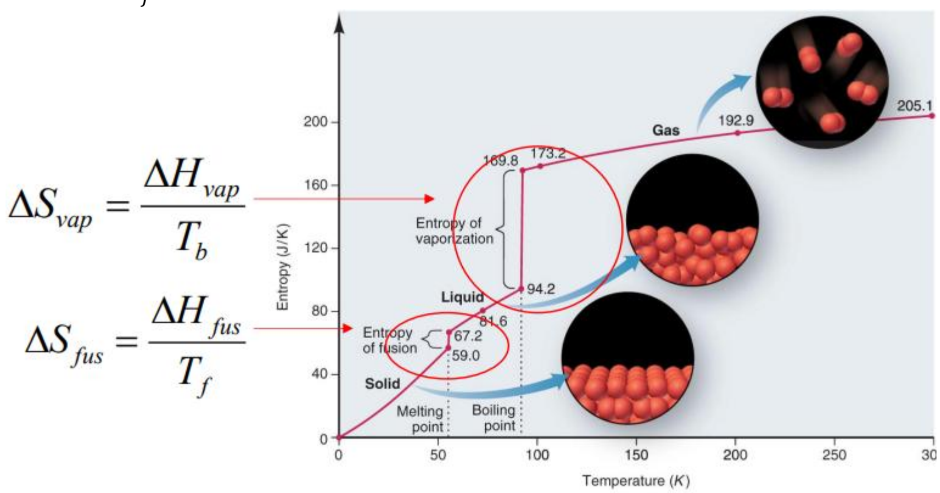
This entire expression is called a **thermochemical equation.**

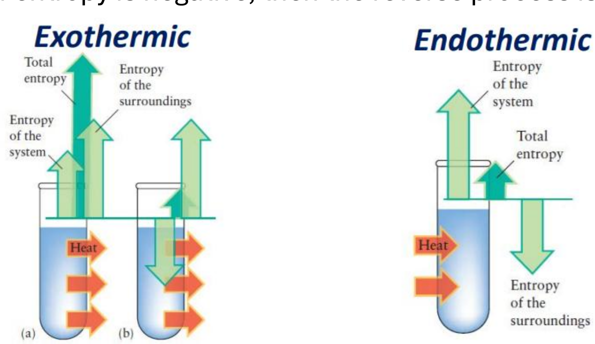
The **stoichiometric coefficients** indicate the number of moles that react to give the reported change in enthalpy.

- If gas is formed in a reaction, it is sometimes necessary to convert ΔU to ΔH differently
  - $\Delta H = \Delta U + \Delta n_{gas} RT$
- Hess' Law argues that enthalpy change is the sum of all ΔH of all reactions, hence ΔH is a state function
- Enthalpy of reaction ($\Delta H_{rxn} [kJ \cdot mol^{-1}]$) is the difference in enthalpy between products and reactants
  - The magnitude of ΔH_{rxn} depends on the physical states of reactants and products and their enthalpies of fusion and vaporization.
- Standard enthalpy of formation $\Delta H°_f$ of a substance is the enthalpy per mole to form the substance from its elements in their pure and most stable form
- Molar enthalpies of formation are zero in stable elemental form

Lecture 10

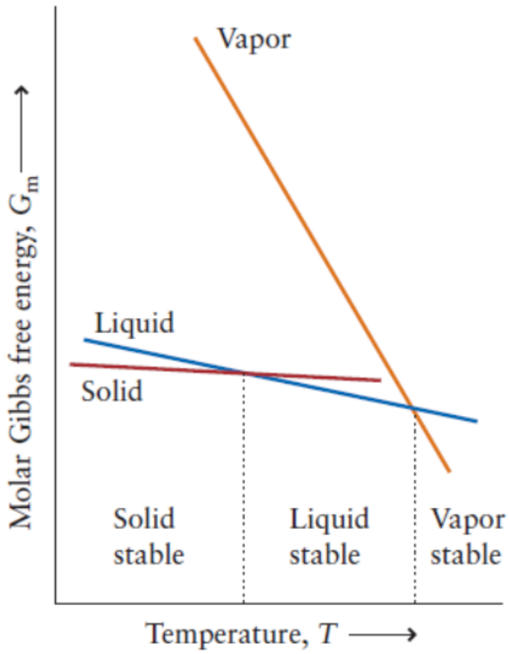
- Endothermic processes can sometimes spontaneously occur
    - To do with lattice energy
- Gibbs free energy ΔG
    - $\Delta G = \Delta H - T\Delta S$
        - ΔG is a state function related to the energy of a chemical or physical process
        - ΔH is enthalpy change
        - T is temperature
        - ΔS is change in entropy
    - If $\Delta G > G$ then the process is not spontaneous
    - If $\Delta G < G$ then the process is spontaneous
    - If $\Delta G = 0$ then the process is in equilibrium
- Entropy is a measurement of dispersion of energy and number of microstates
    - For formation of solutions $\Delta S > 0$
    - Greater enthalpy is favored
- A spontaneous process is one that has the tendency to occur without additional energy from the outside
- $w = -nRT \cdot \ln \frac{\mathrm{V_{final}}}{V_{initial}}$
    - Work done is not a state machine: it depends on the intermediate steps
- A reversible process is one that can be reversed with an infinitesimal change of a variable
- Second law of thermodynamics:
    - "A cyclic transformation whose only final result is to transfer heat from a body at a given temperature to a body at a higher temperature is impossible."
- The entropy is the thermal energy per unit temperature that is unavailable for doing useful work
    - $\Delta S = \frac{\Delta q}{T}$
- Clausius inequality:
    - Entropy cannot decrease in a closed environment
        - Entropy in the universe is increasing
- Heat flowing in or out of a system: $\Delta S \propto -\Delta q_{sys}$
    - For isothermal processes:
        - $\Delta S = -\frac{\Delta q_{sys}}{T}$
    - Entropy increases more with low temperatures
- A reversible process in a closed system has no entropy change
- $\Delta S = C \cdot \ln \frac{T_2}{T_1}$
    - The greater the heat capacity, the greater entropy changes with a certain temperature change
- Dispersion of molecules over a larger volume increases entropy
    - $\Delta S = nR \ln \frac{V_2}{V_1}$
- For state changes at their transition temperatures:

- $\Delta S = \frac{\Delta H}{T}$
- $\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}$
- $\Delta S_{\text{fus}} = \frac{\Delta H_{fus}}{T_f}$
- 

- Trouton's rule states that many liquids have $\Delta S°_{vap} \approx 85JK^{-1}mol$
- Third law of thermodynamics:
  - The entropies of all perfect crystals approach zero as temperature approaches 0K
- Statistical entropy:
  - $S = k \ln W$
    - $k = 1.381 \times 10^{-23} JK^{-1}$ is the Boltzmann constant
    - W is the number of microstates: the number of ways that atoms can be arranged to give the same energy
    - W increases with temperature and volume
- $\Delta S = \int_{T_1}^{T_2} \frac{CdT}{T}$
  - C often depends on T
- A process is spontaneous only if the total entropy is positive
  - $\Delta S_{tot} = \Delta S_{sys} + \Delta S_{sur}$
- If entropy is negative, then the reverse process is spontaneous
- 

Gibbs Free Energy

- $G = H - TS$

- $\Delta G = \Delta H - T\Delta S$
- For processes at constant temperature:
    - $\Delta G = -T\Delta S_{tot}$
- G decreases as temperature increases
- 

- $$\Delta G = \sum nG_{products} - \sum mG_{reactants}$$
- $$\Delta G^{o}_{298} = \sum nG^{o}_{products} - \sum mG^{o}_{reactants}$$
    - 298 refers to the temperature
- Standard Gibbs free energy of formation ΔG_f is the standard Gibbs free energy of reaction per mole for the formation of a compound from its elements in their most stable form.
- A thermodynamically stable substance is one with negative $\Delta G°_f$
    - Nonlabile substances last for a long time (sometimes inert)
    - Labile substances decompose or react rapidly
-

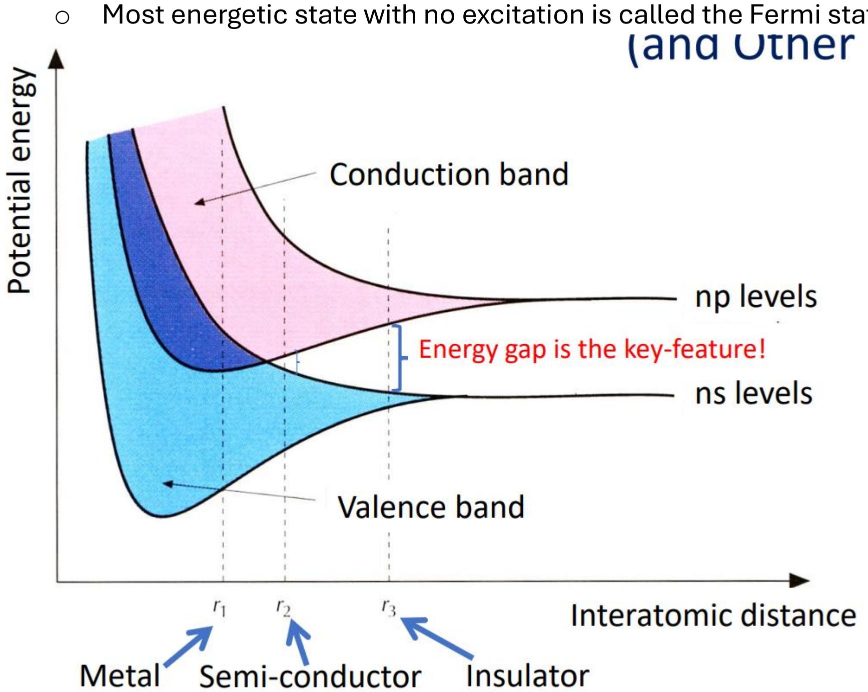
ΔH	*ΔS*	*-TΔS*	*ΔG*	Spontaneity
+	-	+	+	Nonspontaneous
-	+	-	-	Spontaneous
-	-	+	+ or -	Low Temp: Spontaneous High Temp: Nonspontaneous
+	+	-	+ or -	Low Temp: Nonspontaneous High Temp: Spontaneous

Lecture 13*

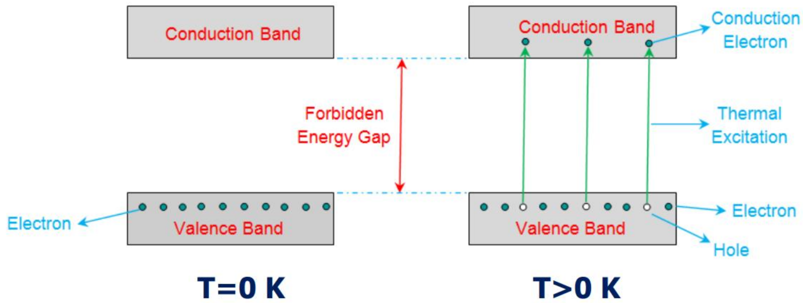
- Free electron model for metals explains:
    - Conductivity (thermal and electrical)
    - Malleability & ductility
    - Opacity and reflectance

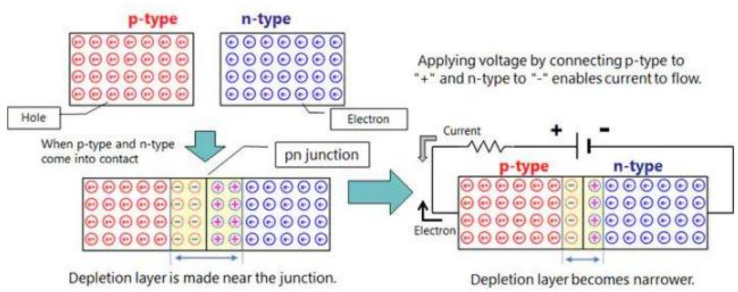
Band Theory

- When bonding, energy levels get very close together, forming bands of energy levels
    - Bands are named after the orbitals that created them (e.g. 2s band)
- The Pauli exclusion principle states that each energy state can only hold 2 electrons
    - Most energetic state with no excitation is called the Fermi state



-
- $\overline{E_K} = k_b T$
- If the energy gap is much greater than $k_b T$, then the material is an insulator
- If the energy gap is Close to or less than $k_b T$, the material is a conductor
- If the energy gap is about $10 \times k_b T$, the material is a semi-conductor
- In alkali metals, the valence s band is half full, meaning that it can conduct
    - The valence band for alkali metals is also the conduction band
- Alkali earth metals have a full valence band; however, the conduction band (xp band) overlaps the valence band, allowing for conduction
- Intrinsic semiconductors naturally have a small energy gap
    - Electrons from the valence band can jump to the conduction band, allowing for both bands to conduct electricity since electrons can move through the available spaces

- 

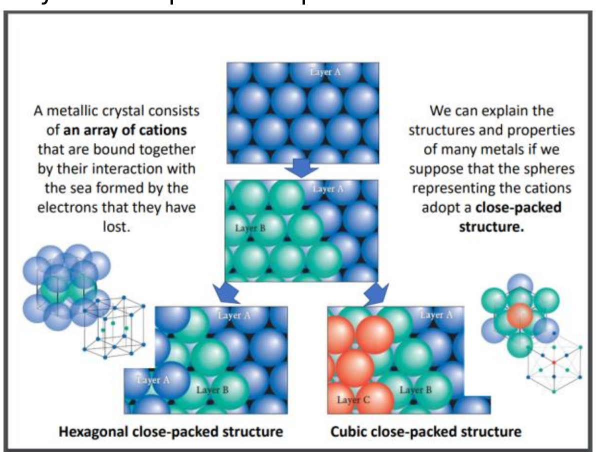
- Extrinsic semiconductors require impurities (doping) in order to conduct electricity. These dopants can provide:
    - More electrons (n-type)
    - More spaces (p-type)
- When n type and p type semiconductors are in contact, they form a depletion layer in between
    - 

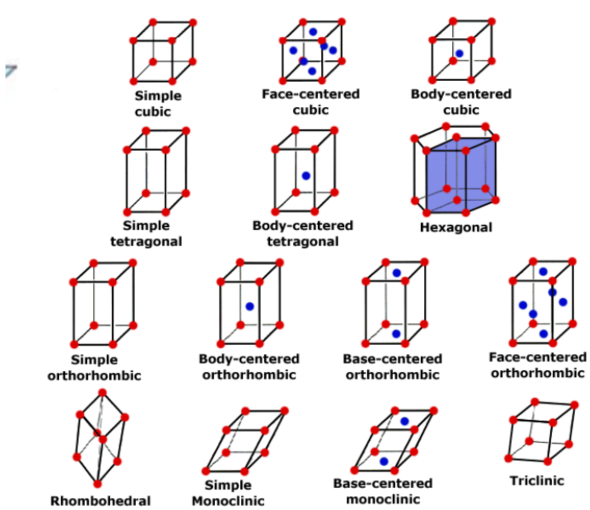
- In diodes, when electrons flow into the n-type, electrons replenish so current flows, if they flow into the p-type, they pile up and stop current
- Photodiodes conduct electricity when the p-type is excited by light
- Solar cells work similarly
- LEDs work with the principle of electroluminescence
    - When electrons rejoin at the junction, they emit light

The Solid State

- Crystals are ordered and symmetrical
- Amorphous solids are unorganized
- Crystals have flat, well-defined planar surfaces with definite angles between them
- 4 types of solids:
    - Covalent network
    - Molecular
    - Ionic
    - Metallic

Type of solids	Constituting particles	Type of bonding forces	Properties	Examples
Ionic	Positive (+) and negative (-) ions	Electrostatic attractions	⇒ Hard ⇒ High melting point ⇒ Electric conduction in molten and solute states ⇒ Brittleness.	NaCl, $CaCO_3$
Covalent (molecular)	Molecules	Intermolecular forces (van der Waals)	⇒ Soft ⇒ Low melting point ⇒ Isolating	CO_2, H_2O, I_2
Covalent (lattice)	Atoms (equal or different)	Covalent bond	⇒ Very hard ⇒ High melting point ⇒ Isolating	C (diamond), SiO_2
Metallic	Positive ions + electrons	Electrons cloud – ions lattice interactions	⇒ Electric conductors ⇒ Glossy ⇒ Ductile	All metals

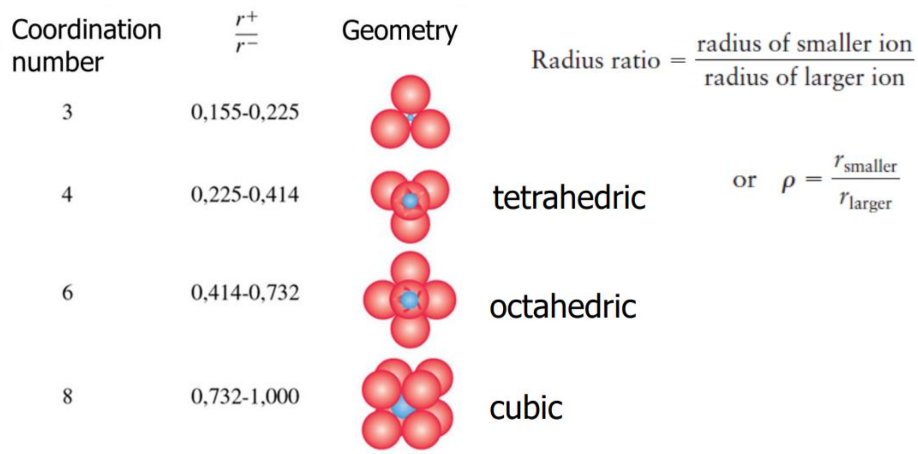
-
- Metallic crystals adopt a close-packed structure.
  - 

- A Bravais lattice is a structure of atoms that can repeat to form a crystal.
  - There are 14 possible unit cells that can produce one
  - 

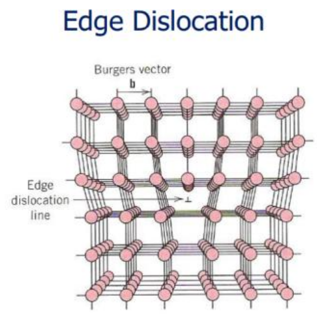
- X ray diffraction can provide information about crystalline solids

    - With single molecules, waves are scattered in random directions.
    - With multiple molecules/atoms, destructive/constructive interference occurs in certain directions.
        - When the material is unorganized, this will be random and no pattern can be observed
        - When the material is organized in a lattice, distinct diffraction patterns can be observed
    - BRAGG LAW

      $$2d(\sin\theta) = \lambda_o$$

      where:
      d = lattice interplanar spacing of the crystal
      θ = x-ray incidence angle (Bragg angle)
      λ = wavelength of the characteristic x-rays
- For ionic structures:
    - 

- Allotropes are elements that can exist in different forms
    - E.g. carbon can exist as diamond, fullerene, graphite etc.
- Polymorphism is the same for molecules (not elements) that can exist in crystal forms
- Liquid crystals are solids that can flow like liquids
    - Mesophases: intermediate between solid and liquid
- Thermotropic liquid crystals are formed by melting solids and adjusting temperature to a very precise value
- Lyotropic liquid crystals are the results of the action of a solvent
- Crystals can have defects:
    - Punctual
        - Vacancies: missing molecules in some places
        - Interstitials: extra molecules in some places
    - Linear
        - Edge dislocation: a plane is interrupted, making two sections uneven

- 

  - Superficial
    - Poly-crystalline materials: solids composed of more than 1 crystal connected by grain boundaries

Lecture 14

- For reversible reactions, after some time, the amount of substances does not change.
  - At equilibrium, forward and reverse reactions occur at the same rate
- For a reversible reaction $aA \rightleftharpoons bB$
  - $K_c = \frac{[B]_{eq}^b}{[A]_{eq}^a}$
  - K_c is the equilibrium constant for the reaction at a given temperature
  - $K = \frac{P_B^b}{P_A^a} \times P^{a-b}$
    - P_x is the partial pressure of x
    - P is the total pressure
    - This applies to reactions with only gases
  - To simplify, at 1bar (standard pressure),
    - $K = \frac{P_B^b}{P_A^a}$
- For reversible reaction $aA + bB \rightleftharpoons cC + dD$
  - $K = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$
    - At standard pressure $P = P° = 1bar$
  - If the reaction does not only involve gases, molarities can be used (standard molarity is $M = M° = Mmol \cdot L^{-1}$
  - Generally, with concentration expressed in different forms,
    - $$K = \frac{\left(c_C/c°\right)^c \cdot \left(c_D/c°\right)^d}{\left(c_A/c°\right)^a \cdot \left(c_B/c°\right)^b}$$
    - $$K = \frac{(c_C)^c \cdot (C_D)^d}{(c_A)^a \cdot (c_B)^b}$$
      - With standard concentration
- Activity a_J of a substance J can be expressed as follows:
Substance	Activity	Simplified form
ideal gas	$a_J = P_J/P°$	$a_J = P_J$
solute in a dilute solution	$a_J = [J]/c°$	$a_J = [J]$
pure solid or liquid	$a_J = 1$	$a_J = 1$
  - It is a measure of how it affects K
  - It allows for the following general formula:

$$aA(g) + bB(g) \rightleftharpoons cC(g) + d(D)(g)$$

$$K = \frac{(a_C)^c \cdot (a_D)^d}{(a_A)^a \cdot (a_B)^b}$$

- When all reactants and products are of the same state of matter, it is called a homogeneous equilibrium
  - When they are different, it is called a heterogeneous equilibrium
  - Activity allows for heterogeneous equilibria to be found
- When a reaction involves fully dissociated ionic compounds dissolved in a solvent, the net ionic equilibrium can be used, by using the activity for each ion.

$$2AgNO_3(aq) + 2NaOH(aq) \rightleftharpoons Ag_2O(s) + 2NaNO_3(aq) + H_2O(l)$$

$$K = \frac{[Ag_2O] \cdot [Na^+]^2 \cdot [NO_3^-]^2 \cdot [H_2O]}{[Ag^+]^2 \cdot [NO_3^-]^2 \cdot [OH^-]^2 \cdot [Na^+]^2}$$

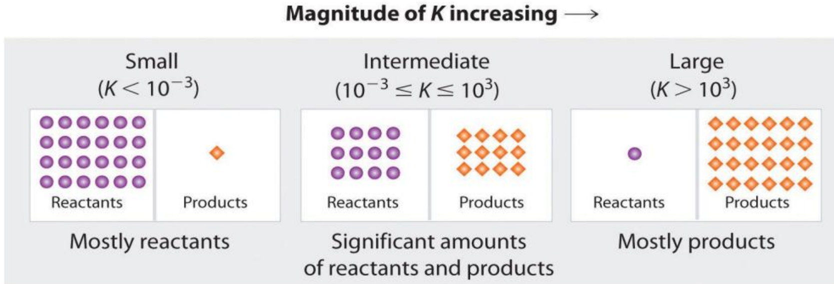
This can be greatly simplified

$$K = \frac{1}{[Ag^+]^2 \cdot [OH^-]^2}$$

- $\Delta G_r = \Delta G° + RT \cdot \ln \frac{a_C^c a_D^d}{a_A^a a_B^b}$
  - $\Delta G_r = \Delta G + RT \ln K$
  - At equilibrium $\Delta G_r = 0$:
    - $\Delta G°_r = -RT \ln K$

General guidelines to K evaluation:

Magnitude of K increasing ⟶



Composition of equilibrium mixture

- The equilibrium constant for the overall reaction is the product of those of the component reactions
- $K_C = \frac{K_P}{(RT)^{\Delta n}}$
  - K_C is the equilibrium constant in terms of concentration
  - K_P is the equilibrium constant in terms of partial pressure

- Δn is the difference between the total stochiometric coefficients in the reaction
  - $\Delta n = c + d - a - b$
- Reaction quotient:
  - $$Q_C = \frac{[C]_i^c \cdot [D]_i^d}{[A]_i^a \cdot [B]_i^b}$$
  - If $Q < K$, then the reaction tends towards the products
  - If $Q > K$, then the reaction tends towards the reactants
  - If $Q = K$, then the reaction is in equilibrium

- $\Delta G_r = RT \ln \frac{Q}{K}$
- Le Chatelier Principle:
  - When stress is applied to a system in dynamic equilibrium, the equilibrium tends to minimalize the effect of the stress
- A shift in equilibrium may be caused by:
  - A change in concentrations of reactants or products
    - The system will reach the equilibrium ratio
  - Variation in P, V, T
    - By increasing P, there is a tendency for the system to minimalize the increase in P, so the number of particles will tend to decrease, favouring the direction with less particles
      - K does not change
    - An increase in T will result in a shift towards where heat is absorbed
      - K changes
  - By adding a catalyst
    - Equilibrium does not change, it will only be reached sooner
- The inclusion of an inert gas at constant volume will not change the equilibrium.

Lecture 15

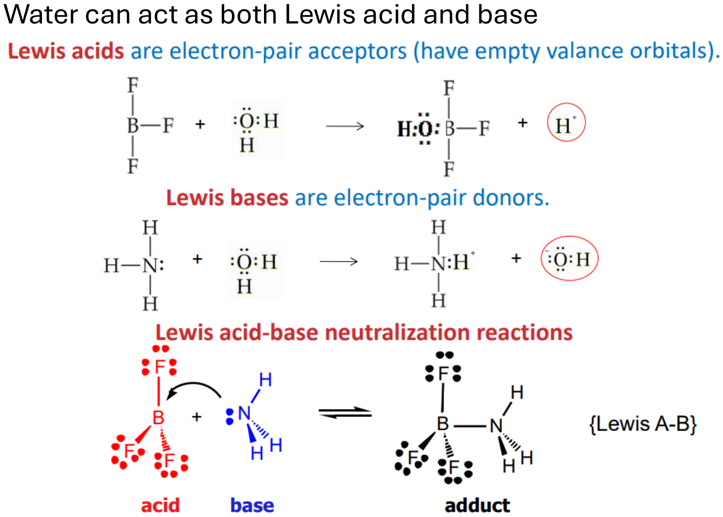
- Acids ionize in water to produce H^+ ions.
  - $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$
- Bases dissociate in water to produce OH^- ions
  - $NaOH(aq) \rightarrow OH^-(aq) + Na^+(aq)$
- H^+ is unstable and reacts with water to produce hydronium
  - $H_2O + H^+ \rightarrow H_3O^+$

Brønsted-Lowry Theory

- Brønsted-Lowry Theory states that acids are H^+ donors and bases are H^+ acceptors
- Acid-base reactions are reversible.
  - The original acid acts as a base and the original base acts as an acid, since the proton has been transferred.
- Each reactant and the product it becomes is called a conjugate pair.
  - $H - A + :B \rightleftharpoons :A^- + H - B^+$
  - $H - A^+$ and A^- are acid and conjugate base

Lewis Theory

- Lewis acid: A substance that accepts an electron pair (electrophile)
  - Has vacant orbital
- Lewis base: A substance that donates an electron pair (nucleophile)
  - Has lone pair electrons
- All cations are Lewis acids since they can accept electrons
- An ion, molecule or atom with incomplete octets can act as Lewis acids
- Molecules where the central atom can have more than 8 valence electrons can be a Lewis acid
- Molecules with multiple bonds between atoms with different electronegativities can be Lewis acids
- Water can act as both Lewis acid and base



- A basic oxide is an oxide which reacts with water to create a solution of hydroxide ions

- $CaO\ (s)\ +\ H_2O\ (l)\ \rightarrow\ Ca\ OH_2\ (aq)$
- Basic oxides are ionic compounds that react with acids to form salts and water
  - $MgO\ (s)\ +\ 2HCl\ (aq)\ \rightarrow\ MgCl_2\ (aq)\ +\ H_2O\ (l)$
- Metals typically form basic oxides and non-metals typically form acidic oxides
  - Elements in between form amphoteric oxides, which can act as either basic or acidic
    - These are some transition metals and metalloids
- In pure water, some molecules act as acid and some as basic.
  - Autoionization occurs
  - $2H_2O\ (l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$
- Amphiprotic means that it can also donate protons (H^+).

Strength of Acids and Bases

- Commonly, the strength of acids and bases is determined by the equilibrium position of when they react with water.
  - $H - A + H_2O \rightleftharpoons A^- + H_3O^+$
  - $B + H_2O \rightleftharpoons H - B^+ + OH^-$
  - The further the equilibrium is from the products, the stronger the acid or base
  - Stronger attraction between the base and the H^+ means more basic.
  - The stronger the acid, the more willing it is to donate H^+ by using water as standard base

Strong and Weak Acids

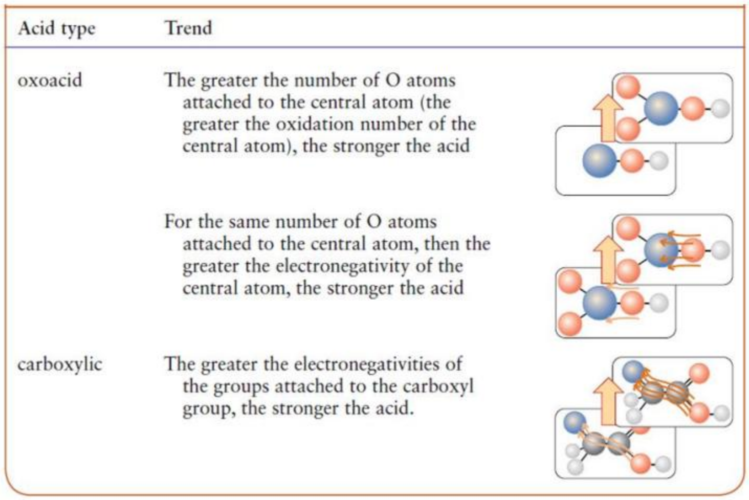
- Strong acids have wea conjugate bases
  - Weak acids have very strong conjugate bases
- Generalized acid dissociation:

$$HA\ (aq) + H_2O\ (l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

  - Equilibrium:

$$K_A = \frac{[H_3O^+] \cdot [A^+]}{[HA]}$$

  - K_A is the acid dissociation (ionization) constant
  - $pK_A = -\log K_A$
    - Other way of expressing acidity
    - The lower pK_A the stronger the acid
    - $K_A = 10^{-pK_A}$
    - Greater K_A means lower pK_A and stronger acid
- In oxoacids, the greater the electronegativities, the stronger the acid
- Strength of acids increases with the number of oxygens in the organic acid
  - Carboxylic acids are stronger acids than alcohols (but still weak acids)
- For binary acids, the weaker and more polar the A-H bond, the stronger the acid

- 

Acid type	Trend
oxoacid	The greater the number of O atoms attached to the central atom (the greater the oxidation number of the central atom), the stronger the acid
	For the same number of O atoms attached to the central atom, then the greater the electronegativity of the central atom, the stronger the acid
carboxylic	The greater the electronegativities of the groups attached to the carboxyl group, the stronger the acid.

Strong and Weak Bases

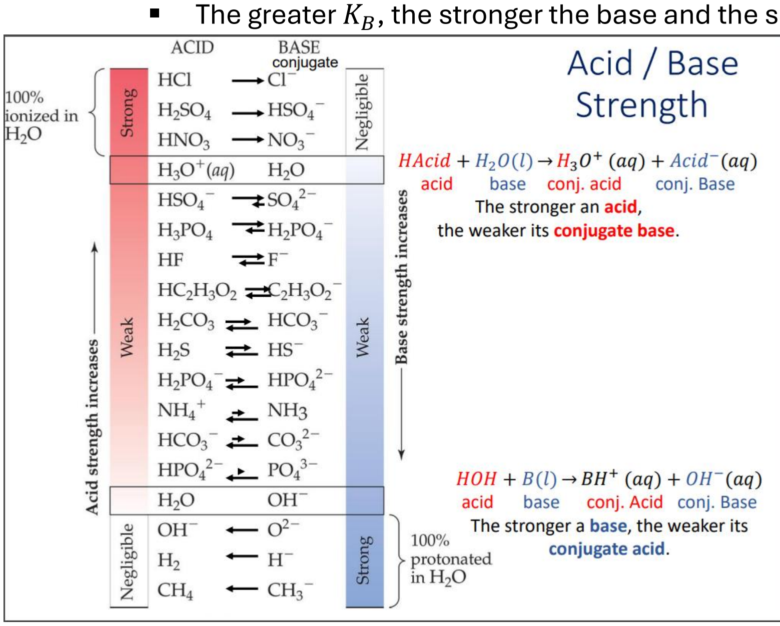
- Strong bases either dissociate fully into OH^- ions or fully accept H^+ ions

$$MOH + H_2O(l) \longrightarrow Na^+ + H_2O\ (aq) + OH^-(aq)$$

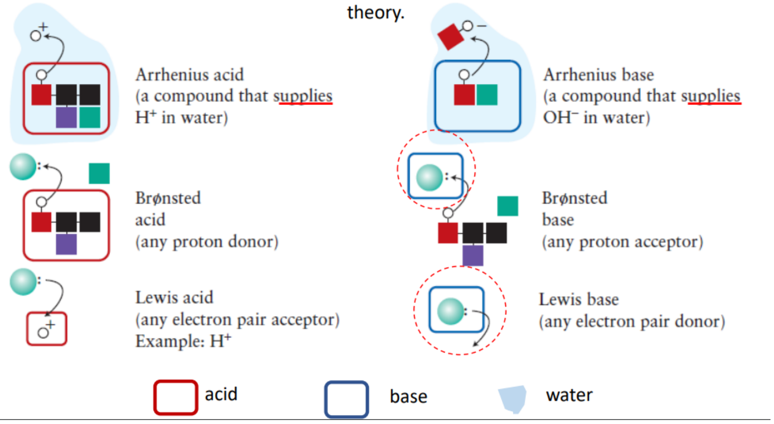
- Base acid conj. acid conj. base
- Generalized base dissociation:

$$H_2O\ (l) + B\ (aq) \rightleftharpoons BH^+\ (aq) + OH^-\ (aq)$$

  - $K_b = \frac{[BH^+]\cdot[OH^-]}{[b]}$
  - K_b is the base dissociation (ionization) constant
  - $pK_b = -\log K_b$
    - The greater K_B, the stronger the base and the smaller pK_b

- 

A Note on Good Practice: The entities that are regarded as acids and bases are different in each theory.

- 

Auto-dissociation of Water

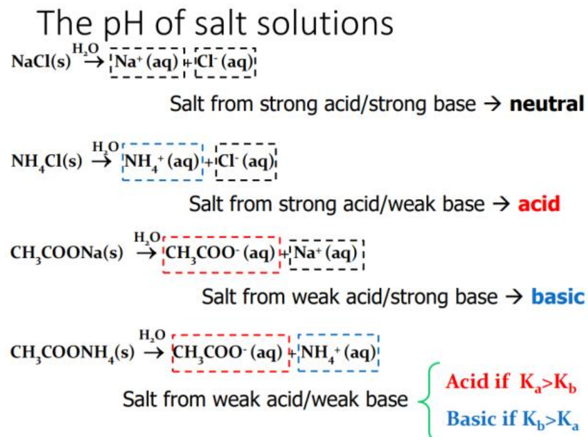
- Water is amphiprotic
    - Some act as basic and some as acids
    - Autoionization
    - $2H_2O \rightleftharpoons H_3O^+ + OH^-$
    - Equilibrium:

$$K_W = \frac{a_{H_3O^+} \cdot a_{OH^-}}{a_{H_2O}^2} = a_{H_3O^+} \cdot a_{OH^-} = [H_3O^+] \cdot [OH^-] = 10^{-14} \text{ @ } 25°C$$

- More OH in a solution means more basic, more hydronium means more acidic
- $pH = -\log[H_3O^+]$
- $pOH = -\log[OH^-] = 14 - pH$
- In strong acids, the contribution of water to the amount of hydronium is negligible
    - In weak acids K_A and K_b must be considered
    - If more than around 5% of the acid/base has been ionized, then K_A and K_b must be considered and solved for
        - For x small:
        - $K_A = \frac{x^2}{[HA]_{init} - x} \approx \frac{x^2}{[HA]_{init}}$
            - x is "small" when $\frac{x}{[HA]_{init}} < 5\%$
            - Same for K_B
        - We ignore the contribution of water when $x > 10^{-6} M$

pH of Salt Solutions

- Highly charged metals (for example Fe^{3+}) can act as Lewis acids when dissolved in water
- Al^{3+} dissolves in water to produce $Al(H_2O)_6^{3+}$ which is a monoprotic acid
- Very few anions containing hydrogen act as acids
    - There exists some, such as Sulfate ion and dihydrogen phosphate ion
    - This is because it is hard for a proton to escape a negatively charged ion



Polyprotic Acids

- Acids can have more than 1 ionizable proton
  - 1H →Monoprotic (HCl)
  - 2H → Diprotic (H_2SO_4)
  - 3H → Triprotic (H_3PO_4)
- Hydrogens are ionized in sequence
  - When the first is removed, the removal of the second becomes more difficult
- Polyprotic acids tend to be more acidic than monoprotic
  - $pH_{HSO_4} < pH_{H_2SO_4}$

Polyprotic Base

- Base that can accept more than 1 proton

pH of Highly Diluted Strong Acids

- Autoprotolysis is a chemical reaction where a molecule donates a proton to an identical molecule
  - One acts as a Bronsted acid and one as a Bronsted base
  - When strong acids are diluted strongly, this needs to be considered when calculating pH
  - This is to be considered when the concentration of the strong acid is less than around $10^{-6}M$
  - Idk where this comes from:

$$[H_3O^+]^2 - [H_3O^+]\cdot[HA]_{initial} - K_w = 0$$

Similarly for a strong base

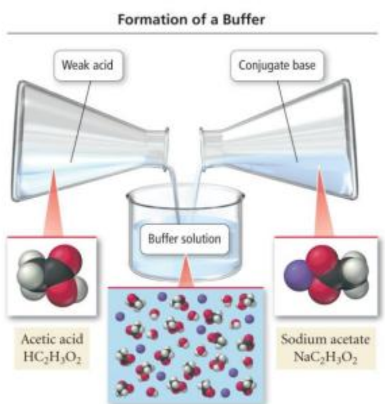
$$[H_3O^+]^2 + [H_3O^+]\cdot[B]_{initial} - K_w = 0$$

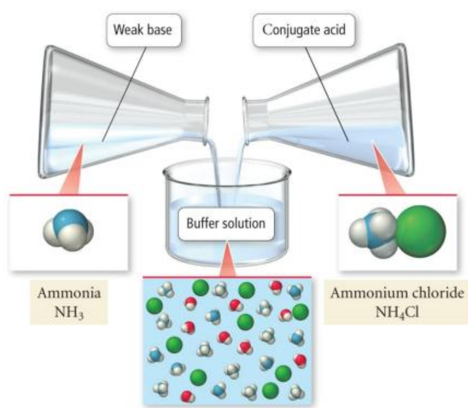
$$K_a = \frac{[H_3O^+] \cdot \left([H_3O^+] - \frac{K_w}{[H_3O^+]} \right)}{[HA]_{initial} - [H_3O^+] + \frac{K_w}{[H_3O^+]}}$$

▪

Lecture 16

Buffers

- Buffers are substances that resist a change in pH
    - They act by neutralizing the added acid or base
    - Once limit is reached, the buffer will also change its pH
    - Many are made with solution of weak acid and a solution of soluble salt containing its conjugate base anion
- Buffers work by applying Le Châtelier's Principle to weak acid equilibrium
    - The weak acid reacts with added bases to produce more water and the conjugate base
    - The conjugate base reacts with protons from added acid to produce the weak acids
- Formation of acid buffer:
    - 

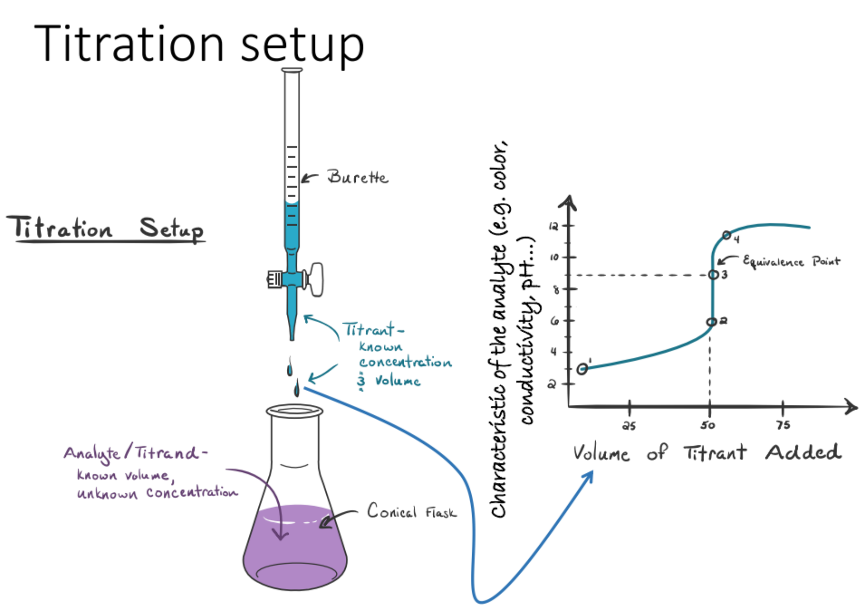
- Formation of basic buffer:
    - 

- If multiple salts with a common ion are added to a weak acid or base, the equilibrium will be restored, and the reaction will tend towards the weak acid/base
    - Reduces the ionization of the weak acid/base by increasing the products of the ionization reaction.
- Buffers are often prepared with equal concentrations of acid and conjugate base
    - Acid with pK_A close to the desired one and prepare solution with conjugate base.
    - Adequate "source" and "sink" to resist pH changes

- Henderson-Hasselbalch equation:
$$pH = pK_A + \log \frac{[A^-]_{init}}{[HA]_{init}}$$
    - The concentrations refer to the weak acid and conjugate base used as buffer
    - Used to calculate the pH of a buffer
    - Buffering occurs because of the logarithmic relationship between pH and the concentration ratio of the buffer's weak acid and base
- Buffers resist pH change but their pH does change
- Buffer effectiveness depends on its capacity and range. It is affected by:
    - Relative amounts of acid/base
    - The concentrations of the acid/base
    - Buffer range:
        - The pH the buffer can work at
    - Buffer capacity:
        - The amount of acid/base the buffer can neutralize
- Range of effectiveness is:
    - $0.1 < \frac{[A^-]}{[HA]} < 10$
    - Most effective buffer is one who's pK_A is closest to the target pH
- Buffers that need to work more with acids will have more base and vice-versa

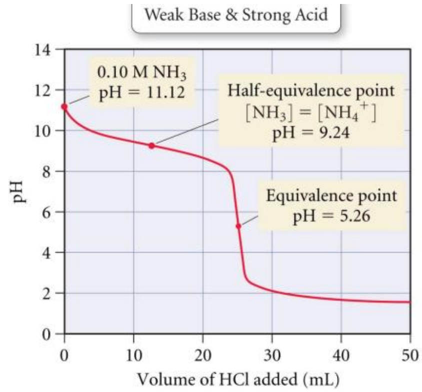
Titration

- Titration is the process of adding a solution of a known concentration (titrant) to a known volume of a solution of unknown concentration (titrand/analyte) until neutralization is achieved (observed by colour change
    - Objective is to find the unknown concentration

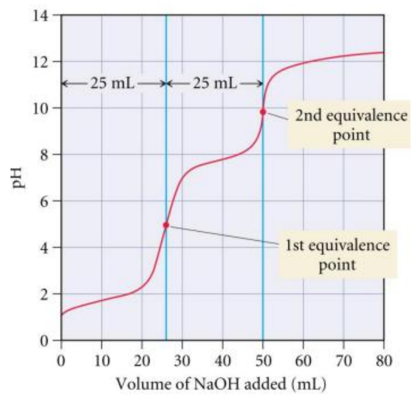


- In an acid-base titration, the equivalence point is where $[OH^-] = [H_3O^+]$
- An indicator is used to detect the change in pH

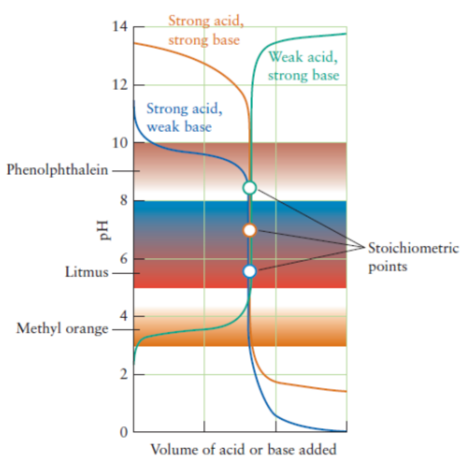
- Strong acid – strong base titration is the simplest type.
    - Equivalence point will be where pH is 7



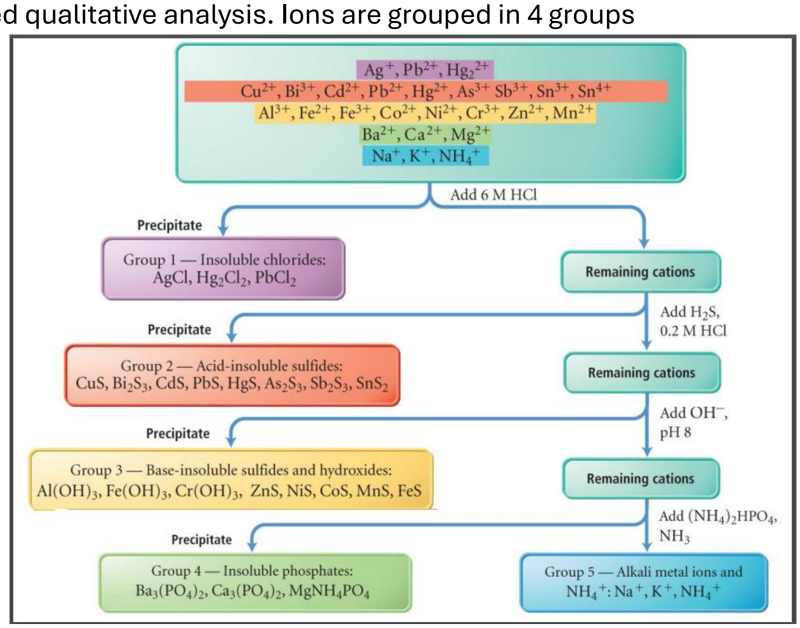
-
- For polyprotic acids, there will be more equivalence points



    -
- Automatic titrators will use the change in conductivity due to hydronium to measure pH
- Indicators are weak acids that change colour depending on their dissociation
- It is important to choose an indicator who's end-point is close to the stochiometric point of titration



    -
- Examples of indicators:
    - Phenolphthalein turns magenta in bases but colourless in acids
    - Methyl red turns red under pH of 4.4 and yellow over 6.2 (orange in between)
    - Universal indicators are mixtures of different indicators to cover pH 0-14

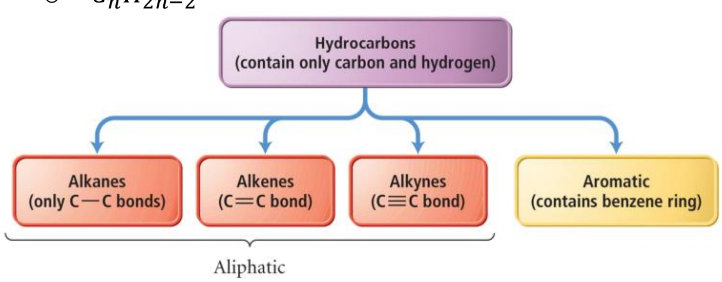
- All ionic compounds dissolve in water, but some have such low solubility that they are considered insoluble
    - Solubility product K_{sp} is a constant to show the dissociation equilibrium when dissolving compounds
    - For an ionic solid M_nX_m, the dissociation reaction is:
      $$M_nX_m(s) \rightleftharpoons nM^{m+}(aq) + mX^{n-}(aq)$$
      the solubility product would be
      $$K_{sp} = [M^{m+}]^n[X^{n-}]^m$$
- To compare K_{sp}, the compounds must have the same dissociation stochiometric coefficients
- Addition of a salt that contains a common ion with an insoluble salt, decreases the solubility of the insoluble salt
- For insoluble ionic hydroxides, the higher the pH, the lower the solubility
    - Higher pH means more OH^- ions, therefore shifting equilibrium towards the precipitate
- For insoluble ionic compounds that contain weak acid anions, the lower the pH, the higher the solubility
- $Q = K_{sp}$, the solution is saturated, no precipitation
  $Q < K_{sp}$, the solution is unsaturated, no precipitation
  $Q > K_{sp}$, the solution would be above saturation, the salt above saturation will precipitate
    - Some solutions will not precipitate even if $Q > K_{sp}$ unless disturbed
        - These solutions are supersaturated
- A solution with different ions can be separated using selective precipitation
    - A substance is added that will react with a selected ion and form a precipitate
- A scheme that uses selective precipitation to determine what ions are present in a solution is called qualitative analysis. Ions are grouped in 4 groups
    - 

Lecture 7*

- Carbon is most stable with 4 bonds
    - Double and triple bonds are more reactive than single bonds
- Carbon uses sp^3, sp^2, sp hybrid orbitals for single, double and triple bonds respectively
    - sp^3 means 4 σ bonds
    - sp^2 means 3 σ bonds and 1 π bond
    - sp means 2 σ bonds and 2 π bonds

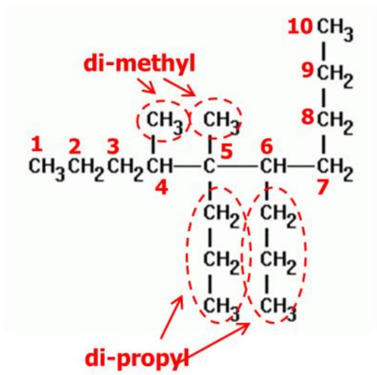
Hydrocarbons

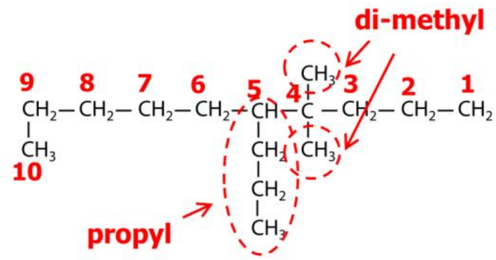
- Hydrocarbons only contain carbon and hydrogen (aliphatic or aromatic)
- Insoluble in water
- Aliphatic hydrocarbons have saturated or unsaturated bonds
    - They can be cyclical (cyclo-)
    - Chains may be straight or branched
- Aromatic hydrocarbons have a 6-carbon benzene ring
- A saturated hydrocarbon has all C-C single bonds
- Saturated aliphatic hydrocarbons are called alkanes
    - C_nH_{2n+2}
    - Can come in rings
- Alkanes have unsaturated C=C bonds
    - C_nH_{2n}
- Alkynes have unsaturated $C \equiv C$ bonds
    - C_nH_{2n-2}



-
- Molecular formula says what atoms contain a molecule
- Structural formula explains the bonding structure
- Models show the general shape of the molecule
- Line-angle formulas show the shape with lines
    - End of line is a carbon
    - Hydrogens are omitted EXCEPT for in functional groups
    - Functional groups are shown explicitly
    - Double/triple bonds are shown
- Iso- shows branching in equal branches
- Naming alkanes:
    - Find longest chain to give the -ane suffix to
    - Find lengths of branches and give them -yl suffix.

- Give branches numbers (minimizing the total of these numbers) depending on their positions
- Order alphabetically depending on number group (without Greek prefix)
- Add di,tri etc if there are multiple
- To indicate multiple branches, insert comma between numbers

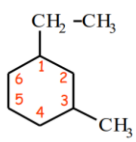




4,4-dimethyl- 5-propyl decane

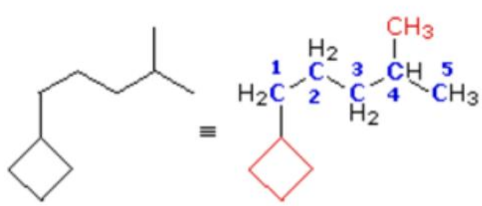
4,5-dimethyl- 5,6-dipropyl decane

- Cycloalkanes (C_nH_{2n}) have cyclical structures with all single bonds and sp^3 orbitals
  - Naming these is similar, but numbering starts at a branch



1-ethyl-3-methyl cyclohexane

  - If there is only 1 branch, then the 1 is omitted



1-cyclobutyl-4-methylpentane

  - Above is disubstituted pentane with cyclobutyl group on 1st carbon
- Hydrocarbons are non-polar
  - Their main force is London dispersion forces
  - The larger the molecule, the greater this force and therefore the greater the boiling point
- Branched molecules tend to have lower melting/boiling points than their chain isomers
- Alkanes (once paraffins) are not very reactive
  - Unaffected by most acids and bases

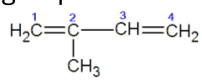
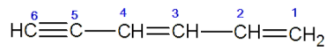
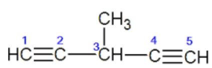
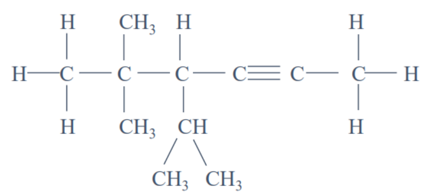
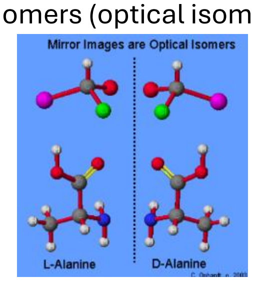
Alkenes

- Aka olefines
- Aliphatic containing C with sp^2 hybrid orbitals (at least a double bond)
  - Polyunsaturated

- Trigonal shape around C
    - Flat
- More reactive than alkanes

Alkynes

- Aka acetylenes
- Aliphatic containing sp hybrid orbitals (at least a triple bond)
- Linear shape along the hybridized sp C
- More reactive than alkenes

- For alkynes and alkenes, numbering on the naming preferably starts on the double or triple bond, or groups named by prefixes
    - 
      2-methylbuta-1,3-diene
      
      Hexa-1,3-dien-5-yne
      
      3-methylpenta-1,4-diyne
    - Good example:
        - 4-isopropyl-5,5-dimethyl-2-hexyne 
- Structural isomers have different attachments
- Stereoisomers have same attachments but different orientations
- Enantiomers (optical isomers) are non-superimposable on their mirror image
    - 

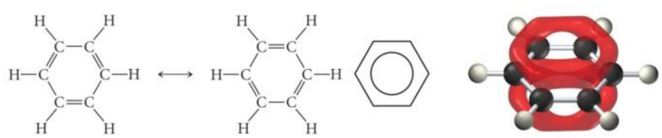
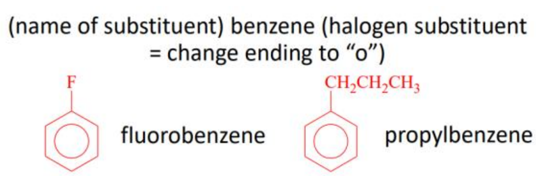
    - Meaning that when mirrored, not all molecules can be aligned with their original
    - Pairs of enantiomers only have 1 physical difference: the direction they polarize light
        - Each will rotate polarized light by the same amount but in opposite directions
        - A racemic mixture contains an equimolar mixture of the two
    - Same reactivity but their compatibility with enzymes may differ if around the chiral centre
- Geometric isomers are stereoisomers that are not enantiomers
- A molecule with a non-superimposable mirror image is called chiral
    - Any carbon with 4 different substituents will be a chiral centre

- Rotation about a double bond is restricted
    - Cis-trans isomerism shows rotational isomerism around a double bond:
        - 
          trans-Dichloroethene, $C_2H_2Cl_2$ *cis*-Dichloroethene, $C_2H_2Cl_2$
    - Cis-trans isomers have different properties, including boiling point and density
- C-C has free rotation but C=C has locked rotation (allows only 2 rotation states)

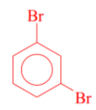
Reactions of Hydrocarbons

- All hydrocarbons undergo combustion
- Substitution is the substitution of H with a halogen, initiated with added heat or UV light
- Addition reactions add a molecule across the unsaturated bond
- Hydrogenation saturates the unsaturated bonds with hydrogen
    - Halogenation adds X_2 where X is a halogen
    - Hydrohalogenation adds HX where X is a halogen
        - HX is polar, so the positive part attaches to the carbon with the most Hs

Aromatic Hydrocarbons

- Benzene ring structure
- Do not behave like alkenes even though they are drawn with C=C
    - True structure of benzene is a resonance hybrid of two structures:
        - 
- Naming:
    - 

- When benzene is not the main group, it is called a phenyl group
- Positions of numbers when named must make the total as small as possible
    - Alternatively, a prefix indicating the position can be used:
        - Ortho-: 1,2
        - Meta: 1,3
        - Para-: 1,4



1,3-dibromobenzene
or *meta*-dibromobenzene
or *m*-dibromobenzene

- Polycyclic aromatic hydrocarbons share a common bond, therefore containing multiple rings
- Arenes are stable, and are therefore unreactive
  - Substitution reactions are the most common, with the pi bonds in the ring left intact
- Aliphatic and aromatic hydrocarbons are mainly found in oil and coal, as well as organic compounds with S and N
- Quantity of gasoline can be increased with:
  - Cracking (shortening chains with catalyst and heat)
  - Alkylation (combining chains with a catalyst)
  - Aromatization (converting alkanes into arene)
- Quality of fuel is measured by octane rating
  - Long chains are less effective as fuel, so they are converted into their branched-chain isomers for a higher rating via isomerization

Functional Groups

- A functional group is a part of the molecule that determines the properties of the molecule
- Many times, the length of the hydrocarbon is irrelevant in reactions, so it is indicated by R

Functional Group*	General Formula*	Class of Compound	Examples
F, Cl, Br, I	RF, RCl, RBr, RI	haloalkane	CH_3CH_2Cl, chloroethane
OH	ROH	alcohol	CH_3CH_2OH, ethanol
OR′	ROR′	ether	$(CH_3CH_2)_2O$, diethyl ether
$NH_2^{\dagger}$	RNH_2	(primary) amine	$CH_3CH_2NH_2$, ethylamine
$-\overset{O}{\overset{\Vert}{C}}H$	RCHO	aldehyde	CH_3CHO, ethanal (acetaldehyde)
$-\overset{O}{\overset{\Vert}{C}}-R'$	RCOR′	ketone	CH_3COCH_3, propanone (acetone)
$-\overset{O}{\overset{\Vert}{C}}-OH$	RCO_2H	carboxylic acid	CH_3CO_2H, ethanoic acid (acetic acid)
$-\overset{O}{\overset{\Vert}{C}}-OR'$	RCO_2R'	ester	$CH_3CO_2CH_3$, methyl acetate
$-\overset{O}{\overset{\Vert}{C}}-NH_2$	$RCONH_2$	amide	CH_3CONH_2, acetamide

- Haloalkanes are alkanes in which at least a hydrogen has been replaced with a halogen

    - Naming involves treating the halogen as a substituent
- Alcohols are R-OH
    - Suffix -ol
    - If OH is not on the last carbon, the number is specified
    - -diol is used when there are multiple OH groups
        - Eg. 1,3-butandiol
    - Alternative naming involves treating OH as a group with name hydroxy
        - Eg. 1,3-dihydroxybutana
    - Phenol is a phenyl group attached to a hydroxy group
    - 3 classes (primary, secondary, tertiary) depending on how many carbons are attached to the carbon connected to the OH group
- Ethers are R-O-R'
    - Naming means naming both Rs followed by word ether at the end
    - Not very reactive
    - More volatile than alcohols with same chain lengths
- Ketones and aldehydes have the carbonyl group (C=O)
    - C=O is highly polar
    - Many reactions involve addition across C=O, attaching the positive part to the O
    - Aldehydes have H on one side, while ketones have 2 hydrocarbons on either side of the C in C=O.
    - Often have nice taste
    - Naming includes replacing the final e in the alkane name with -al for aldehydes and -one for ketones
- Carboxylic are R-COOH
    - Sour and weak acids
    - Prefix + -ic acid
- Esters are R-COOR
    - Obtained by reacting carboxylic acids with an alcohol (esterification)
    - Parent alcohol -yl + main group + -oate
- Condensation reactions are organic reactions driven by the removal of a small molecule, like water in esterification
    - OH is removed from 1 side and H is removed from the other, combining to form water and an ester
- Amines are organic compounds containing nitrogen
    - Smell bad
    - -amine suffix
    - $-NH_2$ group is called amino
    - 3 groups depending on how many carbon groups are attached to the N
    - Alkaloids are plant products that are amines and are biologically active
    - Weak bases. React with strong acids to form ammonium salts
    - React with carboxylic acids to form amides via condensation reaction
- Amino acids contain amine group and carboxylic acid group
    - Has acid part and basic part

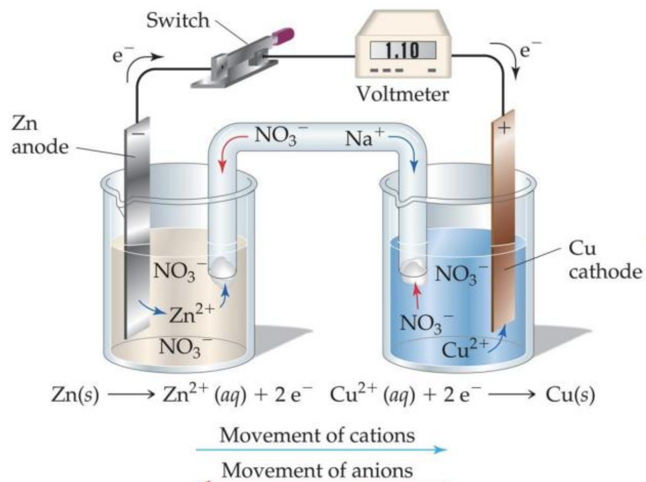
Macromolecules

- Polymerization is the process of combining monomers into polymers
- Polymers can be:
  - Linear (eg HDPE)
  - Branched (eg LDPE)
  - Cross-linked (eg rubber)
  - Network (eg Kevlar)
- In addition polymerization, the chain is created by adding 1 monomer at a time to a chain. The reaction starts with heat or an initiator
- Condensation polymerization removes parts from the combining units in order to form the chain.
  - Chains can grow in 2 directions since each monomer has 2 reactive ends

Lecture 17

- Oxidizing agent gets reduced and reducing agent gets oxidized in redox reactions
- When balancing redox reactions, remember to add H^+ or OH^- in the products when in acid/basic solution
    - Then balance with water

Electrochemistry

- Redox reactions transfer electrons, meaning that they can generate electric current
    - The places where oxidation ad reduction occur need to be separated
- $Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$
    - Redox reaction due to difference in electronegativity between Cu and Zn
- An electrochemical cell uses a redox reaction to generate current. Current flows through electrodes into an external circuit
    - A bridge allows for ion exchange to balance charge
- Spontaneous redox reactions take place in a voltaic cell (aka galvanic cell)
    - Oxidation occurs at the anode
    - Reduction occurs at the cathode
    - Cations move towards the cathodes and anions towards the anode
    - 

        - Daniell Cell
- Non-spontaneous redox reactions take place in an electrolytic cell with the addition of electrical current
- Cell notation
    - Anode (electrode) | Cation (electrolyte) || Anion (electrolyte) | Cathode (electrolyte)
        - | indicates a phase barrier
        - || indicates a salt bridge
        - For multiple electrodes in the same state a comma is used rather than |
            - (Inert electrode)
- Pairs of ions in a solution are usually written in order Ox, Red

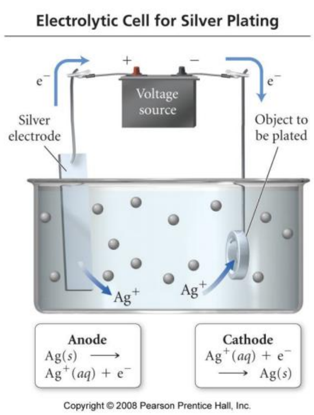
Standard electrode potential, standard reduction potential, standard cell potential

- Electrons flow from high potential to low potential
- Maximum work is $W = IV$
  - $V\ (unit) = JC^{-1}$
- The voltage required to make electrons flow through an external current is called electromotive force (emf)
- Standard electrode/reduction potentials are properties of redox half-reactions
  - Written in reduction half-reaction
  - $E°_{red}$
- $E°_{red}$ cannot be measured absolutely, so it is compared to that of $2H^+\ (aq, 1M) + 2e^-, \rightarrow H_2(g, 1\ atm)$ which we assign a value of 0
  - The above setup, with platinum electrodes, is the standard hydrogen electrode (SHE)
  - Half reactions that have a stronger tendency towards reduction compared to SHE have a positive $E°_{red}$ and those who have a stronger tendency towards oxidation have negative
- Most strongly reducing tend to be towards the left of the periodic table and more oxidizing towards the right
  - Strongest oxidizers have positive $E°_{red}$ and strongest reducers have most negative
- The electrochemical series shows that molecules with greater $E°_{red}$ tend to be able to oxidize ones with a lower value
- Cell potential is the maximum potential produced with two electrodes
  - Sometimes called emf of cell
  - $E°_{cell} = E°_{ox} + E°_{red} = E°_{red}\ (cathode) - E°_{red}\ (anode)$
- Greater difference between standard electrode potential, the greater the cell potential
- A metal will dissolve in an acid if its reduction potential is below that of H^+ (0)
- $\Delta G° = -nFE°_{cell}$
  - $F = eN_A = 9.6485 \times 10^4\ C\ mol^{-1}$ is Faraday's constant
- $E°_{cell} = \frac{0.0592V}{n} \log K$
  - K is the equilibrium constant
- A dead battery is one in which the reaction is at equilibrium
- Nernst Equation:
  - $E_{cell} = E°_{cell} - \frac{RT}{nF} \ln Q$
  - At standard conditions:

$$E_{cell} = E°_{cell} - \frac{0.0592V}{n} \log Q$$

- In concentration cells, the two sides of the cell have the same substance but in different concentrations.
  - This works as a cell because there can be a spontaneous reaction
- There are 2 types of batteries:
  - Disposable (irreversible reaction)

- Rechargeable (reversible reaction with the use of a current)
  - Battery turns into an electrolytic cell when charging and galvanic cell when discharging
- Lead acid batteries (often found in cars) use lead and sulphate ions
  - Cheap, high potential and can store large amounts of energy
- Leclanché Acidic Dry Cells use zinc chloride and ammonium chloride
  - Expensive, easily corroded, heavy and non-rechargeable
- Alkaline dry cells use a hydroxide of an alkali metal (often KOH)
  - Rechargeable, cheap, not easily corroded
- Fuel cells are ones where the reactants are constantly being replenished as fuel
- Some electrolysis reactions require more voltage than E_{cell}, this is called overvoltage or overpotential
  - Electrolysis of water requires 0.6V of overvoltage, so 1.8V total voltage with platinum electrodes
- Electroplating:



- Faraday's law of electrolysis:
  - $n = \frac{Q}{F} = \frac{It}{F}$
- Corrosion is the spontaneous oxidation of metals from chemicals in the environment
- Rust is hydrated iron (III) oxide

Lecture 18

- Chemical kinetics is the study of reaction rates
- Speed of reaction is influenced by:
  - Nature of reactants
  - Temperature
  - Catalysts
  - Concentration
- Rate of reaction:
  - $Rate = \frac{\Delta[Product]}{\Delta t} = \frac{\Delta[Reactant]}{\Delta t}$
- As time increases, rate of reaction (ror) slows down because concentration decreases
- 3 types of rates:
  - Initial
  - Average
  - Instantaneous
- Stochiometric coefficients are taken into account when measuring ror
  - If 2 hydrogens are produced, then $ROR = \frac{1}{2}\frac{\Delta[H_2]}{\Delta t}$

$$aA + bB \rightarrow cC + dD$$

The **unique rate is:**

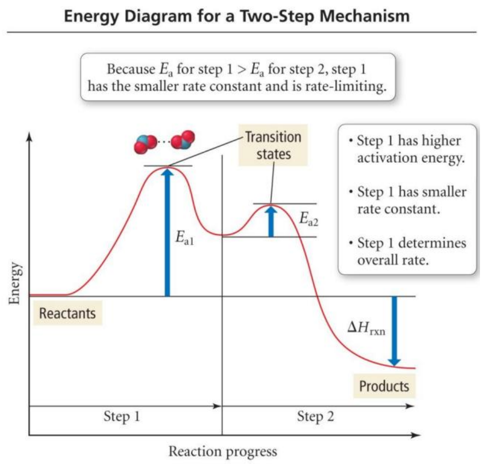
- $$-\frac{1}{a}\cdot\frac{\Delta[A]}{t} = -\frac{1}{b}\cdot\frac{\Delta[B]}{t} = \frac{1}{c}\cdot\frac{\Delta[C]}{t} = \frac{1}{d}\cdot\frac{\Delta[D]}{t}$$
- For instantaneous rates, ΔX becomes dX
- If the reaction is quick (less than an hour) ROR can be measured continuously
  - Otherwise, sampling mixtures at intervals can be done, stopping the reaction in the samples
- Continuous monitoring can be done via:
  - Polarimetry
    - Measuring change in polarization angle caused by difference in concentration of certain substances
  - Spectrophotometry
    - Measuring the amount of light of a particular wavelength that a substance absorbs
  - Total pressure
    - With gas reactions, partial pressures change
- For monitoring at intervals:
  - Aliquots are sampled and tested with:
    - Titration
    - Gravimetric analysis
  - Gas chromatography

Factors Affecting ROR

- Nature of reactants
  - Small molecules react faster than large ones
  - Gases react faster than liquids, that react faster than solids
  - Powders react faster than chunks
    - More surface area
  - Certain chemicals are more reactive than others
- Increasing temperature increases ROR
  - For many reactions, increasing temperature by $10°C$ doubles ROR
- Catalysts increase ROR without being consumed
  - Positive catalysts speed up reactions and negative catalysts slow them down
- Higher concentration means more frequent collisions between particles and therefore faster ROR
- Rate law:
  - $aA + bB \rightarrow Products$
  - $Rate = k[A]^n[B]^m$
    - n, m are the orders for each reactant
    - k is the rate constant
    - These are determined experimentally
  - Method of initial rates finds these values by testing different concentrations and their initial ROR
- For decomposition of N_2O_5 and NO_2
  - $ROR = k[A]^n$
  - $n = 1$ for N_2O_5 → First order kinetics
  - $n = 2$ for NO_2 → Second order kinetics
- Exponent on each reactant is the order with respect to the reactant
- The sum of the exponents for all reactants is the order of the reaction
- Integrated rate law gives concentrations at any time after start of reaction
  - Zero-order reactions decrease in rate linearly
    - $ROR = -k$
    - $[A]_t = -kt + [A]_0$
  - First order exponentially
    - $ROR = k[A]$
    - $[A]_t = [A]_0e^{-kt}$
  - Second order inversely
    - $ROR = k[A]^2$
    - $[A]_t = \frac{[A]_0}{1+kt[A]_0}$

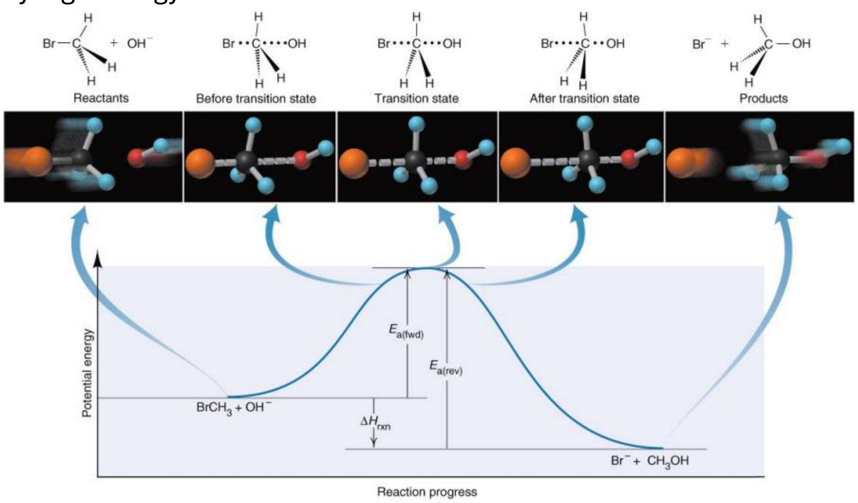
Reaction Mechanisms

- Most reactions occur in a series of small reactions
  - Describing this series is called a reaction mechanism

- A reaction can be autocatalytic, meaning that one of the products is a catalyst for the reaction
- Rate laws for each stem needs to be calculated separately
- In most mechanisms one step occurs slower than the other
  - This will determine the overall speed of the reaction
  - Rate determining step
  - Rate law of this step determines the rate law for the overall reaction
  - Rate determining step has largest activation energy
  - Rate of slowest step is the rate of the overall reaction
  - 

- At equilibrium of $A + B \rightleftharpoons C + D$
  - $k[A][B] = k'[C][D]$
  - $\therefore \frac{k}{k'} = \frac{[C][D]}{[A][B]} = K$
- $k = A\left(e^{-\frac{E_a}{RT}}\right)$
  - T is temperature in K
  - $R = 8.314K\ mol^{-1}K^{-1}$
  - A is a factor called the pre-exponential factor
  - E_a is the activation energy
- Reactions where $\ln k \propto \frac{1}{T}$ are said to show Arrhenius behaviour
- Collision theory: Particles must collide for a reaction to take place
  - Once they collide, they will react if:
    - The collision has enough energy to break the bonds required
    - The molecules collide in the correct orientation
  - These collisions are called effective collisions
  - Higher frequency of effective collisions means faster reaction
  - When two molecules have an effective collision, an unstable, high-energy chemical species is formed, called an activated complex or transition state
- For an endothermic reversible reaction, the activation energy for the forward direction is higher than for the reverse
- A (pre-exponent factor) is called the frequency factor
  - Number of molecules that can approach overcoming the energy barrier

- Two factors
  - Orientation factor (p)
  - Collision frequency factor (z)
- $A = pz$
- $k = A\left(e^{-\frac{E_a}{RT}}\right) = pze^{-\frac{E_a}{RT}}$

- The activated complex has half formed and half broken bonds
  - Very high energy
  - 

- Catalysts provide an alternative mechanism with a lower activation energy
- Cause of ozone depletion is emission of catalysts for the breaking down of ozone
- Homogeneous catalysts are in the same state as the reactants
- Heterogeneous catalysts are in a different state as reactants
- Platinum and palladium are the best catalysts for oxidations and rhodium is the best for reductions
- protein molecules that catalyse biological reactions are called enzymes