

CHEM 112 Fall Exam Guide

Atoms

Related Formulas

$$c = \lambda\nu$$

$$E = nh\nu$$

$$E_{EM} = \phi + \frac{1}{2}mu^2$$

$$r_n = n^2a_0$$

$$E_n = \frac{-R_H}{n^2}$$

$$\Delta E = \frac{-R_H}{n_{top}^2} - \frac{-R_H}{n_{bottom}^2} = R_H \left(\frac{1}{n_b^2} - \frac{1}{n_t^2} \right)$$

$$\lambda = \frac{h}{mu}$$

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

$$F = \frac{-Ze^2}{4\pi\epsilon_0 r^2} \text{ (effective nuclear charge)}$$

Definitions

c is the speed of light in a vacuum,
 $3.00 \times 10^8 \text{ m/s}$

λ is a wavelength

ν is the frequency of EMR

E is the energy of one quanta

n is an integer

h is Planck's constant, $6.626 \times 10^{-34} \text{ J s}$

ϕ is the binding energy (work function)

$\frac{1}{2}mu^2$ is the kinetic energy of the ejected
 electron

a_0 is Bohr's radius, 0.53 Angstroms

R_H is Rydberg Energy, $2.179 \times 10^{-18} \text{ J}$

m is the mass of a particle

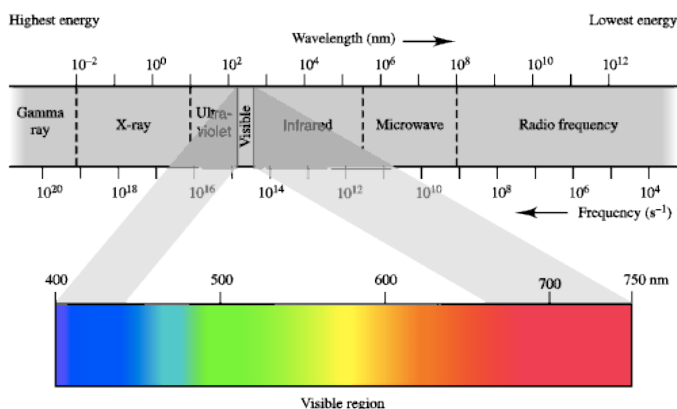
u is the velocity of a particle

Quantum mechanics refers to objects as particle and/or waves in which we cannot know positions and velocity exactly. Energy is transferred in discrete units. In chemistry, interactions between electrons and nuclei lead to chemical bond formation. If we want to understand chemistry, we must understand electrons and if we want to understand electrons, we must understand quantum mechanics.

Electromagnetic Radiation

Electromagnetic radiation refers to the oscillation of electric and magnetic fields through space and matter. These fields are perpendicular to each other and are in phase. This includes light, x-rays, infra-red, microwaves, etc. Electromagnetic waves are characterized by the following:

- Wavelength, λ : distance between two consecutive crests
- Frequency, ν : number of oscillations per second



In Blackbody radiation, the intensity is proportional to the number of possible waves multiplied by the probability that a wave is emitted. In classical mechanics, all waves are equally likely to be emitted, so as frequencies are higher, the intensity goes to infinity. This requires infinite energy and thus is wrong. If

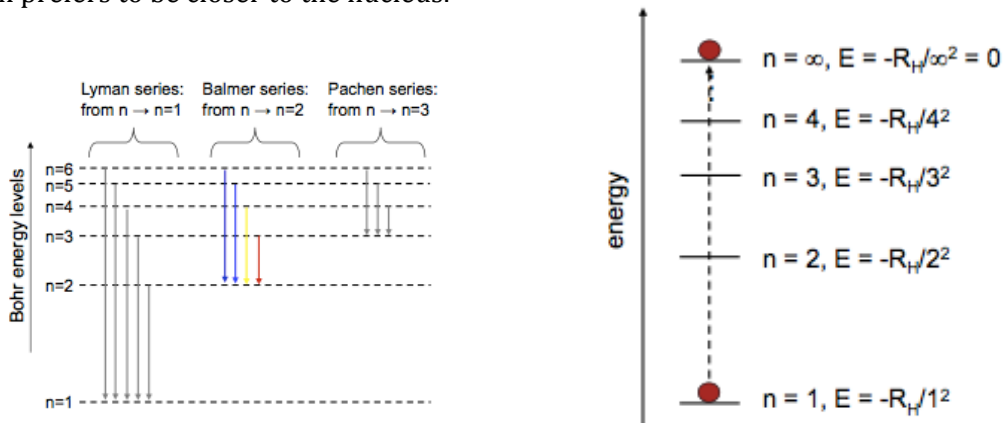
energy is transmitted in quanta, a systems energy can only be integer multiples of Planck's constant and the frequency, allowing discrete changes in energy called quantization.

Quantum theory dictates that in a quantized model, absorption and emission causes the system to jump between energy levels. The system's energy increases in amount of $nh\nu$ with energy input and decreases in amounts of $nh\nu$ with emission. The emitted electromagnetic wave has energy $nh\nu$. The quantized model predicts that a finite amount of energy is in the box and yields an intensity curve that matches the experimentally observed curve.

In the photoelectric effect, incoming electromagnetic waves deliver energy to electrons in the surface. If the electron's energy exceeds the energy binding it to the surface, it is ejected from the material.

Bohr Model of the Atom

Bohr suggested applying quantum theory to atoms. In his model, electrons move in circular orbits around the nucleus. There is only a fixed set of orbits that an electron can occupy. An electron can move between orbits by accepting or emitting fixed, discrete amounts of energy. This is quantization of the energy. Using various physical constants to determine the angular velocity of the electron, you can find the radius of each orbit. Lower energies mean the atom is more stable. Smaller n values correspond to smaller radii. Energetically, the electron prefers to be closer to the nucleus.



Each line represents an energy level associated with a particular orbit. The electron is normally in the $n=1$ state (ground state). To remove the electron from the atom, it has to 'move' to the $n=\infty$ through a process called **ionization**. Ionization energy is equal to the Rydberg energy and is always positive. Jumps between energy levels are called transitions and can be quantified. If an electron jumps up levels, the electron must absorb energy, called electron excitation. If an electron drops down levels, it must release energy, called electron relaxation.

The energy of the photon is equal to the difference in the energy levels. We can use absorption and emission spectra to determine the energy needed for electrons to jump between energy levels.

Wave Particle Duality

de Broglie asks if light waves can also be particles, can matter particles also be waves? Waves bend when they pass through slits, which lead to characteristic diffraction patterns, only a property of waves. Shooting electrons through a double slit screen showed the same pattern of diffraction.

Heisenberg's Uncertainty Principle

In general, we cannot know both the position and velocity of a particle with exact precision; there is always an error that exists.

Quantum Numbers

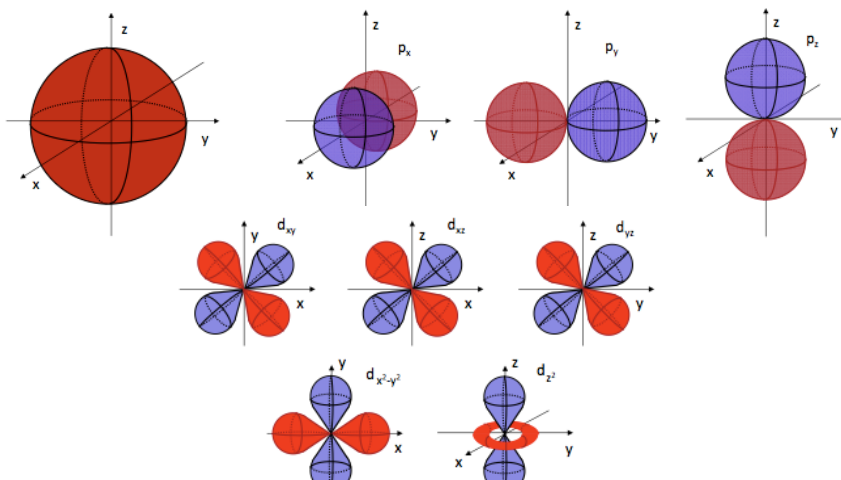
The radial function changes as we move from the nucleus, whereas the angular function describes how the wavefunction changes as we move around the nucleus.

- n is the principle quantum number
 - can take on positive integer values
 - determines the energy of the orbital
 - determines the most probable distance of finding an electron from the nucleus
- l is the angular momentum quantum number
 - determined by the value of n
 - can take on positive integer values from 0 to $n-1$
 - determines the shape of the orbital
- m is the magnetic quantum number
 - determined by the value of l
 - can take on integer values from $-l$ to l
 - determines the orientation of the orbital
- spin factors
 - either $\frac{1}{2}$ or $-\frac{1}{2}$
 - only one electron can occupy each spin factor

Each set of n , l and m is an orbital. All orbitals with the same value of n are in the same principle shell. All orbitals with the same values of n and l are in the same sub-shell. Each principle shell contains n sub-shells and n^2 orbitals. Each sub-shell contains $2l+1$ orbitals.

Multiple orbitals have the same energies, called degenerate orbitals. Their shapes are the only factor that differentiates them from each other.

Orbital Shapes



Pauli's exclusion principle states that in a system, two electrons cannot have the same set of quantum numbers. Atoms will try to minimize their energies by filling lowest energy orbitals first. If there are orbitals of identical energy, electrons initially occupy these orbitals singly (Hund's rule). Spin is assigned to maximize the total spin and all singly occupied orbitals should have the same spin. Filling orbitals according to these rules is called the aufbau process.

Periodic Table

The periodic table lists the elements in order of increasing atomic number. Increasing the number of protons and electrons in the previous element by 1 makes the next element in the periodic table.

Atomic Radii

- covalent radius: half the distance between two identical atoms that are bonded
- metallic radius: half the distance between two identical atoms in a metal
- ionic radius: part of the distance between nuclei in an ionic bond

The more shells in an element, the larger the radius. Thus, atomic radius increases as you go down a column in the periodic table. Atomic radius also decreases with higher effective nuclear charge. The size of the atom is a balance between nucleus-electron attraction and electron-electron repulsion.

Ionic Radii

Ions are atoms that have gained or lost electrons. Losing one or more electrons causes the ion to have a positive charge, called a cation. Gaining one or more electrons causes the ion to have a negative charge, called an anion. Atoms with higher maximum values of n have more electronic shells and thus are larger. Atoms with a higher effective nuclear charge attract the electrons more closely to the nucleus and decrease the size. The decrease in the maximum value of n causes the ionic radius to decrease. Many atoms lose all of the electrons in their outermost shell to form cations dropping n by 1. No atoms typically gain enough electrons to increase n by 1. Electron-electron repulsion helps us predict what happens when an atom gains or loses electrons without changing n . Anions have larger radii than their respective atoms because of the increased electron-electron repulsion. Cations on the contrary have smaller radii than their respective atoms because of the decrease in electron-electron repulsion. If two ions have the same number of electrons, but a different nuclear charge, they are **isoelectic**. In general, if two ions have the same electronic configuration, the ion with the high nuclear charge is smaller. **Ionization energy** refers to the amount of energy required to remove an electron from an atom in the ground state. First ionization energy is the amount to remove the first electron, whereas second ionization energy is the amount to remove the second most-weakly held electron. Ionization energy depends on both effective nuclear charge and value of n . A larger value of n means larger distance between nucleus and outer electron and thus weaker attraction. Ionization energy decreases left across the period and down the column.

Electron Affinity

The amount of energy emitted when an electron is added to an atom in the gaseous state is termed **electron affinity**. A strong electron affinity (more negative value of EA) means the added electron is attracted strongly to the nucleus. Electron affinity increases with effective nuclear charge and decreases with radius, thus electron affinity decreases to the left across the period and down a column.

Chemical Bonding

A chemical bond is an interaction that holds two or more atoms together in a molecule. The valence electrons are very important for bonding interactions.

Lewis Dot Structures

1. Write atomic symbol.
2. Determine the number of valence electrons.
3. Place electrons as dots around atomic symbols.
 - a. Each dot represents one valence electron.
 - b. Dots are placed on each of four sides.
 - c. Single dots are placed first, paired only if there are more than 4 valence electrons.

Ionic bond: for one atom to accept an electron, another atom has to give up an electron. In most cases, ionic bonding does not lead to simple molecules. Typically, each positive ion is surrounded by several negative anions. For molecules, we are usually interested in cases where electrons are shared between atoms (**covalent bonding**).

Expanded Valence Table

Group	1	2	3	4	5	6	7	8
Standard valence	1,0	2,0	3,0	4,0	3,1	2,2	1,3	0,4
Expanded Valence	-	-	-	-	5,0	4,1	3,2	2,3
	-	-	-	-	-	6,0	5,1	4,2
	-	-	-	-	-	-	7,0	6,1
	-	-	-	-	-	-	-	8,0

**Expanded valences are only accessible for elements with n greater than 3.

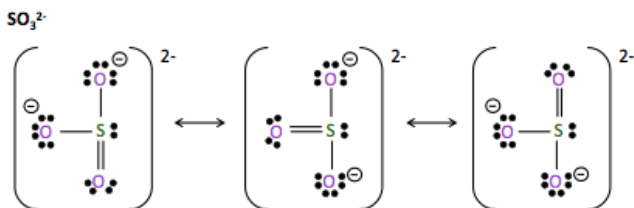
Lewis Dot Structures

1. Sketch out atomic positions.
 - a. Hydrogen atoms are always terminal atoms
 - b. Halogens are usually terminal atoms
 - c. C, Si ... N, P are usually central atoms
 - d. O, S ... can be terminal or internal atoms
2. Add bonds and lone pairs using standard valences.
3. If standard valences are not all satisfied, consider using expanded valences for atoms with n greater than 3.

In some molecules, individual atoms bear formal charges. These are charges assigned to individual atoms in a molecule. The sum of all formal charges in a molecule must equal the molecular charge. Formal charge can be calculated by the core charge minus the number of valence electrons.

4. If standard and expanded valences are not all satisfied, place formal charges on atoms.
5. If formal charges on any atom are -1, 0 or +1, you are probably OK. Otherwise, consider redoing the structure.

Resonance



Sometimes, more than one Lewis structure is correct. The actual structure is a combination of all the resonance structures. In resonance structures, the atomic positions don't change, but the bonds and electrons move. The most likely structure will have no formal charges.

Molecular Shapes

Related Formulae

$$\text{Bond order} = \frac{\# \text{ of bonding } e - \# \text{ of antibonding } e}{2}$$

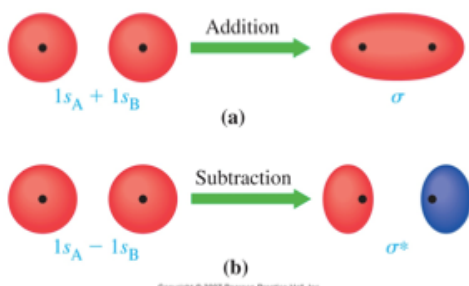
$$\mu = \delta d$$

Definitions

μ is the dipole moment

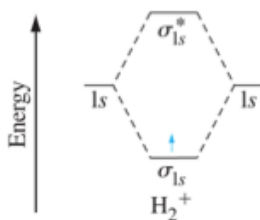
δ is the charge separation

d is the distance between atoms



Covalent bonds involve atomic orbitals containing unpaired electrons interacting with each other. Overlap indicates sharing. Atomic orbitals tell us how an electron is distributed in an atom – molecular orbitals tell us how electrons are distributed in molecules. Electron density between nuclei holds atoms together in bonds, this is called a **bonding orbital**. **Anti-bonding orbitals** decrease electron density between

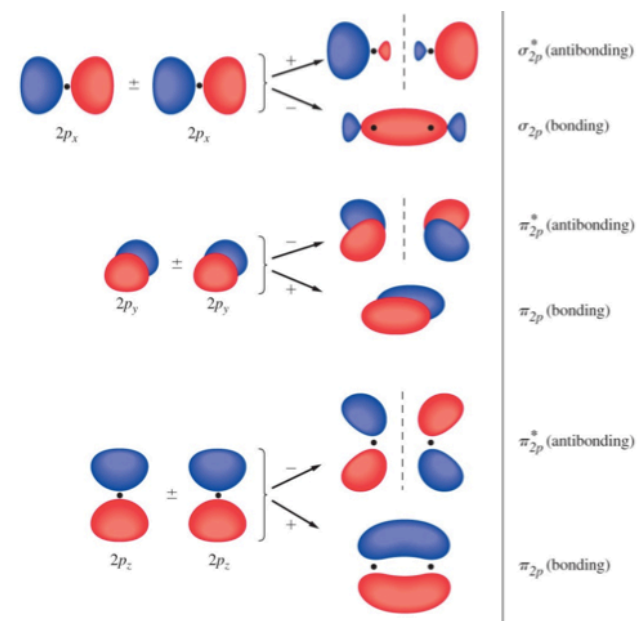
orbitals. Molecular orbital theory lets us predict many properties of molecules.



1. The number of molecular orbitals formed is equal to the number of atomic orbitals that are combined.
2. When two MOs are formed from two AOs, 1 MO is bonding and has a lower energy than the AOs and 1 MO is anti-bonding and has higher energy than the AOs.
3. In molecules, electrons go into the lowest energy MOs.
4. The maximum number of electrons that can go into an MO is 2 because of the Pauli exclusion principle.

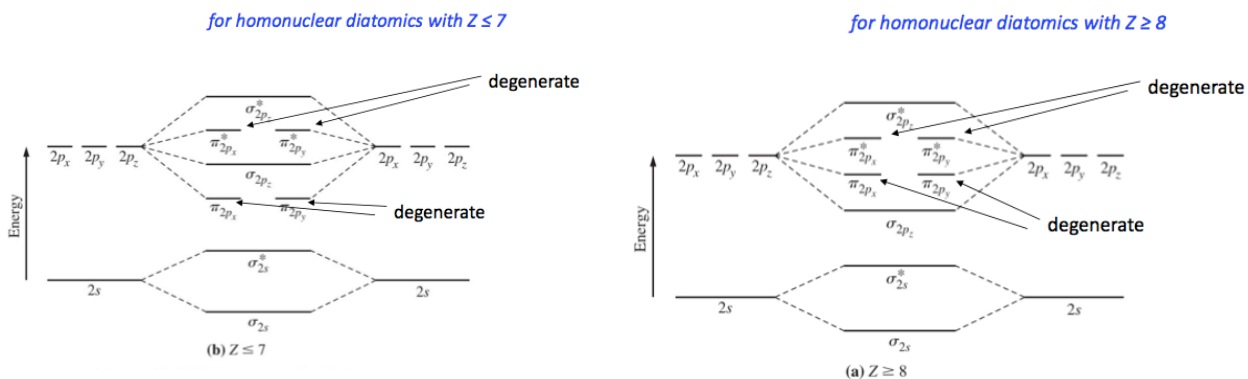
5. If two MOs have the same energy, each gets 1 alpha electron first, and the electrons are paired (Hund's rule)

With MOs, we define the bond order in terms of bonding and non-bonding orbitals.



Sigma vs. Pi Orbitals

In sigma orbitals, bonding involves atomic orbitals directed along line between atoms. This can occur between s orbitals or p orbitals. Pi orbitals involve atomic orbitals perpendicular to the line between atoms. This occurs only between p orbitals. In bonding orbitals, there are no nodes between atoms. In anti-bonding orbitals, there is at least one node between atoms.



Electronegativity and Dipole Moments


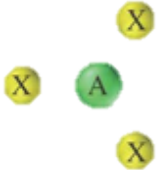


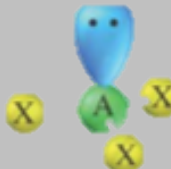
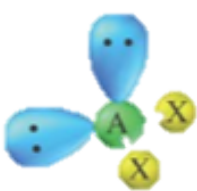
To share electrons, each atom must partially give up an electron and partially accept one. Whichever electron 'wants' electrons the most, gets more of the shared electron density. **Electronegativity** is the ability of an atom in a bond to attract electron density to itself. In a bond, the atom with the larger electronegativity bears a slightly negative charge. The larger the difference, the larger the charge separation. A **dipole moment** is a property exhibited by molecules that have a charge separation. A vector pointing toward the more negative atom represents it. Only bonds with charge separation exhibit a dipole moment, which has units of Coloumb meter. Molecules with large molecular dipole moments are called **polar**

molecules. Molecules with small molecular dipole moments are called **non-polar molecules.**

- **Bond length:** distance between atoms at the potential energy minimum
- **Bond energy:** energy required to break the bond
- **Bond order:** a measure of the number of electrons shared between bonded atoms

VSEPR

Electron pairs repel each other and can be found in bonds or in lone pairs. Electron pairs assume orientations to minimize electron repulsions.

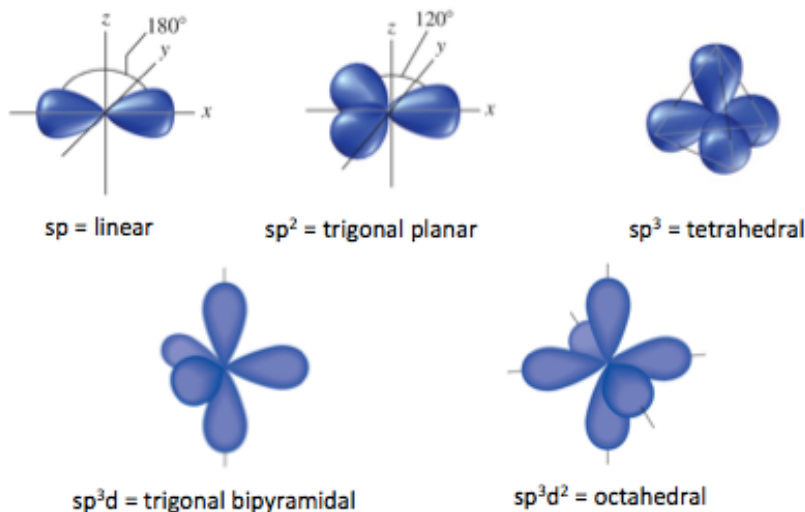
Number of Electron Groups	Electron Group Geometry	Number of Lone Pairs	VSEPR Notation	Molecular Geometry	Ideal Bond Angles (degrees)	Diagram
2	Linear	0	AX_2	Linear	180	
3	Trigonal planar	0	AX_3	Trigonal planar	120	
	Trigonal planar	1	AX_2E	Bent	120	
4	Tetrahedral	0	AX_4	Tetrahedral	109.5	
	Tetrahedral	1	AX_3E	Trigonal Bipyramidal	109.5	
	Tetrahedral	2	AXE_2	Bent	109.5	

5	Trigonal Bi-pyramidal	0	AX_5	Trigonal Bi-pyramidal	90, 120	
	Trigonal Bi-pyramidal	1	AX_4E	Seesaw	90, 120	
	Trigonal Bi-pyramidal	2	AX_3E_2	T-shaped	90	
	Trigonal Bi-pyramidal	3	AX_2E_3	Linear	180	
6	Octahedral	0	AX_6	Octahedral	90	
	Octahedral	1	AX_5E	Square pyramidal	90	
	Octahedral	2	AX_4E_2	Square-planar	90	

Hybridization

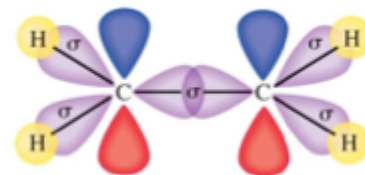
Combining the s and p orbitals to form sp^3 orbitals is called **hybridization**. Four hybrid orbitals point toward the corners of a tetrahedron. 1 hydrogen atom can interact with 1 sp^3 orbital.

Combining an s orbital and 2 p orbital gives sp^2 and leaves 1 normal p orbital. Combining an s orbital and a p orbital gives sp and leaves 2 normal p orbitals. Combining 1 s, 3 p and 1 d gives an sp^3d hybrid that can accommodate 5 electrons. 1 s, 3 p and 2 d combined gives a sp^3d^2 orbital that can accommodate 6 electrons.



Identifying Bond Types

Sigma bonds correspond to single bonds and one of the lines in multiple bonds. They involve hybrid orbitals on two different atoms. Pi bonds are the extra lines in multiple bonds and involve p orbitals on two different atoms.



Polymers

Chain Reaction Polymerization

1. Initiation: Bonds are broken to form radical species with lone pairs.
2. Propagation: Radical species react with organic compounds to produce more radical species.
3. Termination: Radical species react with other radical species to form stable polymers.

Step-Reaction Polymerization

Step-reaction polymerization refers to a type of polymerization mechanism in which bi-functional or multifunctional monomers react to form first dimers, then trimers, longer oligomers and eventually long chain polymers. Many naturally occurring and some synthetic polymers are produced by step-growth polymerization, e.g. polyesters, polyamides, polyurethanes, etc. Due to the nature of the polymerization mechanism, a high extent of reaction is required to achieve high molecular weight.

Stereospecific Polymers

- Atactic polymer: lack of order, random placement of side groups
- Isotactic polymer: side groups are ordered all one side of the molecule

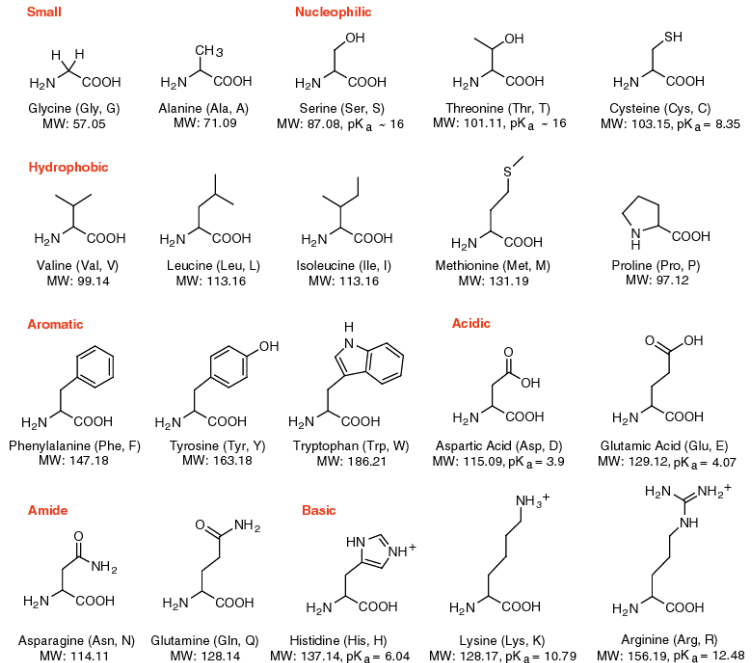
- Syndiotactic polymer: order as well, but slightly different than isotactic in that side groups are alternating

Proteins

Nucleic acids include deoxyribonucleic acid and ribonucleic acid. Zwitter ions contain isoelectric points. The amine is protonated in acidic solution, neutral at its isoelectric point and the deprotonated amine end is present in basic solutions.

A peptide bond forms between amino acids to form proteins.

- Primary structure: the order of the amino acids in the protein sequence
- Secondary structure
 - Alpha helix: hydrogen bonding between side chains of amino acids
 - Beta pleats: another secondary structure
- Tertiary structure: complex and irregular folding of the peptide chain in three dimensions
- Quaternary structure: describes the interactions between different peptide chains that make up the protein



Liquids and Solids

Related Formulae

$$\Delta H_{vap} = H_{vapour} - H_{liquid} = -\Delta H_{condensation}$$

$$\ln \frac{P_2^*}{P_1^*} = -\frac{\Delta H_{vap}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \text{ (Clausius-Clapeyron equation)}$$

Van der Waals forces describe a collection of weak attractive forces that exists in atoms or molecules. Displacement of electrons cause polarization giving rises to an instantaneous dipole. This dipole can affect neighbouring molecules causing induced dipoles. In a smaller surface area, there exists less LDF and thus branched molecules have lower boiling points than straight chains.

- Cohesive forces: intermolecular forces between like molecules
- Adhesive forces: intermolecular forces between unlike molecules
- Surface tension: energy or work required to increase the surface area of a liquid
- Viscosity: a liquid's resistance to flow

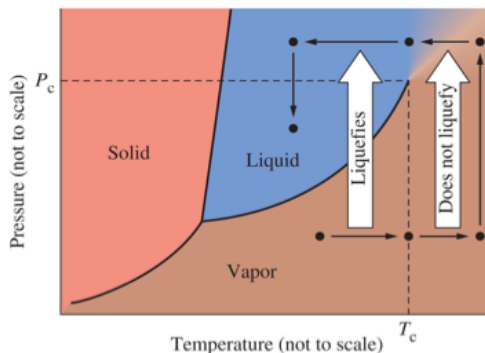
- The stronger the intermolecular forces of attraction, the greater the viscosity. Cohesive forces within the liquid create an internal friction that resists flow.

Vapour Pressure

Increasing temperature, surface area and decreasing intermolecular forces will all cause the likelihood of a liquid to vapourize increase. Vapour pressure refers to the pressure exerted by vapour at this point of equilibrium whereby the rates of evaporation and condensation are equal. Although vapour pressure is independent of volume, it does depend on temperature and increases with temperature increase. This is because as temperature increases, the fraction of molecules with sufficient energy to break the intermolecular forces holding them in liquid phase increases.

Phase Changes

Apply heat to a material at a constant rate and as it reaches a phase change, temperature remains constant even though heat is still being applied. This heat supplied is being used to break intermolecular forces to overcome the phase barrier. Melting involves little breaking of intermolecular forces and is more affected by 'unpacking' of the solid structure. **Entropy** is a measure of disorder or randomness in a system. The 2nd Law of Thermodynamics states any spontaneous change is accompanied by an overall increase in entropy. When boiling, liquids will begin to change phase at the temperature in which atmospheric pressure is equivalent to vapour pressure. Liquids with higher intermolecular forces will have higher boiling points. Bubbles can only start forming around 'nucleation points'. Without these, the rate at which heat is absorbed from the heating element may outstrip the rate at which heat can be given off by evaporation leading to **superheating**.



Phase diagrams can be helpful in aiding visualization of the phase changes. The point where solid, liquid and gas phase lines intersect is called the **triple point**. Where the liquid-gas barrier disappears is called the **supercritical point**.

Thermodynamics

Relevant Formulae

$$E_k = \frac{1}{2}mv^2 \text{ (measured in J)}$$

$$w = fd$$

$$q = mc\Delta T = C\Delta T$$

$$q_{\text{system}} = -q_{\text{surroundings}}$$

$$S = k\ln W$$

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T}$$

$$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right) = nR\ln\left(\frac{P_1}{P_2}\right); T \text{ is constant}$$

$$\Delta S_{\text{sys}} = \frac{\Delta H_{\text{vap}}}{T_{\text{vap}}}$$

$$\Delta S = nC_p \ln\left(\frac{T_2}{T_1}\right) \text{ where } P \text{ is constant}$$

$$\Delta S = nC_v \ln\left(\frac{T_2}{T_1}\right) \text{ where } V \text{ is constant}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G = \Delta H^\circ - T\Delta S$$

$$S = S^\circ - R\ln(P)$$

$$\Delta G = \Delta G^\circ + RT\ln(Q)$$

$$\Delta H^\circ = \sum v_p \Delta H_f^\circ(\text{products}) - \sum v_r \Delta H_f^\circ(\text{reactants})$$

$$\Delta S = \sum v_p S^\circ(\text{products}) - \sum v_r S^\circ(\text{reactants})$$

$$\Delta G^\circ = -RT\ln(K_{eq})$$

$$\ln\left(\frac{K_{eq2}}{K_{eq1}}\right) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \text{ (Van Hoff't)}$$

Definitions

q is the quantity of heat

c is the specific heat capacity

C is the heat capacity

T is the temperature

v_p is the stoichiometric co-efficient of a product

v_r is the stoichiometric co-efficient of a reactant

S is entropy

H is enthalpy

k is the Boltzmann constant; the gas constant per molecule

W is the microstates; the particular way in which particles are distributed amongst the states

C_v is the constant volume

C_p is the constant pressure

G is Gibbs' free energy

Q is the reaction quotient

K_{eq} is the equilibrium constant

The Law of Conservation of Energy states that in interactions between a system and its surroundings, the total energy remains constant: energy is neither created nor destroyed.

- **Energy, U:** the capacity to do work
- **Work, w:** force acting through a distance
- **Kinetic energy, KE:** the energy of motion
- **Potential energy, V:** the stored energy that has potential to do work; associated with forces of attraction or repulsion; energy due to condition, position or composition
- **Thermal energy:** kinetic energy associated with random molecular motion; in general proportional to temperature
- **Calorie:** the quantity of heat required to change the temperature of one gram of water by one degree Celsius
- **Heat capacity:** the quantity of heat required to change the temperature of a system by one degree
 - **Specific heat capacity:** system is one gram of substance
 - **Molar heat capacity:** system is one mole of substance
 - Heat capacity = mass of system x specific heat
- **Chemical energy:** contributes to the internal energy of a system
- **Heat of reaction, q_{rxn} :** the quantity of heat exchanged between a system and its surroundings when a chemical reaction occurs within the system at a constant temperature
- **Function of state:** any property that has a unique value for a specified state of a state
- **Path-dependent functions:** the path from an initial state to the final state is crucial; each part, or segment of the path to the final state is necessary to take into account
- **Standard enthalpy of reaction, ΔH° :** the enthalpy change of a reaction in which all reactants and products are in the standard states
- **Standard state:** the pure element or compound at a pressure of 1 bar and the temperature of interest

- **Standard enthalpy of formation, ΔH_f :** the enthalpy change that occurs in the formation of one mole of substance in the standard state from the reference forms of the elements in their standard states; ΔH_f of a pure element is 0
- **Entropy, S :** a measure of the degree of randomness or disorder in a system; the probability that a certain state will exist
- **Gibbs free energy:** state function that can predict spontaneity of reaction without calculations for surroundings

Bomb Calorimetry

A bomb calorimeter is a type of constant-volume calorimeter used in measuring the heat of combustion of a particular reaction. Bomb calorimeters have to withstand the large pressure within the calorimeter as the reaction is being measured. Electrical energy is used to ignite the fuel; as the fuel is burning, it will heat up the surrounding air, which expands and escapes through a tube that leads the air out of the calorimeter. When the air is escaping through the copper tube it will also heat up the water outside the tube. The temperature of the water allows for calculating calorie content of the fuel.

$$q_{cal} = C_{cal}\Delta T$$

Coffee-Cup Calorimetry

A coffee cup calorimeter is essentially a polystyrene (Styrofoam) cup with a lid. The cup is partially filled with a known volume of water and a thermometer is inserted through the lid of the cup so that its bulb is below the water surface. When a chemical reaction occurs in the coffee cup calorimeter, the water absorbs the heat of the reaction. The change in the water temperature is used to calculate the amount of heat that has been absorbed (used to make products, so water temperature decreases) or evolved (lost to the water, so its temperature increases) in the reaction.

$$q_{rxn} = -q_{cal}$$

Gibbs' Free Energy

- If $\Delta G_{sys} < 0$ the process is spontaneous
- If $\Delta G_{sys} = 0$ the process is at equilibrium
- If $\Delta G_{sys} > 0$ the process is non-spontaneous

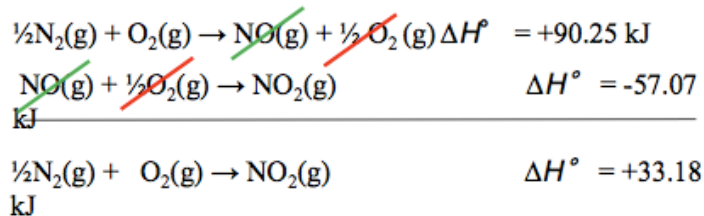
Laws of Thermodynamics

0. If two systems are in thermal equilibrium with a third system, they must be in thermal equilibrium with each other
1. A system only contains internal energy. A system does not contain heat or work. These only occur during a change in the system. $\Delta U = q + w$
 - a. Internal energy can be translational kinetic energy, molecular rotation, bond vibration, intermolecular attractions, chemical bonds, and electrons.
 - b. An isolated system is unable to exchange either heat or work with its surroundings, so we can say that the energy of an isolated system is constant
2. The entropy of any isolated system cannot decrease. Such systems spontaneously evolve towards thermodynamic equilibrium — the state of maximum entropy of the

system. Equivalently, machines that violate the second law (perpetual motion machines) are impossible.

- a. $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$
 - b. all spontaneous processes produce an increase in the entropy of the universe
3. The entropy of any pure substance in thermodynamic equilibrium approaches zero as the temperature approaches zero. The entropy of a system at absolute zero is typically zero, and in all cases is determined only by the number of different ground states it has.

Hess' Law of Constant Heat Summation



If a process occurs in stages or steps (even hypothetically), the enthalpy change for the overall process is the sum of the enthalpy changes for the individual steps.

Spontaneous Change

A spontaneous reaction is one that occurs by itself, given enough time, without outside intervention. If a reaction is spontaneous in one direction, it will be non-spontaneous in the reverse direction. When the driving force or tendency for spontaneous change is expended, equilibrium is established. At equilibrium, what can happen has happened. Entropy provides the basis for predicting the direction of spontaneous change. The direction of spontaneous change, from an energy point of view, is often from a higher to a lower energy, but not always. The greater the numbers of arrangements of the microscopic particles amongst the energy levels in a particular state of a system, the greater the entropy of the system. Entropy can be increased when pure liquids or solutions are formed from solids, gases are formed from solids or liquids, the number of molecules of gas increases as a result of a chemical reaction, or the temperature increases.