Atomic structure

July 7, 2021 5:00 PM

Atomic mass

- u is atomic mass and is equal to $\frac{1}{12}$ mass of $^{12}_{6}C$.
- Proton has mass $1u$, charge $+1$.
- Neutron has mass $1u$, charge 0.
- Electron has mass $0.0005u$, charge -1.

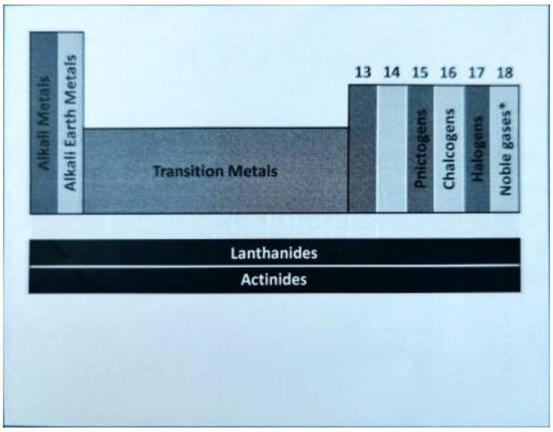
Valence electrons

- Th number of electrons in the s and p subshells of the occupied electronic shell with the largest n for the neutral element
- This shell is the valence shell
- Valence electrons are involved in the formation of bonds
- Hydrogen only has one valence electron, no core electron
- Iso-valent: have the same amount of valence electrons (same column in the periodic table)

Notation:

- $^{A}_{Z}E$
- A is the mass number = #protons + #neutrons.
- Z is the atomic number = #protons
- E is the atomic symbol

Periodic table

- 

- s, d, p, f depend on the electrons
- Columns are called groups - similar properties
- Rows are called periods
- Alkali metals lose the valence electrons easily
- Transition metals
    - Some give up more electrons
    - Some give up 1 electron only

Quantum mechanical model

- Position of an electron in an atom cannot be known with absolute certainty
- The position of an electron in an atom is presented as a probability distribution

Atomic orbitals

- Atomic orbital are the wave representation of electrons in an atom
- Depiction of a region in space where the electron can be found in high probability
- Orbitals can have different sizes, shapes and orientation in space

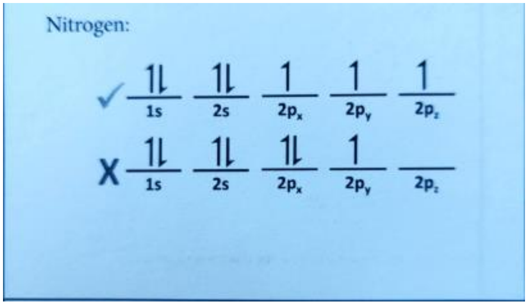
Electronic configurations

- Used to describe different electrons in an atom or ion
- Aufbau principle: Electrons will fill the orbital with the lowest energies possible
- Pauli exclusion principle: there can only be up to two electrons per orbital
- Rules and steps
    - Locate the element in the periodic table noting the period that the element is in (n) and the block (s, p, d, f)
    - Identify the noble gas in the previous period ($n-1$) and write its symbol in square brackets
    - Starting from the left hand side of the periodic table in period n, write the occupancies of the valence electrons until the element is matched
    - For ionic species or the s or p blocks, add or subtract from the configuration for the neutral atom

Ionization of transition metals

- When transition metals form cations, electrons are removed from the s-orbital before removing electrons from the d-orbital
- E.g. Ti: $[Ar]4s^2 3d^2$, Ti^{2+}: $[Ar]3d^2$.

Orbital diagram notation

- Solid horizontal line represents each orbital
- Electrons are represented by arrows
- In an s-orbital, one electron is represented by an up-arrow (spin-up) and the other electron is represented by a down-arrow (spin-down)
    - No two arrows pointing in the same direction in the same orbit
- 3 types of p-orbitals. Each type can hold up to two electrons
    - Electrons are left unpaired if possible
- 

Simple atomic model (Bohr model)

- Let n be the shell number
- The maximum number of electrons in a particular orbit: $\#e_n^- = 2n^2$.
- Shells and subshells
    - $n = 1$, sub-shells s, $\#e_n^- = 2$.
    - $n = 2$, sub-shells s, p, $\#e_n^- = 8$.
    - $n = 3$, sub-shells s, p, d, $\#e_n^- = 18$.
    - $n = 4$, sub-shells s, p, d, f, $\#e_n^- = 32$.
- Electrons travel in perfectly defined orbits around the nucleus
- Energy is quantized (discrete energy level)
    - Electrons can only exist on shells
- Excellent at predicting energy of one electron species
    - $E = -2.718 \times 10^{-18} J \times Z^2 \left(\frac{1}{n^2}\right)$.
    - The further the electron is from the nucleus, the less the electrons feel the positive charge, the less energy it has
- Electron excitation
    - An electron in low-energy orbit n_i can be excited to a higher energy orbit n_f.
    - When an electron is excited, it absorbs energy equal to the energy difference between n_f and n_i.
    - $\Delta E = E_{n_f} - E_{n_i}$.
    - Relaxation is reverse process

Energy and light

- $E_{light} = \frac{hc}{\lambda} = hf.$
- One way in which color arises is through absorbance
    - White light travels through a sample containing atoms or molecules that absorb light of only a given wavelength (color)
    - Light with wavelength corresponding to energy difference between orbits will be absorbed
- Emission
    - When atoms in the gas phase are excited, they relax emitting light of wavelength equal to the energy difference between the orbits

Effective nuclear charge Z_{eff}.

- For multi-electron atoms
- $E \propto \frac{q^+q^-}{r}.$
- Let Z be the total number of protons, S be the number of core electrons.
- $Z_{eff} \sim Z - S.$

Atomic radius

- Calculated by measuring the internuclear distance of a homonuclear diatomic molecule and dividing by 2
- Its cation M^+ is always smaller than the neutral species.
- Its anion N^- is always larger than the neutral species.
- Isoelectronic species
    - Atoms, ions with the same number of electrons
    - The atom or ion with the largest atomic or ionic radii is the most negative atom

Ionization energy (IE)

- The energy required to remove a single electron from an atom or ion in its gaseous state
- $X(g) \rightarrow X^+(g) + e^-.$
- Atoms are not interacting with neighboring atoms in gas state
- IE_1 is the first ionization energy
- Increases from left to right on the periodic table
    - $IE_1\ Be > IE_1\ Li$ because of higher Z_{eff}.
    - $IE_1\ Be > IE_1\ B$ because the adding electrons has higher energy and it is easy to pull off
- Decreases from top to bottom

Electron affinity (EA)

- The energy change that results from the addition of a single electron to an atom or ion in its gaseous state
- $X(g) + e^- \rightarrow X^-(g).$
- Electron affinity increases as we move to top right of the periodic table

Molecule

July 7, 2021 5:36 PM

Chemical bonding

- Ionic
- Covalent (polar or non-polar)
  - Small difference in electronegativity
- Metallic

Electronegativity (χ)

- The attraction of an atom for the shared electrons in a covalent bond
- Has exactly the same trend as electron affinity
- Increases as we move to top right of the periodic table
- Note that oxygen is more electronegative than chlorine.

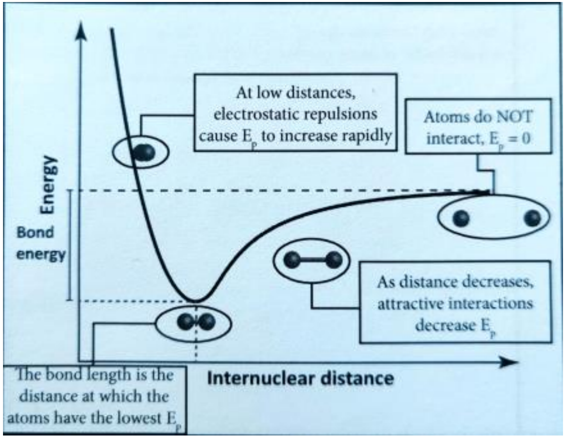
Ionic bonding

- Bonding through electrostatic attraction between oppositely charged ions
- Completely unequal sharing of electrons
- Occurs when the difference in electronegativities is large (≥ 1.7)

Lattice energy

- The energy required to convert one mole of crystalline solid into its constituent ions in the gas phase at infinite separation.
- $E \propto \frac{q^+q^-}{r} \, (kJ/mol)$.
  - Charge and distance matter
  - Charge matters more

Covalent bond

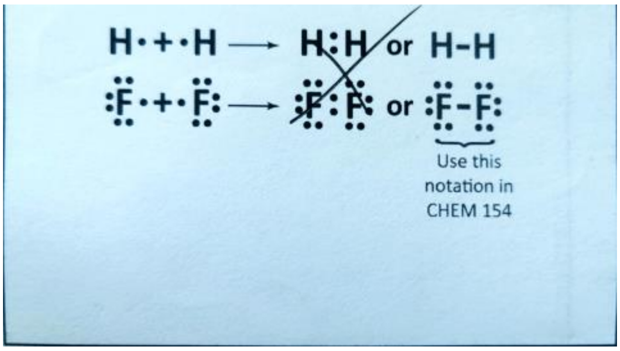
- Formed when a pair of electrons are shared between two atoms with no net electrical charge
- 

Bond energy

- The bond energy is the energy required to break a bond
- The larger the difference of the electronegativity, the higher the bond energy
- The higher the bond order (number of electron pairs shared by two bonded atoms), the higher the bond energy

Lewis structure

- Shows how valence electrons are shared in a molecule
- Valence electrons that form a bond are called bonding pairs
- Valence electrons that do not form a bond are called lone pairs

- 

- Octet rule: main group elements gain, lose, or share electrons to achieve a configuration in which they are surrounded by eight valence electrons
- Formal charge
    - The difference between the number of valence electrons and the number of electrons surrounding an atom in a particular Lewis structure
    - $F.C = \#ve^- - \#L.P.e^- - \frac{1}{2}\left(\#Bonding\ e^-\right)$.
        - $\#ve^-$: number of valence electrons.
        - $\#L.P.e^-$: number of lone pair electrons.
        - $\#Bonding\ e^-$: number of bonding electrons.
- Drawing
    - Count the number of valence electrons
    - Draw the skeletal structure of the molecule
        - The least electronegative atom is generally the central atom
        - Hydrogen is always a terminal atom
        - Unless told, do not form rings
    - Place two electrons in each bond of the skeletal structure
    - Place the remaining valence electrons not accounted for as lone pairs on individual atoms until the octet rule is satisfied
    - Form multiple bonds as needed to complete octets and account for all valence electrons
    - Label formal charges
        - Sum of F.C. is equal to the overall molecular charge
- Remember
    - Hydrogens are always terminal
    - The most stable Lewis structure is the one with the least non-zero formal charges
    - The most stable Lewis structure is the one that places the negative charge on the most electronegative atom and the positive charge on the least electronegative atom
- Exceptions (Incomplete octet)
    - Elements in group 13 follow a sextet rule (only three electron groups surrounding them)
    - E.g. BH_3.
- Exceptions (Hyper-valence/expanded octets)
    - Elements on the third row of the periodic table and below can expand their octets
    - E.g. PCl_5.
    - The octet rule will not be exceeded unless necessary to form bonds with more than four atoms or to minimize formal charges
    - Terminal atoms are not hypervalent

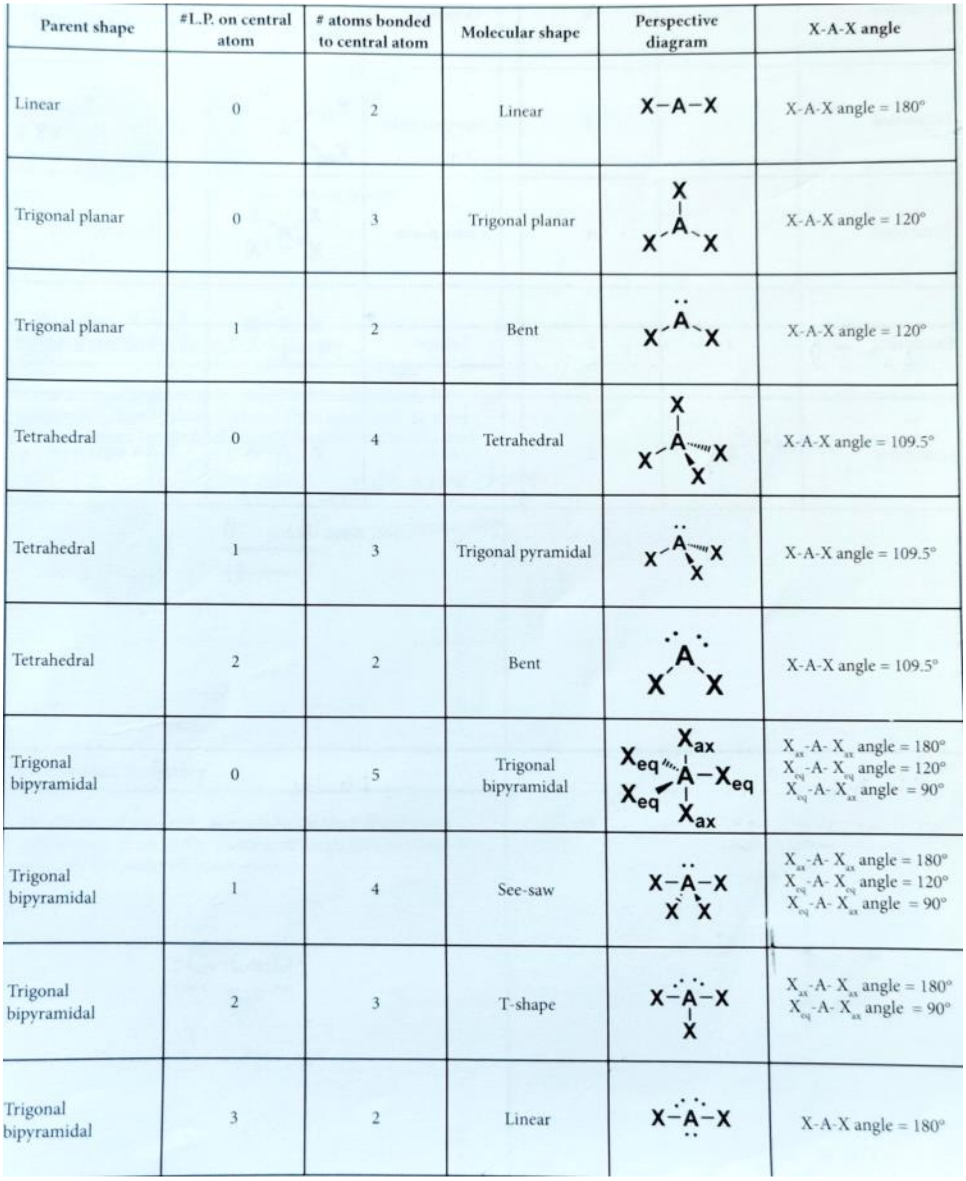
Resonance structures

- One of two or more individual Lewis structures that contribute to the resonance hybrid (actual structure of a molecule)
- Resonance structures differ from one another only in the placement of electrons, but all show the same arrangement of atoms themselves
- Partially represent the true nature of the bonding in a molecule
    - None of the resonance structures can be experimentally observed
- Drawing
    - Only electrons can be moved, nuclei never move
    - Total number of electrons in system is constant, total charge in system is constant
    - All structures should be proper Lewis structures

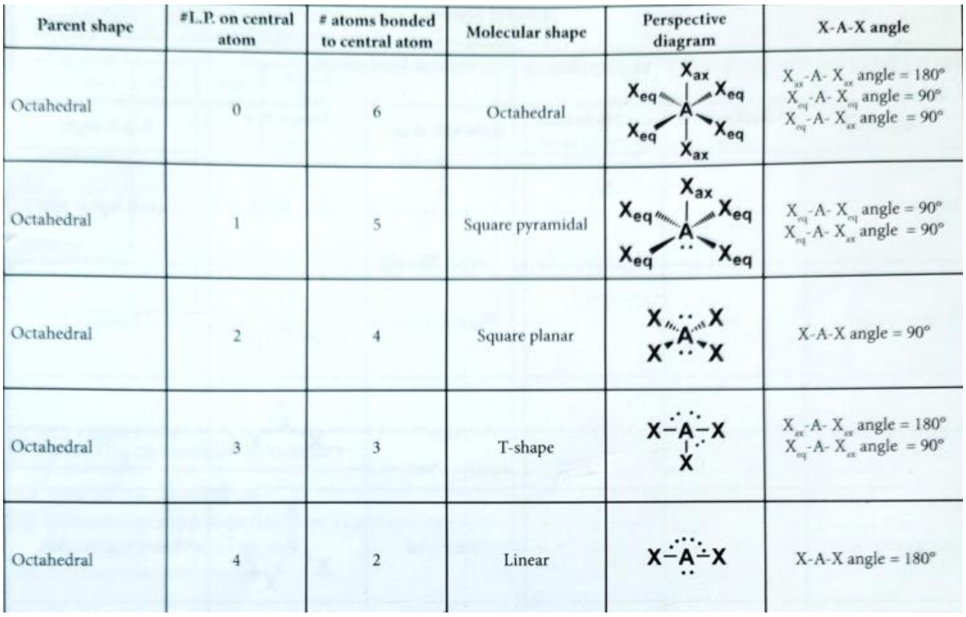
    - Look for lone pair and double-bond electrons
- Note
    - Do not put a negative formal charge on the central atom unless you absolutely have to
    - Never put a double bond on a halogen (VII A)
- Stability
    - Resonance contributors may not all have the same stability
    - Better Lewis structures will make a stronger contribution to structure of the resonance hybrid

Valence shell electron pair repulsion (VSEPR)

- A theory that predicts molecular shape by treating atoms in a molecule as point charges that are favored to be as far away from each other as possible
- Perspective diagram
    - Three dimensional representation of a molecule in space
    - Wedge bond represents an atom coming out of the plane of the molecule
    - Dash bond represents an atom going into the plane of the molecule
-



Parent shape	#L.P. on central atom	# atoms bonded to central atom	Molecular shape	Perspective diagram	X-A-X angle
Linear	0	2	Linear	X–A–X	X-A-X angle = 180°
Trigonal planar	0	3	Trigonal planar		X-A-X angle = 120°
Trigonal planar	1	2	Bent		X-A-X angle = 120°
Tetrahedral	0	4	Tetrahedral		X-A-X angle = 109.5°
Tetrahedral	1	3	Trigonal pyramidal		X-A-X angle = 109.5°
Tetrahedral	2	2	Bent		X-A-X angle = 109.5°
Trigonal bipyramidal	0	5	Trigonal bipyramidal		X_{ax}-A-X_{ax} angle = 180° X_{eq}-A-X_{eq} angle = 120° X_{eq}-A-X_{ax} angle = 90°
Trigonal bipyramidal	1	4	See-saw		X_{ax}-A-X_{ax} angle = 180° X_{eq}-A-X_{eq} angle = 120° X_{eq}-A-X_{ax} angle = 90°
Trigonal bipyramidal	2	3	T-shape		X_{ax}-A-X_{ax} angle = 180° X_{eq}-A-X_{ax} angle = 90°
Trigonal bipyramidal	3	2	Linear		X-A-X angle = 180°

- 

Parent shape	#L.P. on central atom	# atoms bonded to central atom	Molecular shape	Perspective diagram	X-A-X angle
Octahedral	0	6	Octahedral		X_{ax}-A-X_{ax} angle = 180° X_{eq}-A-X_{eq} angle = 90° X_{eq}-A-X_{ax} angle = 90°
Octahedral	1	5	Square pyramidal		X_{eq}-A-X_{eq} angle = 90° X_{eq}-A-X_{ax} angle = 90°
Octahedral	2	4	Square planar		X-A-X angle = 90°
Octahedral	3	3	T-shape		X_{ax}-A-X_{ax} angle = 180° X_{eq}-A-X_{ax} angle = 90°
Octahedral	4	2	Linear		X-A-X angle = 180°

Bond polarity
- Because of differences in electronegativity, electrons are never equally distributed when two different atoms bond
- This charge separation is known as a dipole
- Bonds with a dipole are called polar bonds
- An arrow pointing towards the most electronegative atom is used to show bond polarity
  - End of the arrow with the most electron density has the label δ^-.
  - The other end has the label δ^+.

Molecular polarity
- Depends on the three dimensional arrangement of atoms
- CO_2 is non-polar.
- Determining polarity
  - Draw VSEPR molecular shape of the molecule
  - Draw arrows to show bond dipoles for each bond in a molecule
  - Do a vector addition for each dipole drawn
  - If the vector addition is zero, the molecule is non-polar
  - If the vector addition is non-zero, the molecule is polar

Intermolecular forces
- London dispersion forces
- Dipole-dipole forces
- Hydrogen bonding
- Ion-dipole forces

London dispersion forces
- Dipole-induced dipole forces
- Due to momentary asymmetry of distribution of electron density
- Polarizability
  - The larger an atom is, the more polarizable it is, the larger the London dispersion force is
  - Higher boiling/melting points

Dipole-dipole interactions
- Arise from alignment of dipoles (sum of individual dipole vectors) in molecules
- Both interacting molecules must have dipoles

Ion-dipole interactions
- Solvation of ions
- Molecules orient to stabilize ionic charge

- $E \propto -\frac{|z|\mu}{r^2}$.
    - z is the charge of the ion.
    - μ is the dipole moment.
    - r is the distance between the ion and the molecule.

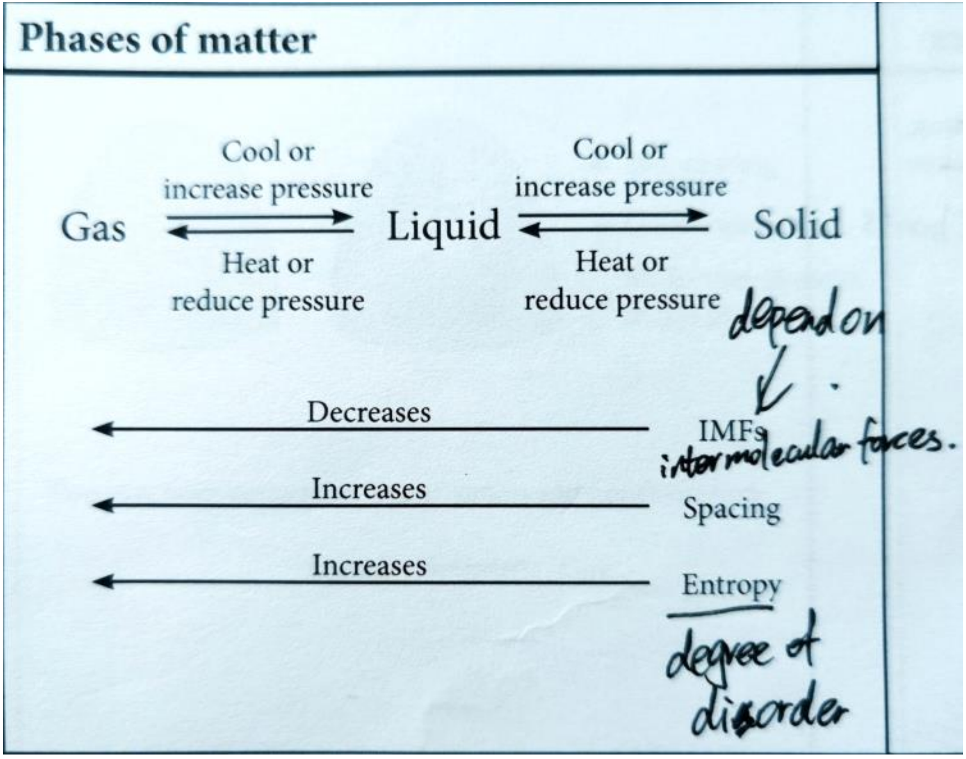
Hydrogen bonding

- Strong type of dipole-dipole forces present in molecules
- Hydrogen atom bonded to an electronegative atom (N, O, F)

Summary

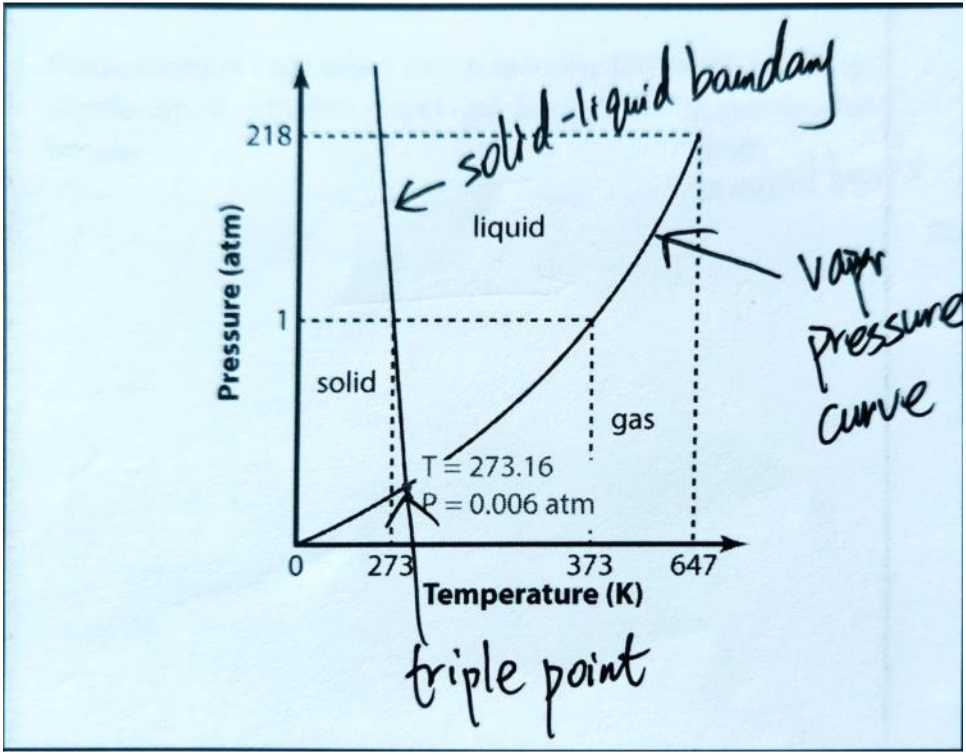
- London dispersion forces
    - Weak
    - Non-polar molecules which develop instantaneous dipoles
    - Strength increases as the number of electrons in the molecule increases (more polarizable)
    - E.g. I_2, Kr, PCl_5.
- Dipole-dipole interactions
    - Strong
    - Polar molecular which have a permanent dipole
    - E.g. PCl_3, ICl, CH_3Cl.
- Hydrogen bonds
    - Strong
    - Molecules in which H is bonded to a F, O, or N atom
    - The large electronegative difference and resulting permanent dipole are responsible for the strength of these forces
    - E.g. HF, H_2O.
    - In water: oxygen atoms in one molecule are attracted to hydrogen atoms in a neighboring water molecule to maximize electrostatic interactions

Phase

- Substance exist indifferent states: solids, liquids, gases
- Simple substance in its various states is called a one-component system (one pure chemical)
- Changes of the states are called phase changes
- 

- Molecules at the surface of a liquid have less neighboring molecules, thus have less IMF and can become vapor easily

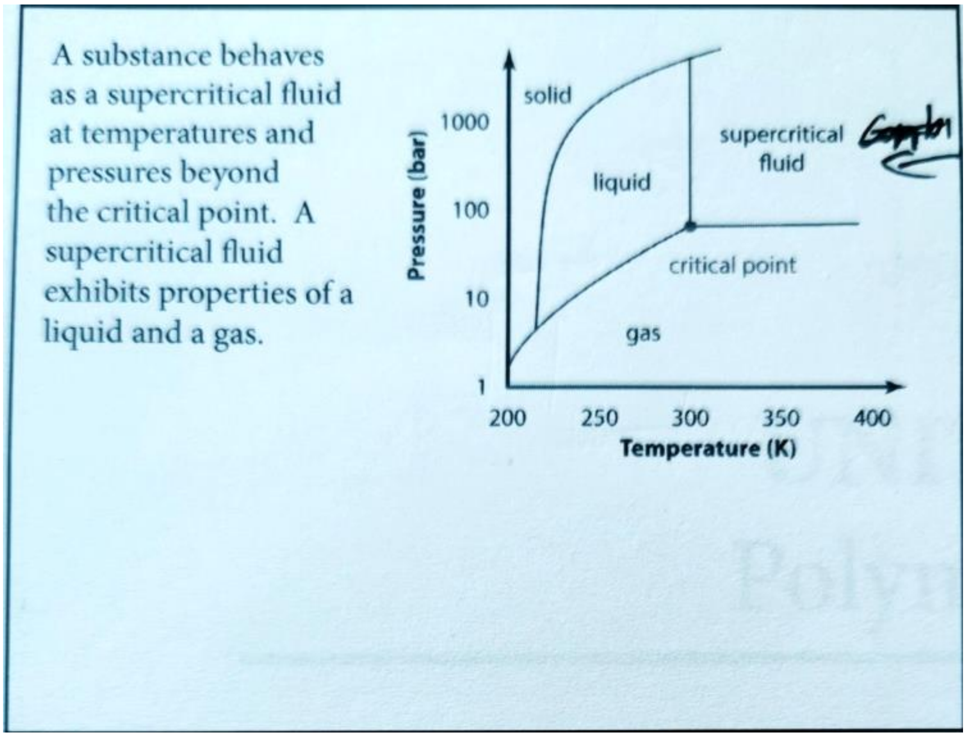
Vapor pressure

- Two process occurring: vaporization and condensation
- Vapor pressure of equilibrium is defined as the pressure exerted by a vapor in thermodynamic equilibrium with its condensed phases at a given temperature in a closed system
- The equilibrium vapor pressure indicates a liquid's evaporation rate
- Vapor pressure increases with temperature
- More molecules escape to gas phase
- Liquids boil when VP=atmospheric pressure
- 

Density and pressure

- If pressure is increased, the stable phase changes from a less dense to a more dense form

Supercritical fluids

- 

A substance behaves as a supercritical fluid at temperatures and pressures beyond the critical point. A supercritical fluid exhibits properties of a liquid and a gas.

- Combination of gas and liquid
- Lower density than gas
- Can dissolve things

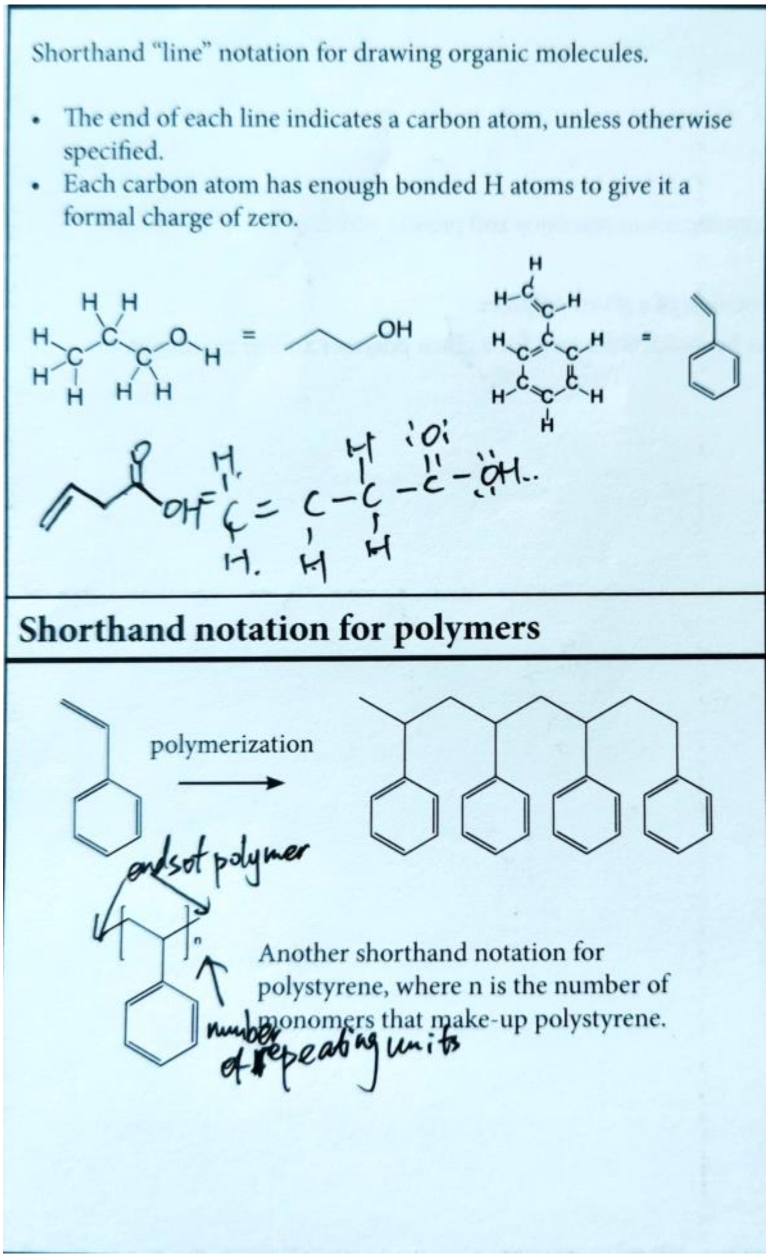
Polymers

July 7, 2021 6:45 PM

Polymers

- Macromolecule constructed by a sequential stringing together of smaller molecules called monomers

Shorthand notations

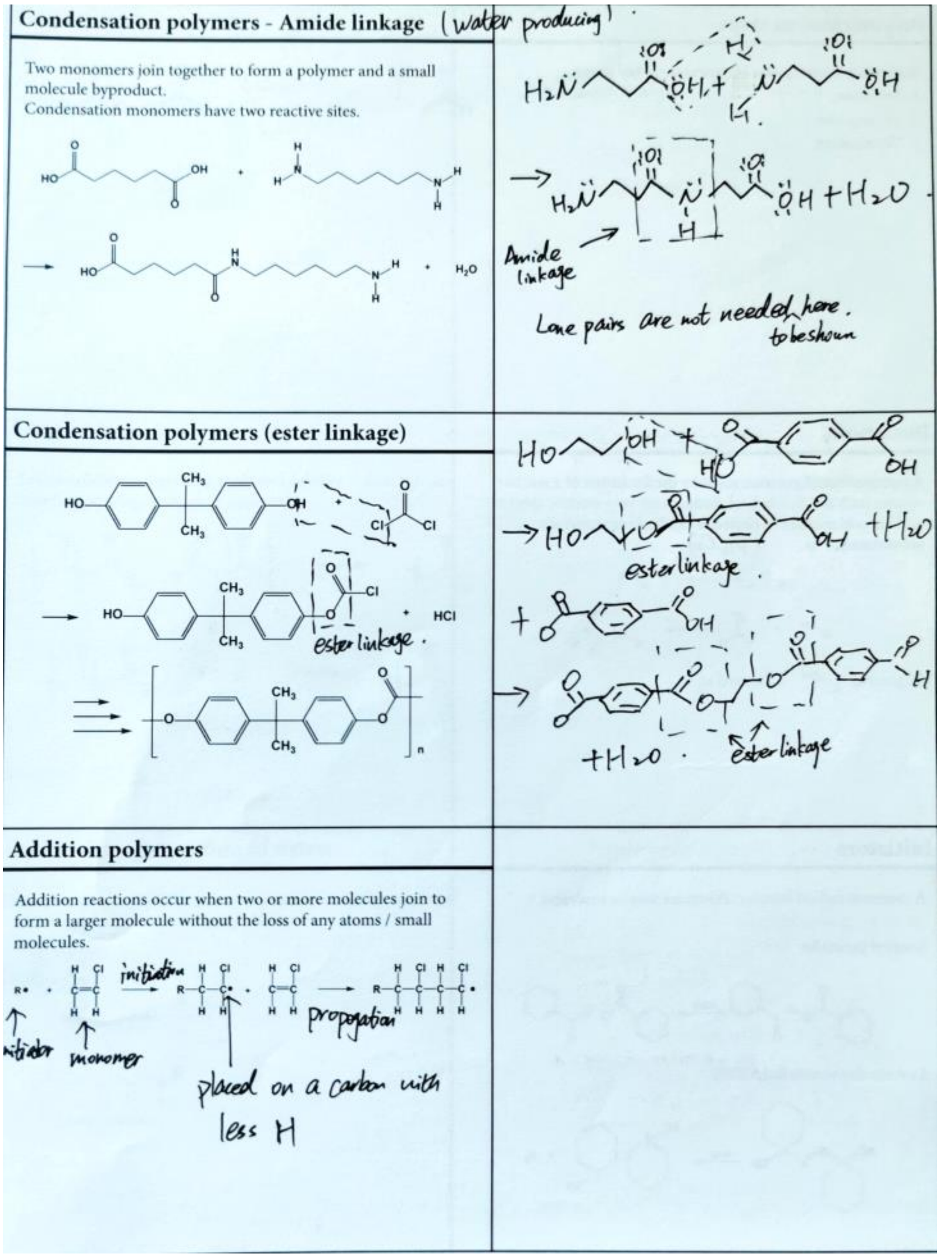


Shorthand "line" notation for drawing organic molecules.

- The end of each line indicates a carbon atom, unless otherwise specified.
- Each carbon atom has enough bonded H atoms to give it a formal charge of zero.

- **Shorthand notation for polymers**

Another shorthand notation for polystyrene, where n is the number of monomers that make-up polystyrene.



Condensation polymers - Amide linkage (water producing)

Two monomers join together to form a polymer and a small molecule byproduct.
Condensation monomers have two reactive sites.

Amide linkage

Lone pairs are not needed here. to be shown

Condensation polymers (ester linkage)

ester linkage.

ester linkage.

+H_2O ester linkage

Addition polymers

Addition reactions occur when two or more molecules join to form a larger molecule without the loss of any atoms / small molecules.

placed on a carbon with less H

Molecular weight distributions

- A synthetic polymer will have a range of chain lengths of differing molecular mass, or a mass distribution
- Differences in molecular weight affect solubility, strength, viscosity
- Number average molecular weight (M_n)
  - Average molecular weight of the mass distribution
  - $M_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$.
  - M_i: molecular weight.
  - N_i:number of polymer chains of a given mass.
- Weighted average molecular weight (M_w)
  - A weighted average of the molecular weight
  - It is affected by the largest polymers
  - It report on mass of ensemble of polymers
  - $M_W = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$.
- Molecular weight distributions
  - $M_w > M_n$.
  - $P(M < M_n) = \frac{1}{2}$.

Polydispersity (PDI)

- A measure of the breadth of the molecular weight distribution
- $PDI = \frac{M_w}{M_n}$.

Degree of polymerization (DP)

- A measure of the average number of repeat units in a chain
- $M_0 = MW$ of monomer.
- $DP_n = X_n = \frac{M_n}{M_0}$.

Molecular weight and mechanical strength

- When MW is below a certain point, the polymer has no mechanical strength
- As MW increases beyond that point, mechanical strength increases rapidly
- At a given chain length, the increase in MW does not significantly change the mechanical strength of the material
- Length of the polymer will affect properties
    - Mass
    - Branches
- Properties of a polymer
    - Stability
    - Fragility
    - Soft/hard
    - Toxicity
    - Response to temperature
    - Conductivity
    - Solubility
    - Transparency
    - Stretchiness
    - Biodegradability

Gases

July 7, 2021 6:56 PM

Useful constants

- Pressure
  - 1 atm=760 mmHg = 760 Torr = 101325 Pa.
  - 100000 Pa = 1 bar
- Gas constant
  - $R = 0.08206\, L\, atm\, mol^{-1}K^{-1} = 8.314\, J\, mol^{-1}K^{-1} = 62.37\, L\, Torr\, mol^{-1}K^{-1}$.
- Standard temperature: $T = 273.15K$.
- Standard pressure: $P = 1\ atm$.

Ideal gas law

- Gases at high temperatures and low pressures can be described by the ideal gas law
- $PV = nRT$.
- P: pressure.
- V: volume.
- n: number of moles.
- R: gas constant.
- T: temperature in K.

Dalton's law of partial pressures

- For a mixture of gases in a container, the total pressure exerted is the sum of the pressures that each gas would exert if it were alone
- $P_{total} = P_1 + P_2 + \cdots$.
- $P_{total}V = (n_1 + n_2 + \cdots)RT$.

Mole fraction (χ)

- Ratio of the number of moles of a given component in a mixture to the total number of moles of the mixture
- $\chi_1 = \frac{n_1}{n_{total}} = \frac{n_1}{n_1+n_2+\cdots}$.
- $\chi_1 = \frac{P_1}{P_{total}} = \frac{V_1}{V_{total}}$.

Kinetic molecular theory

- A gas is made up of vast number of particles which are in constant random motion
- Gas particles occupy no volume
- Gas molecules move in straight lines except when they collide with other molecules or with the walls of the container. These collisions are elastic
- Gas molecules interact with one another only when collisions occur
- Average KE of gas molecules is proportional to the temperature
- KE does not depend on gas identity

Kinetic energy and temperature

- The average kinetic energy increases as the temperature increases
- The identity of the gas affects the speed of the molecules

Real gases

- Ideal gases, assume no intermolecular interactions and zero volume for gas molecules
  - Most likely true for gases at low pressures and high temperature
- At low pressures, distance between particles is larger

Van Der Waals equation

- Takes into consideration the volume occupied by the gas atoms or molecules (b) and the interactions betweeen particles (a)

- a and b are determined experimentally
- $\left(P_{obs} + a\,\left(\frac{n}{V}\right)^2\right)(V - nb) = nRT.$

Energy & theromodynamics

July 8, 2021 4:37 PM

Thermodynamics: determine whether a reaction will happen

- If $\Delta G < 0$, it is spontaneous
- Energy changes in chemical and physical processes using heat and work
- A reaction that may be thermodynamically favored may still not occur due to kinetic reasons
  - Diamond to graphite.

Kinetics: determine the rate of the reaction

Free energy: internal energy of a system that can do work

Definitions

- Universe = system + surrounding
- System
  - Open: a system in which heat and matter can be exchanged with the surroundings
  - Closed: a system in which heat can be exchanged with the surroundings, but no matter can be exchanged
  - Isolated: a system in which neither heat nor matter can be exchanged with the surroundings
- Extensive properties
  - Scale with the size (quantity) of the system
  - E.g. mass, volume
- Intensive properties
  - Do not scale with the system
  - E.g. density
  - The ratio of two extensive properties is an intensive property

Internal energy (U)

- Kinetic energy
  - Translational
  - Rotational
  - Vibrational
- Potential energy
  - Bond energies
  - Intermolecular interactions
  - Potential energy is more substantial

Heat (q)

- The flow of energy from one body to another
- Heat always flow from a hot object to a cold object (not the reverse)

Work (w)

- The transfer of energy that doesn't rely on a temperature difference
- Mechanical, electrical
- Work in a chemical reaction
  - $w = -P_{ext}\Delta V$.
  - $\Delta \mathrm{V} > 0$, expansion, work done by the system
  - $\Delta \mathrm{V} < 0$, contraction, work done on the system
  - Only valid at constant pressure

State function

- Only depends on where you started and where you finished, not on the path

- Changes in the following are path independent
    - Temperature
    - Pressure
    - Volume
    - Internal energy
    - Enthalpy
    - Entropy
    - Gibb's free energy

Path functions
- Depend on the process by which it is performed
- Heat and work

First law of thermodynamics
- $\Delta U = q + w$.
- Law of conservation of energy: Energy cannot be created or destroyed, it can only change form
- System has internal energy. Heat and work are ways to transfer energy to surroundings
    - $\Delta U_{universe} = \Delta U_{surroundings} + \Delta U_{system} = 0$.
- Heat added to system (endothermic) and work done on the system are positive.
- Heat removed from the system (exothermic) and work done by the system are negative.

Constant volume
- $w = \Delta V = 0$.
- $\Delta U = q = q_V$.

Constant pressure
- Some energy used as work to push gas molecules out of the way and expand the environment
- $\Delta U = q_P + w$.

Heat capacity and specific heat
- Temperature changes depend on:
    - Heat delivered (q).
    - Substance presented (m, n).
    - Specific heat (c) or molar heat capacity (C_p).
- $q = cm\Delta T = nC_p\Delta T$.

Enthalpy
- The heat transferred during chemical reaction at constant pressure.
- There is no absolute enthalpy (no reference point)
- $\Delta H = H_{product} - H_{reactants} = q_P = \Delta U + P\Delta V$.
- It is an extensive property, it scales with size/quantity/extent

Phase changes
- Heat is required to overcome intermolecular forces
- Heat is released on the formation of intermolecular forces
- Latent heat: $\Delta H = n\Delta H_{phase\ change}$.

Hess' law
- $\Delta H_{overall} = \Delta H_1 + \Delta H_2$.
- Overall reaction enthalpy is the sum of enthalpy of all steps.

Standard enthalpy of formation
- $\Delta H^{O}_{f,T}$.
    - O: standard state.
    - f: formation.

    - T: temperature.
- The enthalpy change in a reaction where 1 mole of substance formed from elements in their standard states
- $\Delta H_f^O = 0$ for elements in standard state.
    - Enthalpy of an element in its most stable form at $P = 1bar$ for a specified temperature is 0.
- Need to select one allotrope of element as reference form
- ΔH_f^O varies slightly with temperature, use $T = 298K$ as room temperature.
- $\Delta H_{reaction}^O = \sum v\Delta H_f^O(products) - \sum v\Delta H_f^O(reactants)$.
    - ΔH_f^O is the enthalpy of formation for each product, reactant.
    - v is the Stoichiometric coefficient.

Bond enthalpies

- Enthalpy is the energy required to break and form bonds over a reaction
- Not all bond enthalpies are made equal, they are averaged over many compounds
- $\Delta H_{reaction}^O = \sum E_{bond}(products) - \sum E_{bond}(reactants)$.

Entropy

- $S = k \ln W$.
    - $k = \frac{R}{N_A} = 1.38 \times 10^{-23} J/K$.
    - W is the number of equivalent microstates
- Heavier molecules have higher entropies
- Entropy decreases from gas to liquid to solid

Energy dispersal

- Heat flow and temperature affect entropy
- $\Delta S = \frac{q_P}{T} = \frac{\Delta H}{T}$.

Second law of thermodynamics

- $\Delta S_{universe} = \Delta S_{surr} + \Delta S_{sys}$.
- If $\Delta S_{universe} > 0$, the process is spontaneous.
- If $\Delta S_{universe} = 0$, it is equilibrium.
- $\Delta S_{surr} = \frac{q_{surr}}{T_{surr}} = \frac{-q_{sys}}{T_{surr}} = \frac{-\Delta H}{T_{surr}}$.
- $\Delta S_{universe} = \Delta S_{sys} - \frac{\Delta H}{T_{surr}}$.

Entropy always increases

- Increase temperature.
- Increase system volume
- Phase transition to higher entropy species
- Increase number of products
- Increase complexity of products
- Produce higher entropy species in a reaction

Third law of thermodynamics

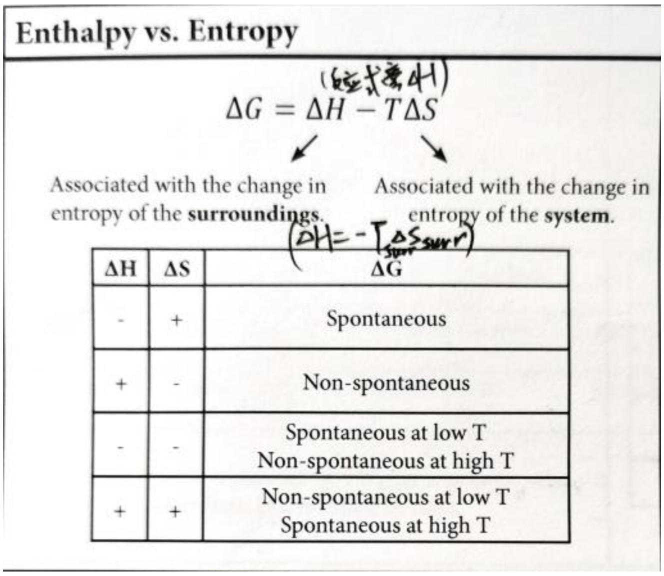
- At $T = 0K$, a crystal is perfect and there is no disorder $S = 0$.
- Provides an absolute reference point for entropy values

Standard molar entropy

- Entropy is a state function
- Standard molar entropy can be used to calculate the entropy of a system
- The standard molar entropy is the entropy of one mole of substance under standard state conditions
- $\Delta S^O = \sum v\Delta S^O(products) - \sum v\Delta S^O(reactants)$.

Gibb's free energy (G)

- $G = H - T_{surr}S = -T_{surr}\Delta S_{universe}$.
- At constant T and P, $\Delta G = \Delta H - T\Delta S$.
- Spontaneity depends on enthalpy and entropy of the system ($\Delta G = -T\Delta S_{universe}$)
  - $\Delta G < 0$, spontaneous.
  - $\Delta G = 0$, equilibrium.
  - $\Delta \mathrm{G} > 0$, non spontaneous.
- Standard free energy of reaction: $\Delta G^O = \sum v\Delta G^O(products) - \sum v\Delta G^O(reactants)$.



Enthalpy vs. Entropy

([illegible]式[illegible]ΔH)

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

Associated with the change in entropy of the **surroundings**.

($\Delta H = -T_{surr}\Delta S_{surr}$)

Associated with the change in entropy of the **system**.

ΔH	ΔS	ΔG
-	+	Spontaneous
+	-	Non-spontaneous
-	-	Spontaneous at low T Non-spontaneous at high T
+	+	Non-spontaneous at low T Spontaneous at high T

Chemical equilibrium & kinetics

July 8, 2021 4:49 PM

Chemical equilibrium

- Chemical reactions are dynamic systems in which reactants are converted to products and products are converted to reactants
- At equilibrium, $[R]$ does not change with time.
  - Rate forward: $k_{forward}[R]$.
  - Rate reverse: $k_{reverse}[P]$.
  - Rate forward = rate reverse at equilibrium
  - $K = \frac{k_f}{k_r} = \frac{[P]_{eq}}{[R]_{eq}}$.
- Given reaction $aA + bB \rightleftharpoons cC + dD$.
  - $K = \frac{[C]_{eq}^c [D]_{eq}^c}{[A]_{eq}^c [B]_{eq}^c}$.
  - $Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{P_C^c P_D^d}{P_A^a P_B^b}$(for gas).
  - At constant temperature, K will not change, Q will change
  - Comparing Q and K tells about the direction of spontaneous change as the system moves towards equilibrium
  - K tells the extent of a reaction
    - Small K, negligible product formation.
    - Large K, reaction goes to completion.
    - Intermediate K, significant products and reactants.

Non standard conditions

- $\Delta G = \Delta G^O + RT \ln Q$.
  - ΔG^O is the free energy change under standard conditions.
  - Q is reqaction quotient under any conditions.
- K and Q are calculated using the activity of each component instead of concentration
- Activities (a) reflect the real availability or effective concentration of a species in a real solution
  - Gases $a_x = \gamma_x P_x$.
  - Solutions $a_x = \gamma_x [X]$.
  - Pure solids $a_x = 1$.
  - Pure liquids $a_x = 1$.
- ΔG and ΔG^O.
  - ΔG: concentrations and pressures can be any value.
  - ΔG^O: concentrations must be 1M and pressures must be 1 bar, liquids and solids must be pure.
  - $\Delta G < 0$, spontaneous in the forward direction.
  - $\Delta G > 0$, spontaneous in the reverse direction.
  - $\Delta G = 0$, equilibrium.
  - ΔG^O tells the equilibrium position, ΔG tells which way a reaction will proceed to reach equilibrium.
- ΔG and K.
  - At equilibrium, $\Delta \mathrm{G} = 0$, $Q = K$.
  - $\Delta G^O = -RT \ln K$.
  - For a reaction, changing temperature changes the value of $K = e^{-\frac{\Delta G^O}{RT}}$.

Van't Hoff equation

- Used to calculate changes in the equilibrium constant as a function of temperature
- Assume that ΔH^O does not change with temperature.

- $\ln\left(\frac{K_1}{K_2}\right) = \frac{\Delta H^O}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$.
- $\ln K = -\frac{\Delta H^O}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^O}{R}$.

Le Chatelier's principle

- When a system at equilibrium is stressed, it responds by re-establishing equilibrium to reduce the applied stress
- Three common means for introducing stresses
    - K stays constant
        - Changes in concentration
        - Changes in pressure
    - K varies
        - Changes in temperature

Coupled reactions

- Important reactions can be non-spontaneous
- To make the reaction happen, couple it with another reaction that is spontaneous

Solubility equilibria

- Solubility: the ability of a compound to dissolve in solution
- E.g. $Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$.
    - $K = 7.9 \times 10^{-6}$.
    - When $[Ca^{2+}][OH^-]^2 > K$, the equilibrium will shift two left and it will precipitate.
- Common ion effect
    - A shift in equilibrium occurs when one or more ions that are part of the equilibrium are introduced from an outside source

Reaction rates

- $rate = \frac{change\ in\ concentration}{time} = \frac{\Delta[substance]}{\Delta t}$.
- For $aA + bB \rightleftharpoons cC + dD$
    - Forward rate: $k_f[A]^a[B]^b$.
    - Reverse rate: $k_r[C]^c[D]^d$.
    - At equilibrium $k_f[A]^a[B]^b = k_r[C]^c[D]^d$.
- Concentration of products increases while concentration of reactants decreases:
    - $rate = \frac{\Delta[product]}{\Delta t} = -\frac{\Delta[reactant]}{\Delta t}$.
    - When concentration changes depend on stoichiometry: $rate = \frac{\Delta[product]}{\mathrm{v}\Delta t} = -\frac{\Delta[reactant]}{\mathrm{v}\Delta t}$.

Differential rate law and concentration

- $rate = k[A]^n[B]^m$.
- n and m are the order of the reaction.
- k is the rate constant, different for different reactions.
- k, n, m are determined experimentally.

Integrated rate laws

- Used to determine the concentration of products at any point during the reaction
- Order of a rate law = sum of exponents of concentration terms.
- Zero order integrated law
    - $rate = k[A]^0 = k$, concentration of A has no effect on reaction rate.
    - $rate = -\frac{\Delta[A]}{\Delta t} = k$.
    - $[A]_t = -kt + [A]_0$.
- First order: $\ln[A] = -kt + \ln[A]_0$.
- Second order: $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$.

- Half life
    - The time it takes for its concentration to fall to one-halt its original value.
    - For first order: $t_{1/2} = \frac{\ln 2}{k}$.

As temperature increases, more collisions between reactants have the energy necessary for reaction to occur

Activation energy

- Minimum energy that reactant molecules must possess to undergo a particular chemical reaction

Collision geometry

- Some collisions may have enough energy but not the right orientation

Arrhenius behavior

- $\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$.

A reaction mechanism is a collection of one or more molecular steps that account for the way reactants become products

- The slowest step determine the rate law

Molecularity

- The stoichiometric coefficients for reactants in an elementary step do provide the order of reaction

Catalysis

- A catalyst is a substance that increases the rate of the reaction but is neither created nor destroyed in the process
- Catalyst is not an intermediate
- The energy of the reactants or products does not change
- The activation energy of the catalyzed reaction is lower than that of the uncatalyzed reaction

Homogeneous and heterogeneous catalysts

- Homogeneous: in the same phase as the reactants
- Heterogeneous: in a different phase from the reactants

Electrochemistry

July 8, 2021 4:49 PM

Standard hydrogen electrode defined as 0V

- $2H^+ + 2e^- \rightarrow H_2$

All electrochemical reactions referenced to this value

Measuring cell potential

- Standard cell potential given by: $E^O_{cell} = E^O_{red} - E^O_{ox}$.
- Use standard reduction potentials for both with both reactions written as reductions
  - Half reaction with more positive standard reduction potential will be cathode

Cell potential and Gibbs energy

- Electrical work made up of
  - Potential difference between electrodes
  - Amount of charge passed between electrode
- Faraday constant relates charge to moles of electrons transferred in a reaction
  - $F = qN_A = 96500C\ mol^{-1}$.
- $\Delta G^O_{rxn} = -nFE^O_{cell}$.
  - $E^O_{cell} = \frac{RT}{nF}\ln K$.

Galvanic cell

- Electrical energy produced from spontaneous redox reactions
- Electrons flow from anode to cathode

Salt bridge

- Without a salt bridge, there is a build-up of cations at the anode and anions at the cathode

Cell notation

- Used to simplify the description of a galvanic cell
- Anode | anode electrolyte || Cathode electrolyte | Cathode
  - | represents a phase boundary
  - || represents a salt bridge

Cell potential depends on conditions

- The Nernst equation is used to determine cell potential under non-standard conditions
- $E = E^O - \frac{RT}{nF}\ln Q = E^O - \frac{0.0592V}{n}\log_{10} Q$ at $T = 298K$.
- One half-cell provides a reference while the other half-cell measures the concentration of H^+
  - $pH = -\log[H^+]$.
  - $E = L + 0.0592V \log[H_3O^+] = L - 0.0592V\ pH$.

Electrolysis

- An external source of electricity is used to drive a non-spontaneous reaction
- Commonly: used to accomplish chemical change (plating of metals)
  - $2Cl^- \rightarrow Cl_2 + 2e^-$.
  - $2Na^+ + 2e^- \rightarrow Na(l)$.
- The amount of chemical changed produced depends on the charge passed which us related to the quantity of electrons
  - $Q = It$.
  - $\#electrons = \frac{charge}{Faraday\ constant} = \frac{Q}{F}$.
  - We can get from current and time to moles of electrons
  - From moles of electrons, we can find the mass of substance oxidized/reduced