

GENERAL CHEMISTRY "CRACK" MASTER NOTES

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- First law ($\Delta E = q + w$, conservation of energy)
- Equivalence of mechanical, chemical, electrical and thermal energy units
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- Temperature scales, conversion
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- Heat of fusion, heat of vaporization
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Rate Processes in Chemical Reactions - Kinetics and Equilibrium – Page 72

- Reaction rates
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 - reaction order
- Rate determining step
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 - activation energy
 - activated complex or transition state
 - interpretation of energy profiles showing energies of reactants and products, activation energy, ΔH for the reaction
 - Arrhenius equation
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- Relationship of the equilibrium constant and standard free energy change

Solution Chemistry – Page 82

- Ions in solution
 - Anion, cation (common names, formulas and charges for familiar ions; e.g., NH_4^+ , ammonium; PO_4^{3-} , phosphate; SO_4^{2-} , sulfate)
 - Hydration, the hydronium ion
- Solubility
 - Units of concentration (e.g., molarity)
 - Solubility product constant, the equilibrium expression
 - Common-ion effect, its use in laboratory separations
 - Complex ion formation
 - Complex ions and solubility
 - Solubility and pH

Acids/Bases – Page 87

- Acid / base equilibria
 - Bronsted definition of acid, base
 - Ionization of water
 - K_w , its approximate value ($K_w = [H^+][OH^-] = 1 \cdot 10^{-14}$ at 25°C)
 - definition of pH; pH of pure water
 - Conjugate acids and bases (e.g., amino acids)
 - Strong acids and bases (common examples, e.g., nitric, sulfuric)
 - Weak acids and bases (common examples, e.g. acetic, benzoic)
 - dissociation of weak acids and bases with or without added salt
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 - calculation of pH of solutions of salts of weak acids or bases
 - Equilibrium constants K_a and K_b : pK_a , pK_b
 - Buffers
 - definition and concepts (common buffer systems)
 - influence on titration curves
- Titration
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 - Interpretation of titration curves
 - Redox titration

Electrochemistry – Page 98

- Electrolytic cell
 - electrolysis
 - anode, cathode
 - electrolyte
 - Faraday's law relating amount of elements deposited (or gas liberated) at an electrode to current
 - electron flow; oxidation, and reduction at the electrodes
- Galvanic or voltaic cell
 - half reactions
 - reduction potentials; cell potential
 - direction of electron flow

Electronic Structure and Periodic Table

Electronic structure

- Orbital structure of hydrogen atom, principal quantum number n , number of electrons per orbital
 - In the Bohr model, the hydrogen electron orbits the nucleus.
 - In quantum mechanics, hydrogen electron exists in a spherical probability cloud around the nucleus.
 - The principle quantum number, n , defines what shell the electron is in.
 - n values start from one: 1,2,3 ...etc.
 - Higher n shells are higher in energy (if subshells are the same).
 - There are n^2 orbitals per shell.
 - There are 2 electrons per orbital.
 - Thus, there are $2n^2$ electrons per shell.
- Ground state, excited states
 - Electrons are normally in their ground state.
 - When they absorb energy, they get promoted to excited states.
 - Excited states are higher in energy than ground states.
 - Excited state electrons come back down to the ground state via release of energy.
- Absorption and emission spectra
 - The absorption spectrum shows what wavelengths of light are absorbed.
 - The absorption spectrum looks like black lines on a rainbow background.
 - The emission spectrum shows what wavelengths of light are emitted.

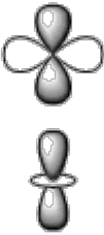
- The emission spectrum looks like colored lines on a black background.
- The absorption spectrum corresponds to the emission spectrum in pattern.
- The emission spectrum shifts to a slightly longer wavelength.
- Quantum numbers l , m , s , and number of quantum states (electrons) per orbital
 - l is the angular momentum quantum number: l are integers that range from 0 to $n-1$.
 - spdf: $l=0,1,2,3$ for s,p,d,f respectively.
 - spdf designates subshells.
 - s subshells hold 1 orbital. p holds 3, d holds 5, f holds 7.
 - each orbital holds a maximum of 2 electrons.
 - s subshells hold a maximum of $1 \times 2 = 2$ electrons, p: $3 \times 2 = 6$, d: $5 \times 2 = 10$, f: $7 \times 2 = 14$.
 - A generalized formula for the above pattern: for any subshell, $4l+2$ electrons can be held.
 - for a given shell, higher subshells have higher energy.
 - a low shell with a high subshell may be higher in energy than a higher shell with a low subshell.
 - m is the magnetic quantum number: m are integers that range from $-l$ to l , including zero.
 - s is the spin quantum number: s is either $+1/2$ or $-1/2$.
- Common names and geometric shapes for orbitals s, p, d

Electron Orbitals

l value name shape orbital info

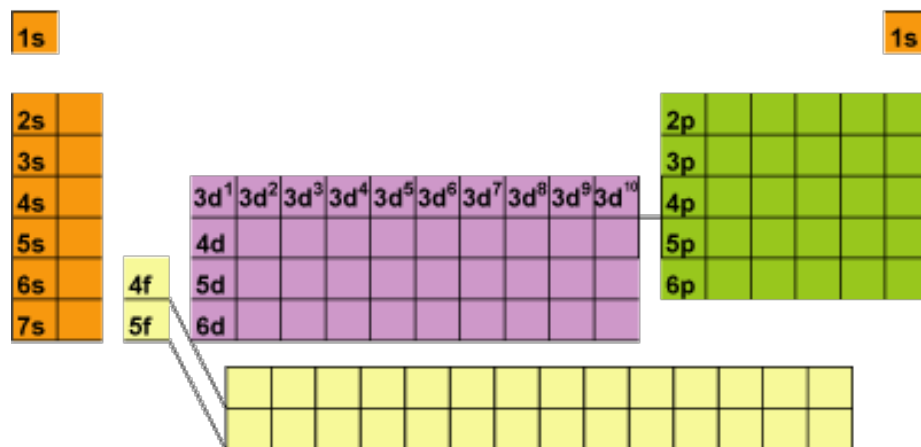
0 s  1 orbital; max e⁻ = 2

1 p  x 3 orientations = 3 orbitals; max e⁻ = 6

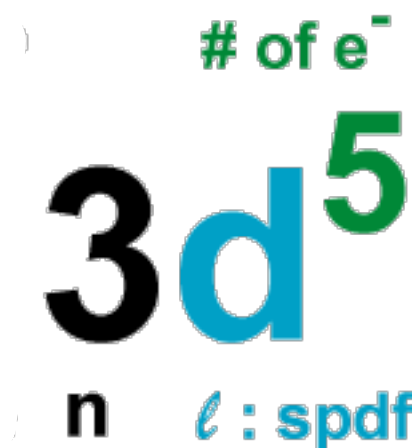
2 d  x 4 orientations
x 1 orientation
4+1 = 5 orbitals; max e⁻ = 10

-
- Electrons are filled by occupying the lowest energy subshells first.
- Subshell arranged in increasing energy: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d
 - The best way to memorize the above is by interpreting the periodic table:

Periodic Table: Orbitals

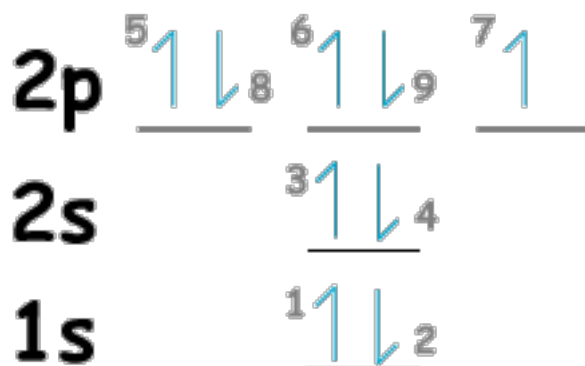


- Starting from the first row, going across, both hydrogen and helium is 1s. Next row: 2s then 2p. Third row: 3s then 3p. Fourth row: 4s, 3d, then 4p. Fifth row: 5s, 4d, then 5p. Sixth row: 6s, 4f, 5d, then 6p. Last row: 7s, 5f, then 6d. The pattern we get from looking at the periodic table is exactly in the order of increasing energy.
- For a given subshell, the columns represent how many electrons are in that subshell. For example, the fifth column of the d subshells contain elements that have 5 electrons in that subshell.
- The number of columns for each subshell indicate the maximum number of electrons that subshell can hold. For example, the d subshells have 10 columns showing that d orbitals can hold 10 electrons total.
- Conventional notation for electronic structure



- Conventional notation:

Orbital diagram for $1s^2 2s^2 2p^5$



$\uparrow$: e^- with spin = $+1/2$

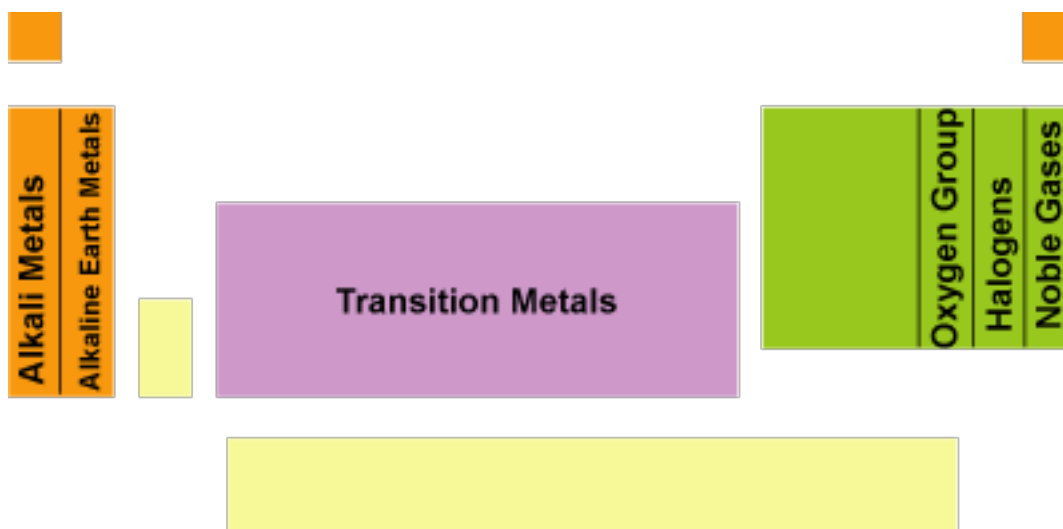
$\downarrow$: e^- with spin = $-1/2$

: order e^- is filled

- Orbital diagrams: _____ : orbital
- Aufbau principle: shells / subshells of lower energy gets filled first (This is the most obvious rule. For example, 1s fills first, then 2s, then 2p ...etc. Review the exact [order](#) of energies because later on, the d subshells get filled after the s.
- Hund's rule: when you fill a subshell with more than 1 orbital (p, d, f), you first fill each orbital with a single electron and with the same spin (check out electrons 5, 6, and 7 in the orbital diagram, which fills according to Hund's rule). The reason for Hund's rule is that electron-electron repulsion in doubly occupied orbitals make them higher in energy than singly occupied orbitals.
- Pauli exclusion principle: 2 electrons in the same orbital must be of different spins (for example, check out electrons 5 and 8 in the orbital diagram).
- Watch out for d^4 and d^9 elements. Instead of s^2d^4 and s^2d^9 , it's s^1d^5 and s^1d^{10} because they want to achieve a half-full or full d subshell.

- Bohr atom
 - Electron orbiting the nucleus in a circular orbit.
 - Larger n values have larger orbiting radii.
- Effective nuclear charge
 - Effective nuclear charge = nuclear charge - shielding electrons.
 - Shielding electrons are those that stand between the nucleus and the electron we are interested in.
 - Shielding electrons are those that are in subshells closer to the nucleus (lower in energy) than the electron we are interested in.
 - Exam questions usually give you a diagram of the Bohr model, in which case, shielding electrons are those that orbits at a smaller radius.
 - The higher the effective nuclear charge for an electron, the more stable it is (higher ionization energy, not easily knocked off).
 - Effective nuclear charge increases for outer electrons as you go across (left to right) the periodic table.

The periodic table: classification of elements into groups by electronic structure; physical and chemical properties of elements



- Alkali metals

- Single valence electron - low ionization energy, very reactive.
- Wants to lose that electron to achieve empty valence shell.
- More reactive as you go down because of increasing radii.
- Reacts with oxygen to form oxides.
- Reacts with water to form hydroxides and releases hydrogen.
- Reacts with acids to form salts and releases hydrogen.
- Most commonly found in the +1 oxidation state.
- Alkaline earth metals
 - 2 valence electrons - relatively low in ionization energy, quite reactive.
 - Wants to lose both electrons to achieve empty valence shell.
 - More reactive as you go down because of increasing radii.
 - Reacts with oxygen to form oxides.
 - Reacts with water to form hydroxides and releases hydrogen.
 - Reacts with acids to form salts and releases hydrogen.
 - Most commonly found in the +2 oxidation state.
- Halogens
 - 7 valence electrons (2 from s subshell and 5 from p subshell) - high electron affinity, very reactive.
 - Wants to gain one electron to achieve full valence shell.
 - More reactive as you go up because of decreasing radii.
 - Reacts with alkali metals and alkaline earth metals to form salts.
 - Most commonly found in the -1 oxidation state.
- Noble gases
 - Full valence shell of 8 - high ionization energy couple with low electron affinity.

- Don't react.
- Found in the oxidation state of 0.
- Transition metals
 - High conductivity due to free flowing (loosely bound) outer d electrons.
 - In the presence of ligands (when in a chemical complex), the d orbitals become nondegenerate (different in energy).
 - Electron transitions between nondegenerate d orbitals gives transition metal complexes vivid colors.
 - Varied oxidation states - but always +.
- Representative elements
 - Representative elements include the s block and the p block of the periodic table.
 - No free flowing (loosely bound) outer d electrons.
 - Valence shell fills from left (1 electron) to right (8 electrons).
 - Standard nomenclature from left to right: I A, II A, III A, IV A, V A, VI A, VII A, VIII A.
- Metals and non-metals
 - Metals are to the left of metalloids.
 - Non-metals are to the right of metalloids.
 - Metalloids: diagonal line from Boron to Polonium: B, Si, As, Te, Ge, Sb, (Po).
 -

Chemical properties	
Metals	Non-metals
Likes to lose electrons to gain a + oxidation state (good reducing agent).	Likes to gain electrons to form a - oxidation state (good oxidizing agent).

Lower electronegativity - partially positive in a covalent bond with non-metal.	Higher electronegativity - partially negative in a covalent bond with metal.
Forms basic oxides.	Forms acidic oxides.
Physical properties	
Good conductor of heat and electricity	Poor conductor of heat and electricity
Malleable, ductile, luster, solid at room temp(except Hg)	Solid, liquid, or gas at room temp. Brittle if solid and without luster.

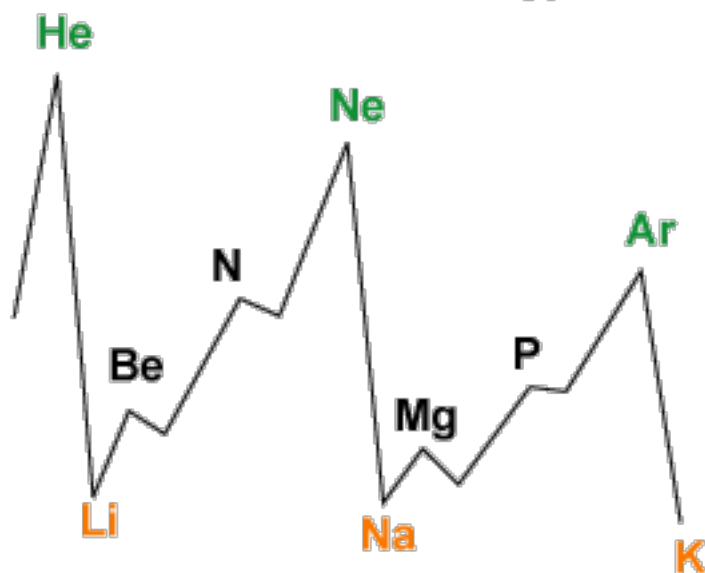
- Oxygen group
 - The group (column) that contains oxygen.
 - Oxygen and sulfur are chemically similar (if a question asks you what element you can substitute for oxygen and still keep the same chemical reactivity, then choose sulfur).
 - Se - Te - Po = non-metal - metalloid - metal (or metalloid).

The periodic table: variations of chemical properties with group and row

- Electronic structure ...[a repeat of electronic structure section above](#)
 - representative elements
 - Representative elements include the s block and the p block of the periodic table.
 - No free flowing (loosely bound) outer d electrons.
 - Valence shell fills from left (1 electron) to right (8 electrons).
 - Standard nomenclature from left to right: I A, II A, III A, IV A, V A, VI A, VII A, VIII A.
 - noble gases
 - Full valence shell of 8 - high ionization energy couple with low electron affinity.
 - Don't react.

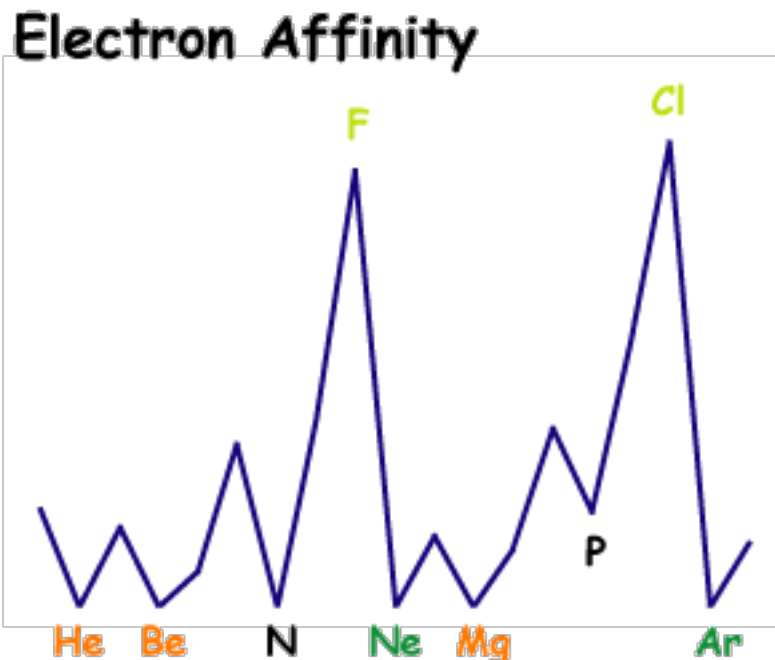
- Found in the oxidation state of 0.
- transition metals
 - High conductivity due to free flowing (loosely bound) outer d electrons.
 - In the presence of ligands (when in a chemical complex), the d orbitals become nondegenerate (different in energy).
 - Electron transitions between nondegenerate d orbitals gives transition metal complexes vivid colors.
 - Varied oxidation states - but always +.
- Valence electrons
 - Electrons in the outer shell.
 - Ranges from 1 to 8 from left to right of the representative elements.
 - The valence electron rule does not apply to transition metals.
- First and second ionization energies
 - definition of first ionization energy: The energy needed to knock off the first valence electron.
 - definition of second ionization energy: The energy needed to knock off the second valence electron.
 - prediction from electronic structure for elements in different groups or rows

Ionization Energy Trend



- - Ionization energy decreases as you go down because of increasing radii.
 - Ionization energy increases as you go right because of decreasing radii.
 - Highest peaks are noble gases.
 - Lowest troughs are alkali metals.
 - Local maxima occurs for filled subshells and half-filled p subshells.
 - Second ionization energy is always higher than the first ionization energy (usually a lot higher).
 - Alkali metals and hydrogen: first ionization energy very low. Second ionization much higher.
 - Alkaline earth metals: first ionization energy low. Second ionization energy also low.
- Electron affinity
 - definition - electron affinity is the amount of energy released when something gains an electron (how easily it can gain an electron).

- variation with group and row



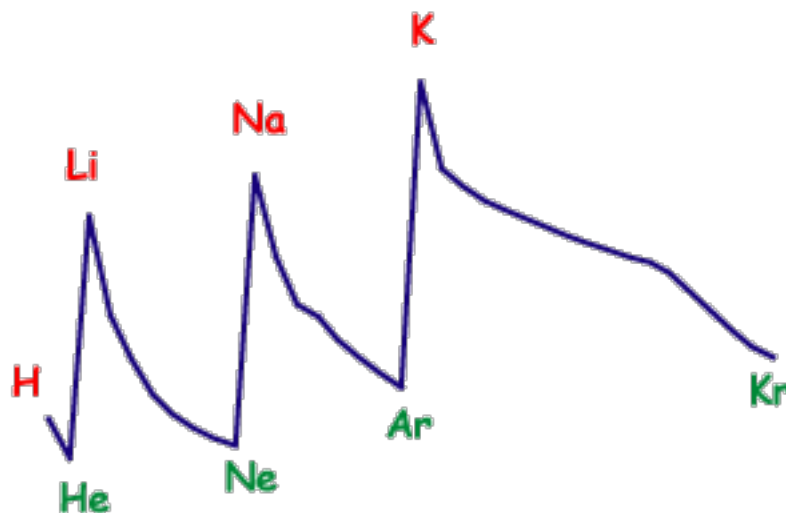
- As you go down a group, electron affinity decreases because of larger radii.
 - As you go across (left to right) a row, electron affinity increases.
 - Highest peaks are for the halogens.
 - Lowest for noble gases.
 - Local minima occurs for filled subshells and half-filled p subshells.
- Electronegativity
 - definition - electronegativity is how much something hoards electrons in a covalent bond.
 - comparative values for some representative elements and important groups
 - Electronegativity increases toward the top right.
 - Fluorine is the most electronegative element.

- Things around fluorine are highly electronegative: N, O, F, Cl, Br.
- Halogens are electronegative, especially toward the top of the group.
- Noble gases can be very electronegative if they participate in bond formation (Kr and Xe).
- Non-metals are more electronegative than metals.
- Covalent bond is a sharing of electrons between elements.
- The more electronegative element in a covalent bond gets a larger share of the electrons and has a partial negative charge
- The less electronegative (more electropositive) element in a covalent bond gets a smaller share of the electrons and has a partial positive charge.
- If the electronegativity difference is too great, an ionic bond occurs instead of a covalent one.
- Ionic bonds result from a complete transfer of electrons from the electropositive element to the electronegative element.
- Electron shells and the sizes of atoms
 - Electron shells
 - Electron shells are defined by the principle quantum number - the n value.
 - Going down the periodic table means jumping to the next shell.
 - As you fill to the next shell (Ne to Na), the effective nuclear charge decreases because the old shell stands in between the nucleus and the new shell.
 - Filling to the next shell causes a jump in atom size because of decreased effective nuclear charge.
 - As you go down a group (Na to K), the atomic size increases even though the effective nuclear charge stays

the same, because higher shells have a larger radius than lower shells.

- Going across the periodic table means filling up the same shell (by going through subshells).
 - As you fill up a shell, the effective nuclear charge increases because the atomic number (protons) is increasing while the same-shell electrons you add do not shield one another.
 - With increasing effective nuclear charge, the electrostatic attraction ($F = kQq/r^2$) between the nucleus and the electrons increases, so the atom becomes more compact.
 - The increasing effective nuclear charge and electrostatic attraction is why going across a periodic table means decreasing atomic size.
- Sizes of atoms

Atomic Radii Trend



Peaks: single electron in valence shell

- **Troughs: filled valence shell**
- Size increases as you go down a column.

- Size decreases as you go across (to the right of) a row.
- Atomic sizes may overlap if you zigzag on the periodic table.

Bonding

The ionic bond (electrostatic forces between ions)

- The ionic bond forms when electrons transfer completely from one atom to another, resulting in oppositely charged species that attract each other via electrostatic interaction.
- Electrostatic energy $\propto q_1q_2/r$
 - Electrostatic Energy = Electrostatic potential $\times$ charge = $kq_1/r \times q_2 = kq_1q_2/r$
 - Electrostatic energy is negative because q_1 and q_2 are opposite in charge (If q_1 and q_2 are not opposite in charge, then they would repel each other, and no ionic bond would form).
 - Frequently, the negative sign is dropped and only the magnitude of the electrostatic energy is used.
 - The greater the magnitude of electrostatic potential, the stronger the ionic bond.
 - Strong ionic bonds are promoted by high charge magnitudes (q values) that are close together (small r value).
 - Ions that form strong ionic bonds have high charge density, that is, the charge to size ratio is high.
- Electrostatic energy $\propto$ lattice energy
 - Lattice energy measures the ionic bond strength.
 - Lattice energy is the energy required to break the ionic bond.
 - The larger magnitude of the lattice energy, the stronger the ionic bond and the harder it is to break.
 - The lattice energy is proportional to the electrostatic attraction between the ions.
- Electrostatic force $\propto q_1q_2/r^2$
 - Coulomb's law: $F = kq_1q_2/r^2$

- Larger charge magnitudes + charges being closer together → greater electrostatic force.
- The Coulomb's constant, k , is $9E9$.
- Opposite charges attract (negative F), same charges repel (positive F).
- If q_1 doubles, the electrostatic force doubles.
- If r halves, the electrostatic force increase by a factor of $2^2 = 4$.
- Coulomb's law is analogous to the universal law of gravitation:
 - $F = Gm_1m_2/r^2$
 - G is analogous to k and m is analogous to q .
 - The big difference is that G is tiny compared to k , because gravitational force is weaker compared to the much stronger electrostatic force.

The covalent bond

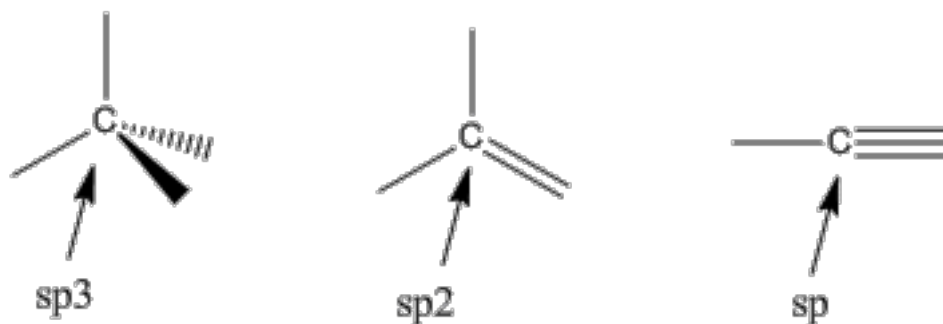
- The covalent bond results when there is a sharing of electrons between two atoms, resulting in the overlap of their electron orbitals.

sigma and pi bonds

- σ bonds are single bonds. They also make up the first bond of double and triple bonds.
- π bonds are double and triple bonds. They make up the second bond in a double bond, and both the second and the third bond in a triple bond.

hybrid orbitals: sp^3 , sp^2 , sp and respective geometries

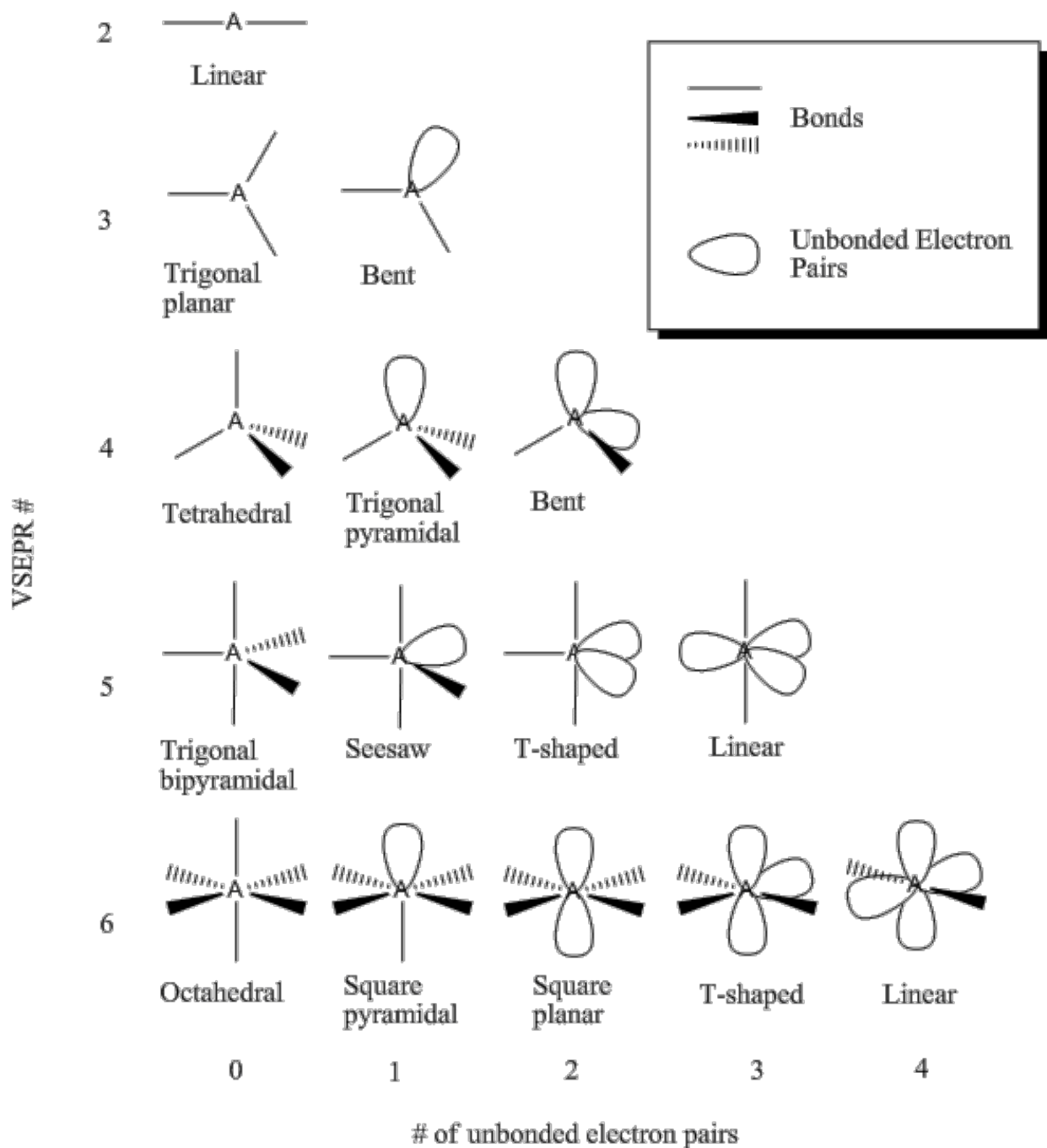
Hybridization of the carbon atom



-
- Hybrid orbitals are produced by hybridizing (mixing) electron orbitals to produce geometries that facilitate bonding.
- sp^3 : a hybrid between one s with 3 p orbitals. Tetrahedral in geometry. Contains single bonds only.
- sp^2 : a hybrid between one s with 2 p orbitals. Trigonal planar in geometry. Contains a double bond.
- sp : a hybrid between one s with one p orbital. Linear in geometry. Contains a triple bond.
- Hybrid orbitals are most commonly used with carbon as the center atom.

valence shell electron pair repulsion and the prediction of shapes of molecules (e.g., NH₃, H₂O, CO₂)

Molecular Geometries

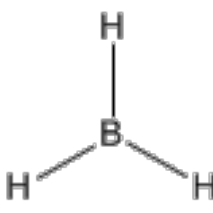
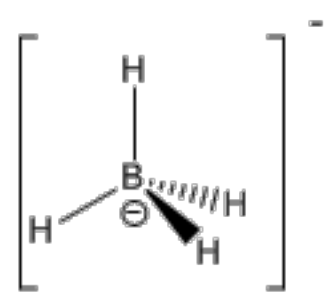


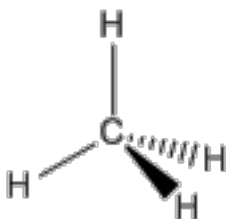
- In short, it is the VSEPR theory.
- The VSEPR theory is used to predict the geometry of molecules.

- The shapes of molecules are determined by the molecular geometry.
- Radicals also count as an electron pair.
- The VSEPR number is the total number of bonds + unbonded electron pairs.
- When calculating the VSEPR number, always use the electron/bond configuration about the central atom.
- NH_3 has a vsepr number of 4 (3 bonds to H and 1 unbonded pair). If you look up the table for VSEPR # = 4 and # unbonded electron pairs = 1, then you'll find that NH_3 is trigonal pyramidal.
- H_2O has 2 bonds, 2 unbonded electron pairs - it is bent.
- CO_2 has 2 double bonds and 0 unbonded electron pairs - it is linear.

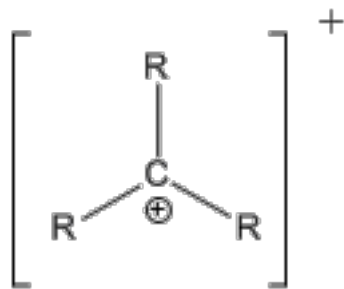
Lewis electron dot formulas

- Every dot represents 1 electron. Every line represents 1 bond (2 electrons). A "lone pair" is represented by two dots.
- Formulas are drawn in such a way that an octet is achieved on each atom. Exceptions include the boron column (they form 3 bonds and have a six-tet), large elements (3rd row and below such as the 10-tet P in PO_4^{3-} and the 12-tet S in SO_4^{2-}), and radicals (compounds with an odd # total electrons that result in a single, unpaired electron).
- All electrons in a bond are shared and can be used to satisfy the octet for both atoms on either side of the bond.
- Rules of thumb for Lewis structures
 - Carbon: 4 bonds total (meaning 4 total bonds. It can either be 4 single bonds or two double bonds ...etc) and no lone pairs. eg. CH_4 , CO_2
 - Oxygen: O can be
 - O: 2 bonds total, 2 lone pairs. eg. H_2O , O_2
 - O^{1-} : 1 bond, 3 lone pairs, formal charge of -1.
 - O^{1+} : 3 bonds, 1 lone pair, formal charge of +1.
 - Nitrogen: N can be

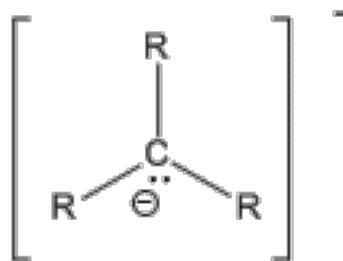
- N: 3 bonds total, 1 lone pair. eg. Amine or ammonia NH_3
- N^+ : 4 bonds, 0 lone pair, formal charge of +1. eg. Ammonium NH_4^+
- Halogens: 1 bond, 3 lone pairs. eg. CCl_4
- Hydrogen: 1 bond, 0 lone pair (exception to octet rule).
- Carbocation: C^+ has 3 bonds, no lone pairs, formal charge +1.
- Carbanion: C^- has 3 bonds, 1 lone pair, formal charge -1.
- Boron: 3 bonds, 0 lone pairs (exception to the octet rule). eg. BH_3
- Common Lewis structures
 - Hydrogen Lewis structures
 - Hydrogen Proton: $\text{H}^{\oplus}$
 - Hydride ion: $\text{H}^{\ominus}$
 - Boron Lewis structures
 - Borane: 
 - Borohydride ion: 
 - Carbon Lewis structures



- Methane:

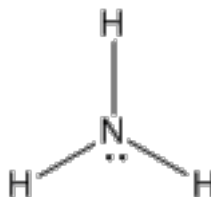


- Carbocation:

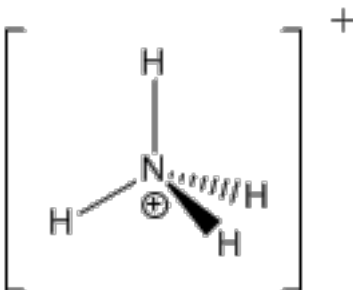


- Carbanion:

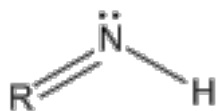
- Nitrogen Lewis structures



- Amine / Ammonia:

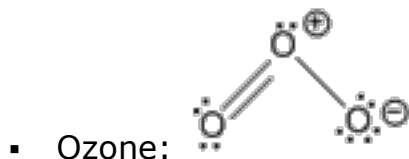
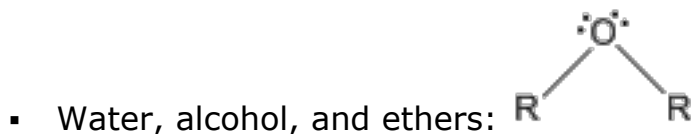
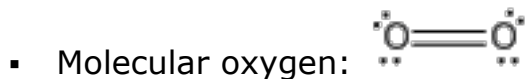


- Ammonium:



- Imine:

- Oxygen Lewis structures



- Halogen Lewis structures

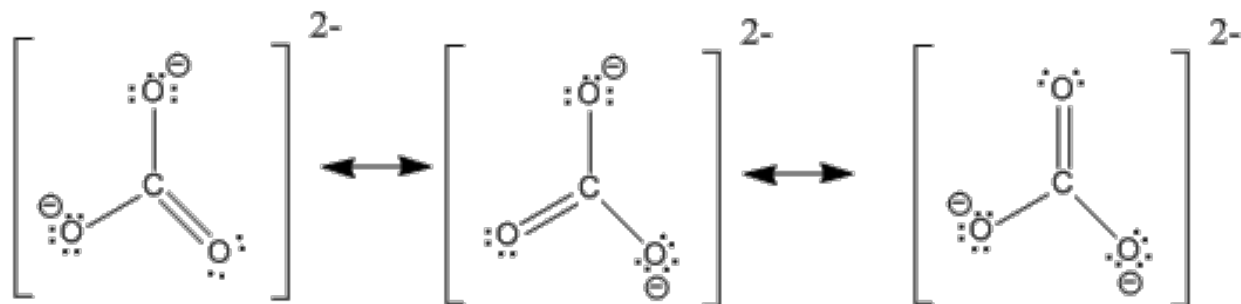


- R in the figures are either carbon or hydrogen.

- Lewis structures for elements in the same column (group) of the periodic table are similar to one another. For example, sulfur can be substituted for oxygen in lewis structures of oxygen.

resonance structures

Resonance structure for CO_3^{2-}



- When there are more than 1 satisfactory Lewis structures for a molecule, they are called resonance structures.
- You can visualize the molecule "shifts" between each of its resonance structures really fast, spending more time in the more stable resonance structures. Or more accurately, the structure of the molecule is a "combination" of its resonance structures, taking on more character from the most stable resonance structures. Eg. The bond length of a molecule that has both a single and a double bond resonance structure is intermediate between a single bond and a double bond.
- The molecule spends most of its time in the most stable resonance structure.
- Stable properties:
 - Octet rule is satisfied in every atom (except for boron group and hydrogen).
 - No formal charges.
 - If there must be formal charges, like charges are apart and unlike charges are close together.

formal charge

- Formal charge = valence electron # in the unbonded atom - electron # in the bonded atom.
- Electron # in the bonded atom = dots around the atom + lines connected to the atom.
- The dots around the atom represent electrons that are held entirely by the atom.
- The lines connected to the atom represent bonding electron pairs, in which the atom only gets one of the two electrons.
- Formal charges (other than 0) must be labeled next to the atom with the formal charge.
- Common formal charges:
 - Oxygen with only a single bond: -1.

- Oxygen with no bond but have an octet: -2. (Oxygen usually exists as the diatomic O_2 and have a double bond to themselves)
- Carbon with only 3 bonds: either +1 if carbocation or -1 if carbanion.
- Nitrogen with 4 bonds: +1.
- Halogen with no bonds, but have an octet: -1. (Halogens usually exist as a diatomic and have a single bond to themselves such as Cl_2)
- Boron with 4 bonds: -1. eg. BH_4^-

Lewis acids and bases

- Lewis acid accept electron pairs. They don't have lone pairs on the central atom. eg. BF_3
- Lewis bases donate electron pairs. They have lone pairs on their central atom. eg. NH_3

Partial ionic character

- Covalent bonds between atoms with dissimilar electronegativities have a partial ionic character.
- role of electronegativity in determining charge distribution
 - The more electronegative atom receives a partial negative charge.
 - The less electronegative atom receives a partial positive charge.
- dipole moment
 - Molecules with asymmetrical partial charge distribution have a dipole moment. eg. H_2O has a dipole moment because the molecule is bent and the oxygen-side of the molecule is partially negative.
 - Dipole moment depends on charge and distance.
 - The greater electronegativity difference, the greater the charge and hence the dipole moment.

- The greater the distance separating the charges, the greater the dipole moment.
- Molecules with symmetrical partial charge distribution do not have dipole moments. eg. CCl_4 do not have a dipole moment because the partially negative chlorine atoms are arranged symmetrically in a tetrahedron. The symmetry cancels out their individual dipole moments.
- Things with a dipole moment are said to be polar.
- Are the individual bonds in CCl_4 polar? Ans: yes.
- Is the entire molecule CCl_4 polar? Ans: no.

Gas phase

Absolute temperature, K scale

-

•	K	°C	°F
Absolute zero	0	-273	-460
Freezing point of water / melting point of ice	273	0	32
Room temperature	298	25	77
Body temperature	310	37	99
Boiling point of water / condensation of steam	373	100	212

- $K = ^\circ C + 273$
- $F = ^\circ C \times 1.8 + 32$

Pressure, simple mercury barometer

- Pressure is the force exerted over an area: $P = F/A$
- Due to gravity, the atmosphere exerts a pressure of 101 kPa at sea level. For convenience, 101 kPa = 1 atm.
- Pressure decreases at higher elevations.
- The mercury barometer measures atmospheric pressure by allowing the atmospheric pressure to "push" on a column of mercury.
- The barometer is open at one end and closed off (vacuum) at the other.
- The atmosphere "pushes" at the open end, which results in the mercury rising up in the closed end.
- The measured atmospheric pressure $P = F/A$. F is the weight of the mercury that got pushed up and A is the cross-section area of the column that the mercury got pushed through.
- Standard mercury barometers are calibrated such that 1 atm of pressure will push the mercury up by 760 mm. For convenience, mm Hg is also called the Torr. So, you don't have to do the $P=F/A$

calculation to find out the pressure reading from a barometer. Just know that $1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr}$.

- $1 \text{ atm} = 101 \text{ kPa} = 101,000 \text{ Pa} = 760 \text{ mm Hg} = 760 \text{ Torr}$.
- When performing $P = F/A$ calculations, make sure that F is in Newtons, A is in meter squared and the resulting P will be in Pascals. You can then convert the Pascals to whatever units the answer choices are in.

Molar volume at 0 degrees Celsius and 1 atm = 22.4 L/mol

- You must memorize this: ideal gases occupy 22.4 L per mol of molecules.
- Do not get this mixed up - it is 22.4 liters per mole, not the other way around.
- The way to remember this is that the mol is a huge number - 6.02×10^{23} molecules. These gazillions of molecules occupy a lot of space - 22.4 L to be exact.
- Another way you can remember this is to look at the periodic table: Air is made up mostly of nitrogen, which has an atomic mass of 14. In the diatomic form, N_2 weighs $14 \times 2 = 28$ grams per mol. Now, air is really light. In order for you to grab 28 grams of air, you need more than just a bottle of air, you need a huge tank totaling 22.4 L.

Ideal gas

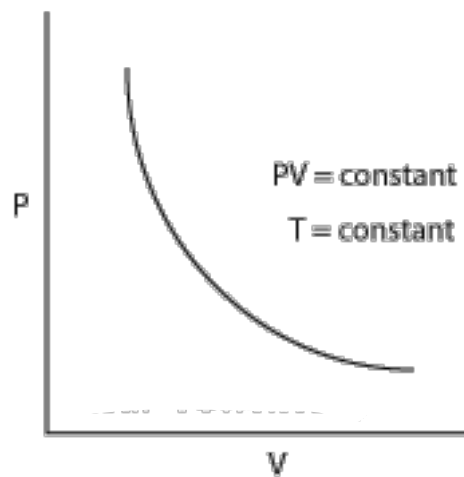
- definition
 - An ideal gas consists of pointy dots moving about randomly and colliding with one another and with the container wall. The ideal gas obeys the kinetic molecular theory of gases and has the following properties.
 - Random molecular motion.
 - No intermolecular forces.
 - No (negligible) molecular volume.
 - Perfectly elastic collisions (conservation of total kinetic energy).
 - You can treat gases as ideal gases at:

- Low pressures
- High temperatures
- Deviation from the ideal occurs at high pressure and low temperature. At these conditions, the gas molecules are "squished" together. When the gas molecules are so close together, they experience intermolecular interactions. Also, the molecular volume becomes significant when the total volume is squished down so much. The intermolecular attractions will cause collisions to be sticky and inelastic. At the extremely high pressures and low temperatures, gases cease to be gases at all - they condense into liquids.
- Ideal gases behave according to the ideal gas law.
- ideal gas law $PV=nRT$, where P is pressure, V is volume, n is # mols of gas, R is the gas constant, and T is temperature.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

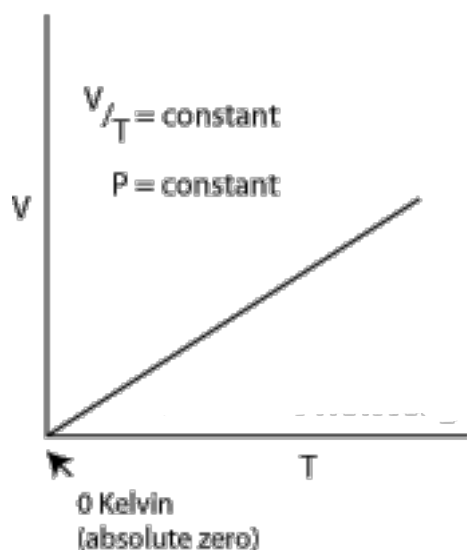
- Combined gas law:
 - Because nR is constant (n is the # mols and R is the gas constant), PV/T must also be constant.
 - Boyle's law and Charles' law can all be derived from the combined gas law.

Boyle's Law



-
- Boyle's law: at constant temperature, $P_1V_1 = P_2V_2$

Charles' Law



-
- $$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$
- Charles' law: at constant pressure,
- Charles' law extrapolates to absolute zero, where volume also goes to zero (this is only an extrapolation).
- Avogadro's law: Equal volumes of two gases will also contain equal number of mols of each gas (given ideal conditions: ideal gas at STP).
 - $PV = nRT$
 - R is constant, and at STP, pressure and temperature is also constant.
 - $V/n = RT/P$
 - If you plug in STP values, you'll end up with $V/n = 22.4$ L/mol.
 - All ideal gases at STP will occupy 22.4 L per mol of gas molecules.

Kinetic molecular theory of gases

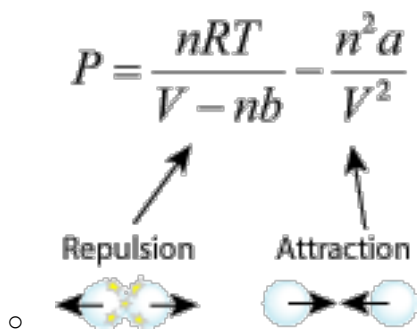
- The ideal gas laws can be derived from the kinetic theory of gases.
- The kinetic theory holds the following assumptions

- Random molecular motion.
- No intermolecular forces.
- No (negligible) molecular volume.
- Perfectly elastic collisions (conservation of total kinetic energy).
- The kinetic theory holds the following concepts:
 - Pressure of a gas is due to its molecules constantly colliding with the walls of its container.
 - Pressure is equally distributed over the walls of the container because molecular motion is random.
 - Temperature is a measure of the average kinetic energy of the gas molecules.
 - Higher temperature means the molecules are traveling faster, lower temperatures means slower molecules.
- Diffusion and Effusion
 - Diffusion: random molecular motion, causing a substance to move from an area of higher concentration to an area of lower concentration (diffusion down its concentration gradient).
 - Effusion: random molecular motion, causing a substance to escape a container through a very small opening.
 - Graham's Law (applies both to diffusion and effusion for the purposes of the exam).
 - $\text{Rate}_1 / \text{Rate}_2 = \sqrt{M_2 / M_1}$
 - Rate = rate of diffusion or effusion. M = molecular weight of gas molecule.
 - A possible question on the exam is two gasses diffuse down a tube from opposite ends. Where will the gases meet? The gist of this is that the lighter gas will travel faster, and the gases will meet at a point that is farther from the end of the lighter gas.
 - Graham's Law is derived from the Kinetic theory

- Temperature = average kinetic energy
- At a given temperature all gases have the same kinetic energy.
- $\frac{1}{2}m_1v_1^2 = \frac{1}{2}m_2v_2^2$
- $m_1v_1^2 = m_2v_2^2$
- $v_1^2/v_2^2 = m_2/m_1$
- $v_1/v_2 = \sqrt{m_2/m_1}$

Deviation of real-gas behavior from ideal gas law

- qualitative
 - When molecules are far apart (under conditions of low P, high T), they are ideal.
 - When molecules are brought close together (higher P, lower T), they experience intermolecular attraction.
 - When molecules are brought so close together that they clash into one another, they experience steric repulsion.
- quantitative (Van der Waals' equation)



- b for bounce. The term with the constant b is the repulsion term. The greater b is, the more repulsion, which leads to greater pressure.
- a for attraction. The term with the constant a is the attraction term. The greater a is, the more attraction, which leads to less pressure.

Partial pressure, mole fraction

- Partial pressure = a component of the total pressure exerted by a species in a gas mixture.
- The total pressure of a mixture of gas = The sum of all the partial pressures.
- Mole fraction = a component (fraction) of the total # mols that belongs to a species in a gas mixture.
- Mole fraction for species A = # mols of A / # mols of the entire gas mixture. = # mols of A / Σ # mols of A, B, C ...
- Dalton's law relates partial pressure to mole fraction.

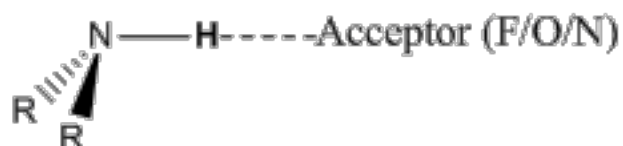
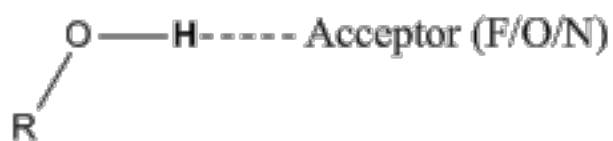
Dalton's law relating partial pressure to composition

- $P_i = \chi_i \cdot P_{\text{total}}$
- $P_{\text{total}} = \Sigma P_i = \Sigma \chi_i \cdot P_{\text{total}}$
- P_{total} is total pressure.
- P_i is partial pressure of species i.
- χ_i is the mole fraction of species i.

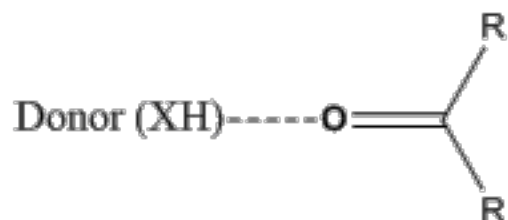
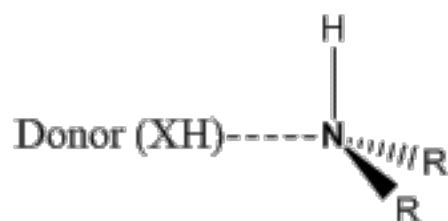
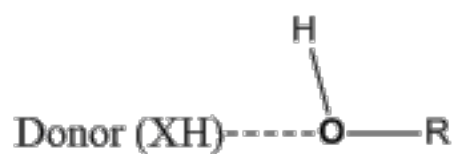
Liquid phase: intermolecular forces

Hydrogen bonding

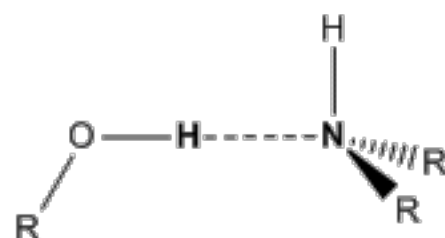
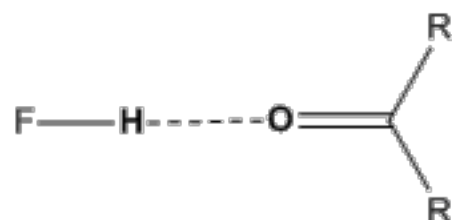
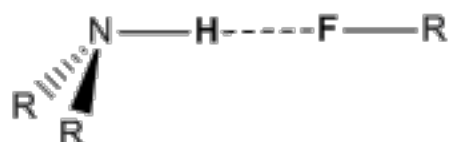
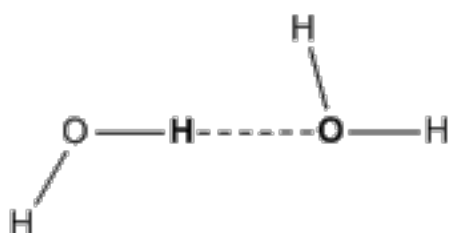
H-bond Donors



H-bond Acceptors

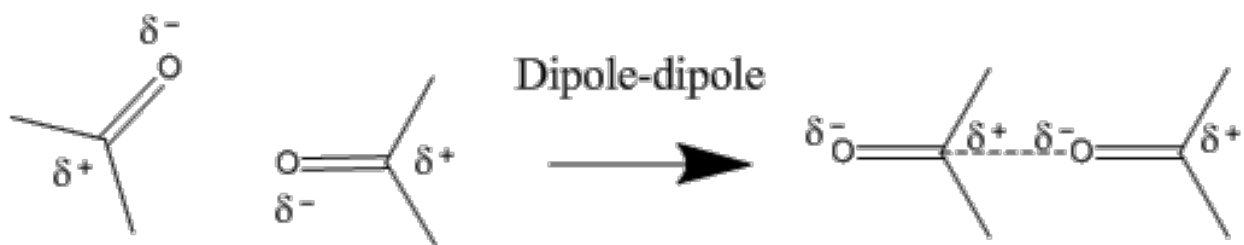


H-bond Examples



- Hydrogen bonding is a weak interaction between a partially positive H and a partially negative atom.
- Technically, hydrogen bonds are a special type of dipole-dipole interaction.
- Hydrogen bonding increases the boiling point.
- Partially positive H are also called hydrogen bond donors. They are hydrogens that are bonded to either F, O, or N.
- Partially negative atoms are also called hydrogen bond acceptors. They are most commonly F, O, or N.
- Do ethers form hydrogen bonds with other ethers? Ans: no, because ethers do not have a partially positive H (donor).
- The more polar a bond is, the stronger the hydrogen bond. The H-F bond is the most polar, followed by the H-O bond, and lastly the H-N bond.

Dipole interactions



- All polar molecules exhibit dipole-dipole interactions. This is where the polar molecules align such that opposites attract.
- Dipole-dipole interactions increase the boiling point, though not as significantly as hydrogen bonding.
- Dipole interactions are stronger the more polar the molecule is.
- Ion-dipole interactions are similar to dipole-dipole interactions, but it's stronger because it is no longer an interaction involving just partial charges. Instead, it is an interaction between a full charge (ion) and a partial charge (dipole).

- Ion-dipole interactions get stronger when you have larger charge magnitude of the ion, and large polarity of the dipole molecule.

Van der Waals' forces (London dispersion forces)

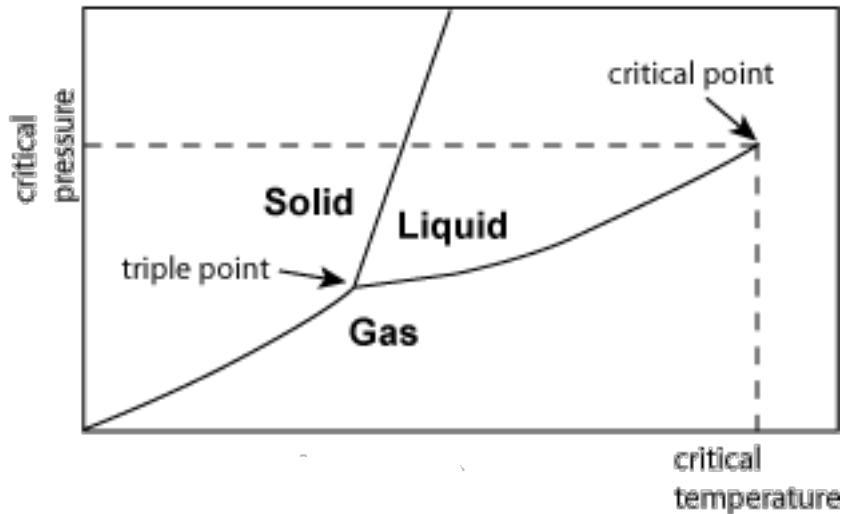
- Also called dispersion forces.
- Dispersion forces exist for all molecules, but are only significant for non-polar molecules. For polar molecules, dipole forces are predominant.
- Dispersion forces result from induced and instantaneous dipoles.
- Induced dipoles: when a polar molecule interacts with a non-polar molecule, then the polar molecule induces a dipole in the non-polar molecule.
- Instantaneous dipoles: Non-polar molecules have randomly fluctuating dipoles that tend to align with one another from one instant to the next.
- Dispersion forces get stronger for larger molecules. For example, decane ($C_{10}H_{22}$) has a stronger dispersion force than ethane (C_2H_6).

Phase equilibria

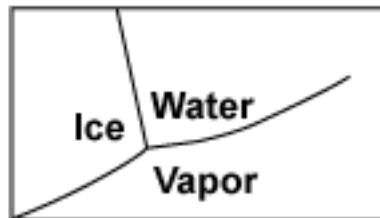
Phases and Phase Equilibria

Phase changes and phase diagrams

Phase Diagram



Phase Diagram for Water



-
- Solid: atoms/molecules vibrate about a fixed position. Hard to compress. Does not flow to fill a container.
- Liquid: atoms/molecules move about, but are close together and bound by intermolecular forces. Hard to compress. Flows to fill a container.
- Gas: atoms/molecules fly about far apart from one another and do not experience intermolecular forces. Easy to compress. Flows to fill a container.
- Solid-liquid boundary: solid and liquid exist in equilibrium.
- Solid-gas boundary: solid and gas exist in equilibrium.
- Liquid-gas boundary: liquid and gas exist in equilibrium.

- Triple point: the temperature and pressure at which all three phases of matter coexist in an equilibrium.
- Critical point: the temperature and pressure at which liquids and gases become indistinguishable.
- Critical temperature: the temperature above which you can no longer get a liquid no matter how much pressure you press on it.
- Water phase diagram is different from others because the solid-liquid boundary is slanted to the left. This is because water (liquid) is more dense than ice (solid), and if you increase the pressure at a given temperature, then you turn ice into water.
- Mnemonic for remembering which section of the phase diagram is for gases: "gas comes out this way."

Freezing point, melting point, boiling point, condensation point

- Freezing point: temperature (at a given pressure) that liquids begins to freeze into a solid.
- Melting point: temperature (at a given pressure) that a solid begins to melt into a liquid.
- Boiling point: temperature (at a given pressure) that a liquid begins to turn into a gas.
- Condensation point: temperature (at a given pressure) that a gas begins to condense into a liquid.
- Freezing point and melting point are the same, they can both be found along the solid-liquid phase boundary.
- Boiling point and condensation point are the same, they can be found along the liquid-gas boundary.
- Sublimation: conversion of a solid directly into a gas. Conditions for sublimation can be found along the solid-gas boundary.

Molality

- Molality is a measure of the concentration of solutes in a solvent.
- Molality is given the symbol m (don't confuse the small case m with the large case M that is molarity)

- Molality = mols of solute / mass (in kg) of solvent.
- Compare molality (mol solute/kg solvent) to molarity (mol solute/L solution).

Colligative properties

- Colligative properties = properties that depend on the # of solute particles, but not on the type.
- Solute particles in solution like to keep the solution in liquid phase. This is why it makes it harder to boil (raises its boiling point) and also makes it harder to freeze (lowers the freezing point). Lowering the vapor pressure is just another fancy name for raising the boiling point.
- Van't Hoff Factor (i): all colligative properties take into consideration of the Van't Hoff factor. Basically, it means convert concentration to reflect the total number of particles in solution. For example, glucose has i of 1 because it doesn't break up in solution. NaCl has i of 2, because in solution, it breaks up into 2 particles Na^+ and Cl^- .
 - vapor pressure lowering (Raoult's law)
 - $P = \chi_{\text{solvent}} \cdot P^{\circ}_{\text{solvent}}$
 - $\Delta P = \chi_{\text{solute}} \cdot P^{\circ}_{\text{solvent}}$
 - P is the vapor pressure.
 - ΔP is the decrease in vapor pressure.
 - $\chi_{\text{solute}} = \text{mol fraction of the solute} = \frac{\# \text{ mols of solute}}{\# \text{ total mols of both solute and solvent}}$
 - $\chi_{\text{solvent}} = \text{mol fraction of the solvent} = \frac{\# \text{ mols of solvent}}{\# \text{ total mols of both solute and solvent}}$
 - $P^{\circ}_{\text{solvent}}$ is the vapor pressure of the pure solvent alone.
 - When you are calculating χ_{solute} , make sure you take into account of van't Hoff. ie. 1 mols of NaCl in solution is actually 2 mols of particles.
 - boiling point elevation ($\Delta T_b = k_b \cdot m \cdot i$)
 - $\Delta T_b = k_b \cdot m \cdot i$

- ΔT_b is the increase in boiling point.
- k_b is the molal boiling point constant (like almost every other constants, the exam will give it to you).
- m is the molality (mol solute/kg solvent).
- i is van't Hoff factor.
- freezing point depression ($\Delta T_f = -k_f \cdot m \cdot i$)
 - $\Delta T_f = -k_f \cdot m \cdot i$
 - ΔT_f is the decrease in freezing point (the negative sign shows that the change is a decrease).
 - k_f is the molal freezing point constant.
 - m is the molality (mol solute/kg solvent).
 - i is van't Hoff factor.
- osmotic pressure
 - $\pi = MRT \cdot i$
 - π is the osmotic pressure.
 - M is the molarity in mol/L.
 - R is ideal gas constant.
 - T is the temperature in K.
 - Osmotic pressure determines whether and in what direction osmosis will occur.
 - Osmosis is the movement of solvent across a semi-permeable membrane from an area of low solute concentration (high solvent concentration) to an area of high solute concentration (low solvent concentration).
 - Solvent will move from an area with low π value to an area with high π value.

Colloids

- Solution: things are mixed at the molecular level and will always stay mixed. When you use the term dissolve, you are making a solution.
- Colloids: things are mixed at a "semi-molecular level" with solute aggregates that are really really tiny. Colloids will stay mixed until you centrifuge it.
- Suspension: things are mixed at a particle level and will NOT stay mixed.
- The famous colloid example is milk. Also, when you shake water and oil vigorously, you can get an emulsion, which is a colloid.

Henry's Law

- $P_{\text{solute}} = k [\text{solute}]$
- P_{solute} is the partial pressure of the solute at the solution's surface.
- k is a constant.
- $[\text{solute}]$ is the solute concentration in solution.
- The partial pressure of a solute just above the solution's surface is directly proportional to its concentration.

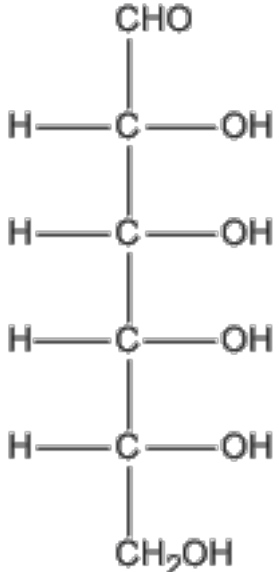
Stoichiometry

Molecular weight

- Molecular weight is numerically equal to molecular mass (amu)
- 1 amu = 1 g/mol
- ^{12}C Carbon has 12 amu and weighs 12 g/mol

Empirical formula versus molecular formula

•

molecular structure	molecular formula	empirical formula
	$\text{C}_6\text{H}_{12}\text{O}_6$	CH_2O

- empirical formula is what you get after dividing everything in the molecular formula by the highest common factor.

Metric units commonly used in the context of chemistry

- Molarity = $M = \text{mol/L}$
- molality = $m = \text{mol/kg}$
- mass = kg. molar mass = g/mol.

Description of composition by % mass

- $\% \text{mass} = \text{mass of species of interest} / \text{total mass} * 100$

Mole concept; Avogadro's number

- 1 mole = 1 mol = 1 Avogadro's number = 6.02×10^{23} molecules

Definition of density

- density = mass / volume = kg/m^3
- often in chemistry, specific gravity is used.
- specific gravity = number of times the density of water = density of substance / density of water
- density of water = $1 \text{ g/mL} = 1 \text{ g/cm}^3$
- specific gravity of water = $1 \text{ g/cm}^3 / 1 \text{ g/cm}^3 = 1$
- density of lead = 11 g/cm^3
- specific gravity of lead = $11 \text{ g/cm}^3 / 1 \text{ g/cm}^3 = 11$
- specific gravity is unitless

Oxidation number

- common oxidizing and reducing agents

oxidizing agents	reducing agents
Oxygen O_2 , Ozone O_3 , Permanganates MnO_4^- , Chromates CrO_4^{2-} , Dichromates $\text{Cr}_2\text{O}_7^{2-}$, peroxides H_2O_2 , lewis acids, stuff with a lot of oxygens	Hydrogen H_2 , metals (such as K), Zn/HCl, Sn/HCl, LAH (Lithium Aluminium Hydride), NaBH_4 (Sodium Borohydride), lewis bases, stuff with a lot of hydrogens

- disproportionation reactions
 - An element in a single oxidation state reacts to form 2 different oxidation states.
 - Disproportionation can occur when a species undergo both oxidation and reduction.

- For example: $2\text{Cu}^+ \rightarrow \text{Cu} + \text{Cu}^{2+}$
 - Here, the Cu^+ acts as both oxidizing and reducing agent and simultaneously reduce and oxidize itself.
 - The oxidized Cu^+ becomes Cu^{2+}
 - The reduced Cu^+ becomes Cu
- redox titration
 - Some terms and concepts
 - A = analyte = stuff with the unknown concentration that you want to find out by titration.
 - A_{ox} = analyte that is an oxidizing agent = analyte in its oxidized state.
 - A_{red} = analyte that is a reducing agent = analyte in its reduced state.
 - T = titrant = stuff that you add drip by drip to determine how much of it is needed to complete the titration.
 - T_{ox} = titrant that is an oxidizing agent = titrant in its oxidized state.
 - T_{red} = titrant that is a reducing agent = titrant in its reduced state.
 - S = standard = something with an accurately known amount or concentration. You use it in a reaction that accurately (stoichiometrically) produces a known amount or concentration of I_2 .
 - S_{ox} = standard that is an oxidizing agent = standard in its oxidized state.
 - S_{red} = standard that is a reducing agent = standard in its reduced state.
 - X = reactions intermediate = a species that is not present in the net equation of the overall reaction.
 - X_{ox} = intermediate that is an oxidizing agent = intermediate in its oxidized state.

- X_{red} = intermediate that is a reducing agent = intermediate in its reduced state.
- Iodimetric titration:
 - $A_{\text{red}} + I_2 \rightarrow A_{\text{ox}} + 2I^-$
- Iodometric titration:
 - 1) $A_{\text{ox}} + 2I^- \rightarrow A_{\text{red}} + I_2$
 - 2) $T_{\text{red}} + I_2 \rightarrow T_{\text{ox}} + 2I^-$
- Using a standard
 - Iodimetric titration with standard:
 - 1) $S_{\text{ox}} + 2I^- \rightarrow S_{\text{red}} + I_2$
 - 2) $A_{\text{red}} + I_2 \rightarrow A_{\text{ox}} + 2I^-$
 - notes: step 1 makes sure that the I_2 produced is of accurate amount/concentration by the use of the standard.
 - Iodometric titration with standard:
 - 1) $S_{\text{ox}} + X_{\text{red}} \rightarrow S_{\text{red}} + X_{\text{ox}}$
 - 2) $X_{\text{ox}} + A_{\text{red}}(\text{limiting reagent}) \rightarrow X_{\text{red}} + A_{\text{ox}}$
 - 3) $X_{\text{ox}}(\text{left over}) + 2I^- \rightarrow X_{\text{red}} + I_2$
 - 4) $I_2 + T_{\text{red}} \rightarrow 2I^- + T_{\text{ox}}$
 - notes:
 - step 1 makes an intermediate of accurately known amount.
 - step 2: the analyte eating up an unknown, but calculatable, amount of the intermediate.
 - step 3: the remaining intermediate going on to make I_2

- step 4: Here, you will find out how much T is needed to eat up all the I_2 produced from step 3. From this, you'll know the amount of X_{ox} (left over). You also can calculate the amount of X_{ox} originally produced by the standard. Thus $X_{ox} - X_{ox}(\text{left over}) = \text{the amount of analyte}$. Important note: this is usually not a simple subtraction because you need to take stoichiometric ratios into consideration.
- Iodine is used in redox titrations because in the presence of starch, I_2 is dark blue while I^- is colorless.
- You can only accurately titrate something going from dark to colorless ($I_2 \rightarrow 2I^-$), but not the otherway round.
- A redox titration does not necessarily need the presence of Iodine. As long as some type of color change can be seen at the equivalence point of the redox reaction, then it will work. For example:
 - $5 H_2O_2 + 6 H^+ + 2 MnO_4^- \rightarrow 5 O_2 + 2 Mn^{2+} + 8 H_2O$
 - Goes from purple to colorless because of $MnO_4^- \rightarrow Mn^{2+}$ transition.
- Redox titrations are similar to acid-base titrations, except instead of measuring pH, you look for a color change.
- Practice question:
 - 1) $S_{ox} + 5X_{red} \rightarrow 3S_{red} + 3X_{ox}$
 - 2) $3X_{ox} + A_{red}(\text{limiting reagent}) \rightarrow 3X_{red} + A_{ox}$
 - 3) $X_{ox}(\text{left over}) + 2I^- \rightarrow 2X_{red} + I_2$
 - 4) $I_2 + 2T_{red} \rightarrow 2I^- + T_{ox}$

after a long time doing drip by drip titration, you finally saw the dark color change to colorless. You noted down the initial and final volume reading of your pippette to be 300 mL and 200 mL, respectively. The concentration of the titrant you used was 10 M. You dissolved 1/2 mols of the standard to begin with. How much analyte was there?

- First, convert everything to mols (amount). $n = MV$. For the titrant (T_{red}) it is $10 M \times (0.3 L - 0.2 L) = 1 \text{ mol}$

- For the standard (S_{ox}), it is already given to you in mols. However, if it's not, you have to convert it to mols.
- We know from the notes above that $X_{\text{ox}} - X_{\text{ox}}(\text{left over}) =$ the amount of analyte, after taking into account of stoichiometric ratios.
- Here are the stoichiometric ratios:
 - From step 4
 $I_2 : 2T_{\text{red}}$
 - From step 3
 $X_{\text{ox}}(\text{left over}) : I_2$
 - From step 2
 $3X_{\text{ox}} : A_{\text{red}}(\text{limiting reagent})$
 - From step 1
 $S_{\text{ox}} : 3X_{\text{ox}}$
- $X_{\text{ox}} = 0.5 \text{ mol } S_{\text{ox}} * 3X_{\text{ox}} / S_{\text{ox}} = 1.5 \text{ mol } X_{\text{ox}}$
- $X_{\text{ox}}(\text{left over}) = 1 \text{ mol } T_{\text{red}} * I_2 / 2T_{\text{red}} * X_{\text{ox}}(\text{left over}) / I_2 = 0.5 \text{ mol } X_{\text{ox}}(\text{left over})$
- For every $A_{\text{red}}(\text{limiting reagent})$, you eat up 3 X_{ox} , thus:
 $X_{\text{ox}} - 3A_{\text{red}}(\text{limiting reagent}) = X_{\text{ox}}(\text{left over})$
 $1.5 - 3 * A_{\text{red}}(\text{limiting reagent}) = 0.5$
 $A_{\text{red}}(\text{limiting reagent}) = 1/3 \text{ mol}$
- This is why you always look at the stoichiometry of the reaction in calculations. It's almost never a simple addition or subtraction.
- The reaction in the question is actually a real redox titration taken from [wikipedia](https://en.wikipedia.org/wiki/Iodine_monocyanide).

Description of reactions by chemical equations

- conventions for writing chemical equations



- Phases
 - (s) = solid
 - (l) = liquid
 - (g) = gas
 - (aq) = aqueous (dissolved in water)
- Coefficient
 - an equation with coefficients is a balanced equation.
- Direction
 - A single head arrow denotes the reaction goes to completion in the direction of the arrow.
 - A double-sided arrow denotes a reaction in equilibrium.
 - A double-sided arrow with one side larger than the other denotes an equilibrium in favor of the side of the larger arrow.
- Charge
 - Denotes charge and magnitude, for example +, -, 2+, 5- ...etc.
 - Neutral charges are not denoted.
- balancing equations, including oxidation-reduction equations
 - balance the combustion of propanol: $\text{C}_3\text{H}_8\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
 - pick out the atom (or group) that is the easiest to balance (usually represented in only 1 term on both side of the equation. In this case it is carbon.
 $\text{C}_3\text{H}_8\text{O} + \text{O}_2 \rightarrow 3\text{CO}_2 + \text{H}_2\text{O}$

- The next easiest to balance is hydrogen

$$\mathbf{C_3H_8O + O_2 \rightarrow 3CO_2 + 4H_2O}$$
- Leave the hardest to last, oxygen. O is present in every term of the equation, so if we tried to balance O first, we'd be having a hard time. However, now that we balanced every other term, this leaves only one term left that contains O and that we haven't balanced yet. Do a quick count of oxygen atoms: there's 1 from C₃H₈O, 3x2 from 3CO₂, and 4x1 from 4H₂O. Set up this equation: 1 + 2x = 3x2 + 4x1, where x would be the coefficient of our last term, O₂. Solve for x

$$\mathbf{C_3H_8O + \frac{9}{2}O_2 \rightarrow 3CO_2 + 4H_2O}$$
- Even though we balanced out every term, we're not done yet. We need to get rid of any fractions, so multiply every term by 2.

$$\mathbf{2C_3H_8O + 9O_2 \rightarrow 6CO_2 + 8H_2O}$$
- Balancing oxidation-reduction (redox) equations
 1. Separate into half reactions.
 - There will be 2 half equations: one will be oxidation, the other reduction.
 - Half equations contain only species of interest - those containing the atom that undergoes a change in oxidation state.
 - Anything that is not covalently attached to the atom is not part of the species of interest.
 - Anything that does not undergo a change in oxidation state is a spectator ion/species.
 2. Balance each of the half reactions.
 - Balance both charge and atoms.
 - To balance one oxygen atom:
 - Under acidic conditions: add H₂O to the side that needs the oxygen atom, then add H⁺ to the other side.

- Under basic conditions: add 2OH^- to the side that needs the oxygen atom, then add H_2O to the other side.
- The Ion-Electron Method: you balance out the atoms first, then charge.
- The Oxidation-State Method: treat the species of interest as a single atom (those that undergo a change in oxidation number) and then balance it.

3. Recombine the half reactions.

- Multiply each half reaction by a factor, such that when you add them together, the electrons cancel out.
- It's like you're trying to solve a simultaneous equation and you want to eliminate the electron term.

4. Finishing touches

- Combine any identical species on the same side of the equation.
 - Cancel out any identical species on opposite sides of the equation.
 - Add back in the spectator ions.
 - For the oxidation-state method, now is also the time to balance out the oxygens and hydrogens.
 - Check to make sure that both sides of the equation have equal number of atoms and neutral net charge.
- Example using ion-electron method: $\text{K}_2\text{Cr}_2\text{O}_7 (\text{aq}) + \text{HCl} (\text{aq}) \rightarrow \text{KCl} (\text{aq}) + \text{CrCl}_3 (\text{aq}) + \text{H}_2\text{O} (\text{l}) + \text{Cl}_2 (\text{g})$

0. Separate into half reactions.

- Reduction: $\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+}$
- Oxidation: $\text{Cl}^- \rightarrow \text{Cl}_2$

- Species of interest for the oxidation reaction is Cl^- , not HCl , because the H^+ is not covalently attached to our atom of interest, and the hydrogen proton breaks off in aqueous solution.
- Similarly, we use $\text{Cr}_2\text{O}_7^{2-}$ and not $\text{K}_2\text{Cr}_2\text{O}_7$
- K^+ is the spectator ion.

1. Balance each of the half reactions.

- The Ion-Electron Method: you balance out the atoms first, then charge.
 - Balancing atoms for the reduction half reaction (Ion-electron method):
 1. $\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+}$
 2. $\text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+}$
 3. $\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$
 - Balancing charge for the reduction half reaction (Ion-electron method):
 1. $\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$
 - Do the same thing for the oxidation half reaction (Ion-electron method):
 1. $\text{Cl}^- \rightarrow \text{Cl}_2$
 2. $2\text{Cl}^- \rightarrow \text{Cl}_2$
 3. $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$

2. Recombine the half reactions.

- $\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$
- $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$
- Multiply everything in the second equation by 3
- $6\text{Cl}^- \rightarrow 3\text{Cl}_2 + 6\text{e}^-$

- Add the two equations together
- $\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6\text{e}^- + 6\text{Cl}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{Cl}_2 + 6\text{e}^-$

3. Finishing touches

- Except for the electrons, there are no like terms to combine or cancel at this time...
- $\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6\text{Cl}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{Cl}_2$
- For the ion-electron method, the equation is already balanced at this stage of the game. However, you need to add back in the spectator ions. When adding back the spectator ions, what ever you do to the left side, you do to the right.
- To the left side: The dichromate came in counter-ioned with K^+ , so add 2 K^+ .
- To the right side: What ever you do to the left side, you do the same to the right side.
- $\text{K}_2\text{Cr}_2\text{O}_7 + 14 \text{H}^+ + 6\text{Cl}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{Cl}_2 + 2\text{K}^+$
- Referring back to the original equation, the Hs and Cls on the left came in as HCl, so in order to balance the extra $14 - 6 = 8$ Hs, you add 8 Cls. As always, if you add 8 Cls to the left, go ahead and add the same to the right.
- $\text{K}_2\text{Cr}_2\text{O}_7 + 14 \text{HCl} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{Cl}_2 + 2\text{K}^+ + 8\text{Cl}^-$
- We're done focusing on the left side. A quick look at the right side shows that we need to combine 2 of the Cl^- with the 2 K^+ , and the remaining 6 Cl^- goes with the Cr. Thus the final balanced redox equation is:
- $\text{K}_2\text{Cr}_2\text{O}_7 (\text{aq}) + 14 \text{HCl} (\text{aq}) \rightarrow 2\text{CrCl}_3 (\text{aq}) + 7\text{H}_2\text{O} (\text{l}) + 3\text{Cl}_2 (\text{g}) + 2\text{KCl} (\text{aq})$

- Example using oxidation-state method: $\text{K}_2\text{Cr}_2\text{O}_7 (\text{aq}) + \text{HCl} (\text{aq}) \rightarrow \text{KCl} (\text{aq}) + \text{CrCl}_3 (\text{aq}) + \text{H}_2\text{O} (\text{l}) + \text{Cl}_2 (\text{g})$

0. Separate into half reactions (same as the ion-electron method).

- Reduction: $\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+}$
- Oxidation: $\text{Cl}^- \rightarrow \text{Cl}_2$

1. Balance each of the half reactions.

- The Oxidation-State Method: you focus on the atom of interest.
 - Balancing the atom of interest for the reduction half reaction (Oxidation-state method):
 1. $\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+}$
 2. $\text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+}$
 3. Each oxygen is 2^- so the 2 Cr on the left must be 6^+
 4. $2\text{Cr}^{6+} \rightarrow 2\text{Cr}^{3+}$
 - Balancing charge for the atom of interest in the reduction half reaction (Oxidation-state method):
 1. $2\text{Cr}^{6+} + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}$
 - Do the same thing for the oxidation half reaction (Oxidation-state method):
 1. $\text{Cl}^- \rightarrow \text{Cl}_2$
 2. $2\text{Cl}^- \rightarrow \text{Cl}_2$
 3. $2\text{Cl}^- \rightarrow 2\text{Cl}^0$
 4. $2\text{Cl}^- \rightarrow 2\text{Cl}^0 + 2\text{e}^-$

2. Recombine the half reactions.

- $2\text{Cr}^{6+} + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}$
- $2\text{Cl}^- \rightarrow 2\text{Cl}^0 + 2\text{e}^-$
- Multiply everything in the second equation by 3:
- $2\text{Cr}^{6+} + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}$
- $6\text{Cl}^- \rightarrow 6\text{Cl}^0 + 6\text{e}^-$
- add the two equations together
- $2\text{Cr}^{6+} + 6\text{e}^- + 6\text{Cl}^- \rightarrow 2\text{Cr}^{3+} + 6\text{Cl}^0 + 6\text{e}^-$

3. Finishing touches

- Except for the electrons, there are no like terms to combine or cancel at this time...
- $2\text{Cr}^{6+} + 6\text{Cl}^- \rightarrow 2\text{Cr}^{3+} + 6\text{Cl}^0$
- Convert the atoms of interest into species of interest by referring back to the original equation.
- $\text{K}_2\text{Cr}_2\text{O}_7 + 6\text{HCl} \rightarrow 2\text{CrCl}_3 + 3\text{Cl}_2$
- Now unlike the ion-electron method, where the equation is balanced and you only add back spectator ions at this stage of the game, the oxidation-state method requires you to balance the equation again. This is because after you convert the atoms of interest back to their species of interest, the equation is no longer balanced.
- Start with the oxygens. On the left you have 7 O, so add 7 H₂O to the right.
- $\text{K}_2\text{Cr}_2\text{O}_7 + 6\text{HCl} \rightarrow 2\text{CrCl}_3 + 3\text{Cl}_2 + 7\text{H}_2\text{O}$
- Now take care of the hydrogens. You have 6H on the left, but 14H on the right. That means you should add 8 more Hs to the left to make a total of 14. All 14 Hs on the left should be in the form of HCl (refer back to the original equation. Note, HCl here is both the species of interest and also the spectator species. Some of the HCl contributes to the $\text{Cl}^- \rightarrow \text{Cl}_2$ oxidation, but the other portion of the HCl doesn't

undergo redox. It merely provides the H^+ for the water and the Cl^- for the KCl and CrCl_3).

- $\text{K}_2\text{Cr}_2\text{O}_7 + 14\text{HCl} \rightarrow 2\text{CrCl}_3 + 3\text{Cl}_2 + 7\text{H}_2\text{O}$
- Now you see there's 14 Cl to the left, and 12 Cl to the right. You need 2 more Cls on the right. Referring back to the original equation, all the right-sided Cls come in the form of KCl (don't modify the Cl_2 since you've already correctly balanced it by the oxidation state method. When balancing equations at this stage, only play around with water and the spectator species).
- $\text{K}_2\text{Cr}_2\text{O}_7 + 14\text{HCl} \rightarrow 2\text{CrCl}_3 + 3\text{Cl}_2 + 7\text{H}_2\text{O} + 2\text{KCl}$
- Upon examination of the equation, every atom is balanced. So the final balanced redox equation is:
- $\text{K}_2\text{Cr}_2\text{O}_7 (\text{aq}) + 14\text{HCl} (\text{aq}) \rightarrow 2\text{CrCl}_3 (\text{aq}) + 3\text{Cl}_2 (\text{g}) + 7\text{H}_2\text{O} (\text{l}) + 2\text{KCl} (\text{aq})$

- limiting reactants

- Limiting reactant is the reactant that will get all used up first.
- What is the limiting reactant for the following reaction?
 - $3\text{X}_{\text{ox}} + \text{A}_{\text{red}} \rightarrow 3\text{X}_{\text{red}} + \text{A}_{\text{ox}}$
 - Given: You use 60 grams of X_{ox} and 63 grams of A_{red}
 - Given: the molecular weight of X_{ox} is 2 amu, and A_{red} is 7 amu.
 - The first thing you do is convert everything in moles. 1 amu = 1 g/mol.
 - X_{ox} : $60 \text{ g} / 2 \text{ amu} = 30 \text{ mols}$.
 - A_{red} : $63 \text{ g} / 7 \text{ amu} = 9 \text{ mols}$.
 - Now here's where stoichiometry comes in: divide the mols by the stoichiometric coefficient of the species:
 - $30 \text{ mols} / 3 = 10$ for X_{ox}

- $9 \text{ mols} / 1 = 9$ for A_{red}
 - Now compare the values. 9 is the smallest, so A_{red} is the limiting reactant.
 - Limiting reactant can also be called the limiting reagent, limiting species, limiting [whatever].
- theoretical yields
 - The theoretical yield is how much of the product will be made based on stoichiometry.
 - In calculating the theoretical yield, first find out what your limiting reactant is. Then, use your limiting reactant as the stoichiometric basis to calculate how much product you will get.
 - In real life, the experimental yield is always less than the theoretical yield because of loss during steps of the reaction (now you can have a higher experimental yield if you're in a chem lab and you accidentally dumped in more reactants than you realized).
 - What is the theoretical yield for $3X_{\text{red}}$
 $3X_{\text{ox}} + A_{\text{red}} \rightarrow 3X_{\text{red}} + A_{\text{ox}}$
 if you react 60 grams of X_{ox} with 63 grams of A_{red} given that the molecular weight of X_{ox} is 2 amu, A_{red} is 7 amu, and X_{red} is 10 amu?
 - First, find who's the limiting reagent.
 - Using the method described above in the limiting reactant section, we find out that A_{red} is the limiting reactant.
 - Next, take the amount in mols of the limiting reactant (9 mols according to the above calculation) and do the stoichiometry to get to how many mols of $3X_{\text{red}}$ this will yield.
 - $9 \text{ mols of } A_{\text{red}} * 3 \text{ mols of } X_{\text{red}} \text{ per } 1 \text{ mol of } A_{\text{red}} = 27 \text{ mols.}$
 - Lastly, convert mols to grams: $27 \text{ mols} * 10 \text{ g/mol} = 270 \text{ g}$
 - The theoretical yield for the above reaction is 270 g of X_{red}

- Say you did an actual experiment of the above reaction and you managed to obtain 243 g X_{red} , then the experimental yield is 243 g.
- Percent yield = experimental yield / theoretical yield x 100
- For the above experiment, the percent yield would be $243 / 270 \times 100 = 90 \%$

Thermodynamics and Thermochemistry

Energy changes in chemical reactions- thermochemistry

- Thermodynamic system, state function
 - A thermodynamic system is just a fancy name for the system that you are studying.
 - Isolated system: no exchange of heat, work, or matter with the surroundings.
 - Closed system: exchange of heat and work, but not matter with the surroundings.
 - Open system: exchange of heat, work and matter with the surroundings.
 - A state function is path-independent and depends only on the initial and final states.
 - State functions include: ΔH (enthalpy), ΔS (entropy), ΔG (free energy change), ΔU (internal energy change).
 - State function is also called state quantity, or function of state.
- Conservation of energy
 - The total energy of an isolated system remains constant.
 - The total energy of a closed or open system plus the total energy of its surroundings is constant.
 - Total energy is neither gained nor lost, it is merely transferred between the system and its surroundings.
- Endothermic/exothermic reactions
 - Endothermic = energy is taken up by the reaction in the form of heat. ΔH is positive.
 - Exothermic = energy is released by the reaction in the form of heat. ΔH is negative.

- enthalpy H and standard heats of reaction and formation
 - enthalpy or H is the heat content of a reaction. Mnemonic: H stands for heat.
 - ΔH is the change in the heat content of a reaction. + means heat is taken up, - means heat is released.
 - Standard heat of reaction, ΔH_{rxn} , is the change in heat content for any reaction.
 - Standard heat of formation, ΔH_f , is the change in heat content a formation reaction.
 - A formation reaction is where a compound or molecule in its standard state is formed from its elemental components in their standard states. The standard state is where things are in their natural, lowest energy, state. For example, oxygen is O_2 (diatomic gas) and carbon is C (solid graphite).
 - The unit for enthalpy is in energy (J), or it can be expressed as energy per mol (J/mol).
- Hess' law of heat summation
 - $\Delta H_{\text{rxn}} = \Delta(\Delta H_f) = \text{sum of } \Delta H_f \text{ (products)} - \text{sum of } \Delta H_f \text{ (reactants)}$
- Bond dissociation energy as related to heats of formation
 - Bond dissociation is the energy required to break bonds.
 - $\Delta H_{\text{rxn}} = \text{Bond dissociation energy of all the bonds in reactants} - \text{bond dissociation energy of all the bonds in products}$
 - $\Delta H_{\text{rxn}} = \text{Enthalpy of formation of all the bonds in products} - \text{Enthalpy of formation of all the bonds in reactants.}$
 - Bond dissociation energy is positive because energy input is required to break bonds.
 - The enthalpy of formation of bonds is negative because energy is released when bonds form.
- Measurement of heat changes (calorimetry), heat capacity, specific heat (specific heat of water = $4.184 \text{ J/g}\cdot\text{k}$)

- Heat capacity = the amount of heat required to raise the temperature of something by 1 °C.
 - Molar heat capacity = heat capacity per mol = $\text{J} / \text{mol} \cdot ^\circ\text{C}$
 - Specific heat (capacity) = heat capacity per mass = $\text{J} / \text{g} \cdot ^\circ\text{C}$
 - Celsius can be replaced by Kelvin here because a change in 1 °C is the same as a change in 1 K.
- It takes 4.2 J of heat energy to raise the temperature of 1 gram of water by 1 °C.
- Some useful conversion factors:
 - 1 calorie = 4.2 J; 1 Calorie (with capital C) = 1000 calorie = 4200 J.
 - For water, 1 gram = 1 cubic centimeter = 1 mL
- Entropy as a measure of "disorder"; relative entropy for gas, liquid, and crystal states
 - Entropy = measure of disorder = energy / temperature = J / K (it can also be expressed as molar entropy in $\text{J} / \text{mol} \cdot \text{K}$)
 - Entropy of gas > liquid > crystal states.
 - At room temperature, the gas molecules are flying around, but the table in front of you is just sitting there. So, gases have more disorder.
 - Reactions that produces more mols of gas have a greater increase in entropy.
- Free energy G
 - Free energy is the energy available that can be converted to do work.
 - $\Delta G = \Delta H - T\Delta S$
 - T is temperature in Kelvin.
- Spontaneous reactions and standard free energy change
 - Spontaneous reactions are reactions that can occur all by itself.
 - Spontaneous reactions have negative ΔG .
 - Do not assume that an exothermic reaction is spontaneous, because a large, negative ΔS can cause it to become nonspontaneous.

- Do not assume that an endothermic reaction is nonspontaneous, because a large, positive ΔS can make it spontaneous.
- Do not assume that spontaneous reactions will occur quickly, because it may take a million years for it to happen, depending on its kinetics.

Thermodynamics

- Zeroth law (concept of temperature)
 - 0th law of thermodynamics basically says that heat flows from hot objects to cold objects to achieve thermal equilibrium.
 - Mathematically, if $T_A = T_B$, and $T_B = T_C$, then $T_A = T_C$. Where T is temperature.
- First law ($\Delta E = q + w$, conservation of energy)
 - 1st law of thermodynamics is based on the principle of conservation of energy, and it basically says that the change in total internal energy of a system is equal to the contributions from heat and work.
 - ΔE is the same thing as ΔU , which is the change in internal energy.
 - Q is the contribution from heat
 - Q is positive when heat is absorbed into the system (ie. heating it).
 - Q is negative when heat leaks out of the system (ie. cooling it).
 - W is the contribution from work.
 - W is positive when work is done on the system (ie. compression).
 - W is negative when work is done by the system (ie. expansion).
- Equivalence of mechanical, chemical, electrical and thermal energy units
 - If it's energy, it's Joules. It doesn't matter if it's potential energy, kinetic energy, or any energy - as long as it's energy, it has the unit Joules.
 - Energy is equivalent even if they are in different forms. For example, 1 Joule of mechanical energy can be converted into 1 Joule of electrical energy (ignoring heat loss) - no more, no less.
- Second law: concept of entropy

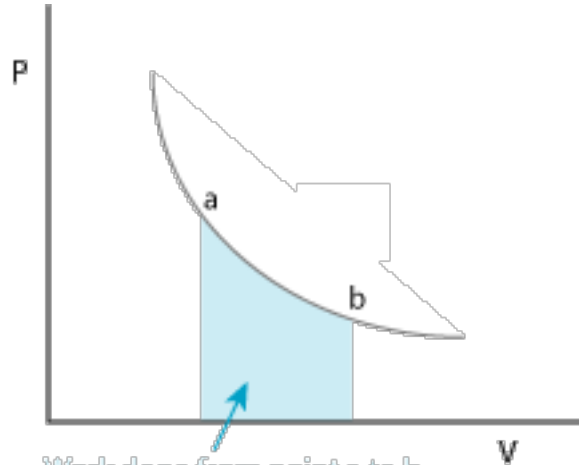
- The 2nd law states that the things like to be in a state of higher entropy and disorder.
- An isolated system will increase in entropy over time.
- An open system can decrease in entropy, but only at the expense of a greater increase in entropy of its surroundings.
- The universe as a whole is increasing in entropy.
- $\Delta S \geq q / T$
 - q is the heat transferred.
 - T is the temperature in Kelvin.
 - For reversible processes $\Delta S = q / T$.
 - For irreversible processes $\Delta S > q / T$.
 - Real processes that occur in the world are never reversible, so entropy change is always greater than the heat transfer over temperature.
 - Because of the irreversibility nature of real processes, as long as anything occurs, the entropy of the universe increases.
- Temperature scales, conversion

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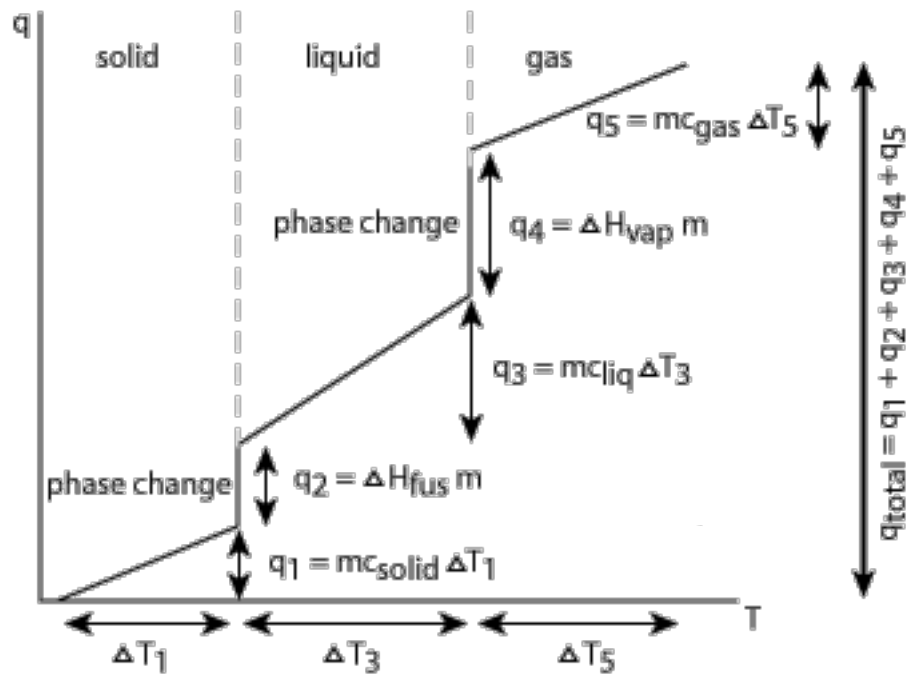
○	K	°C	°F
Absolute zero	0	-273	-460
Freezing point of water / melting point of ice	273	0	32
Room temperature	298	25	77
Body temperature	310	37	99
Boiling point of water / condensation of steam	373	100	212

- $K = ^\circ C + 273$
- $F = ^\circ C \times 1.8 + 32$
- Heat transfer: conduction, convection, radiation

- Conduction: heat transfer by direct contact. Requires things to touch.
- Convection: heat transfer by flowing current. Need the physical flow of matter.
- Radiation: heat transfer by electromagnetic radiation (commonly in the infrared frequency range). Does not need the physical flow of matter, can occur through a vacuum.
- Heat of fusion, heat of vaporization
 - Also called latent heat of fusion, enthalpy of fusion and latent heat of vaporization, enthalpy of vaporization.
 - Heat of fusion = ΔH_{fus} = the energy input needed to melt something from the solid to the liquid at constant temperature.
 - Heat of vaporization = ΔH_{vap} = the energy input needed to vaporize something from the liquid to the gas at constant temperature.
 - Latent heats can be expressed as molar values such as J / mol.
 - The energy it takes to melt a solid is $\Delta H_{\text{fus}} \times \text{\#mols of that solid}$.
 - The energy it takes to vaporize a liquid is $\Delta H_{\text{vap}} \times \text{\#mols of that liquid}$.
 - Latent heats can also be expressed as J / mass, where energy can be obtained by multiplying the latent heats by the mass of the substance.
 - Energy is released when either a gas condenses into a liquid, or when a liquid freezes into a solid. The energy released is the same as the energy of their reverse processes (see formula above).
- PV diagram: work done = area under or enclosed by curve



- Work done from point a to b
- PV diagrams depict thermodynamic processes by plotting pressure against volume.
- Adiabatic process: no heat exchange, $q = 0$. $\Delta E = W$
- Isothermal process: no change in temperature $\Delta T = 0$.
- Isobaric process: pressure is constant, $W = P\Delta V$.
- Isovolumetric (isochoric) process: volume is constant, $W = 0$. $\Delta E = q$
- Calorimetry



- $q = mc\Delta T$
- q is heat absorbed / heat input, m is mass, c is specific heat, and ΔT is change in temperature.
- This formula only works if no phase change is involved.
- Different phases have different specific heats, and on top of that, a phase change requires extra energy such as heat of fusion and heat of vaporization, which is why the above formula does not work across different phases.
- To work problems that involve a phase change, use the calorimetry equation individually for the different phases, then take into account of the heat of fusion or vaporization.
- For example, how much energy does it take to heat ice from $-20\text{ }^{\circ}\text{C}$ to water at $37\text{ }^{\circ}\text{C}$. There's 3 components to this question:
 - For the ice phase from $-20\text{ }^{\circ}\text{C}$ to $0\text{ }^{\circ}\text{C}$, use $q = mc_{\text{ice}}\Delta T$, where ΔT is 20.
 - For the phase transition, use heat of fusion: $q = \Delta H_{\text{fus}} \times \text{\#mols of ice/water}$, where ΔH_{fus} is in energy per mol. (note: if the heat of fusion is given in energy per mass, then you should multiply it by the mass to get energy)
 - For the water phase from $0\text{ }^{\circ}\text{C}$ to $37\text{ }^{\circ}\text{C}$, use $q = mc_{\text{water}}\Delta T$, where ΔT is 37.

Old topics

The topics below are outdated. They have been either modified or replaced by the most recent aamc publication.

- Measurement of heat changes (calorimetry); heat capacity; specific heat (specific heat of water = 1 cal per degrees Celsius)
 - Heat capacity = the amount of heat required to raise the temperature of something by $1\text{ }^{\circ}\text{C}$.
 - Molar heat capacity = heat capacity per mol = $\text{J} / \text{mol}\cdot^{\circ}\text{C}$
 - Specific heat (capacity) = heat capacity per mass = $\text{J} / \text{g}\cdot^{\circ}\text{C}$

- Celsius can be replaced by Kelvin here because a change in 1 °C is the same as a change in 1 K.
- It takes 1 cal, or 4.2 J, of heat energy to raise the temperature of 1 gram of water by 1 °C.
- 1 calorie = 4.2 J; 1 Calorie (with capital C) = 1000 calorie = 4200 J.
- For water, 1 gram = 1 cubic centimeter = 1 mL
- First law: $\Delta E = Q - W$ (conservation of energy)
 - 1st law of thermodynamics is based on the principle of conservation of energy, and it basically says that the change in total internal energy of a system is equal to the energy absorbed as heat minus the energy lost from doing work.
 - $\Delta E = Q - W$
 - ΔE is the same thing as ΔU , which is change in internal energy.
 - Q is the heat absorbed *into* the system.
 - W is the work done *by* the system.
 - An alternative expression for the first law is $\Delta E = Q + W$, where work is either positive if done *on* the system, or negative if done *by* the system (this is the classical expression of $\Delta E = Q - W$).
 - Expansion = work done *by* the system $\rightarrow \Delta E = Q - W$
 - Compression = work done *on* the system $\rightarrow \Delta E = Q + W$
- Specific heat, specific heat of water ($^1\text{cal} / \text{g}\cdot^\circ\text{C}$)
 - $1 \text{ cal} / \text{g}\cdot^\circ\text{C} = 4.2 \text{ J} / \text{g}\cdot^\circ\text{C} = 0.001 \text{ Cal} / \text{g}\cdot^\circ\text{C} = 4200 \text{ J} / \text{kg}\cdot^\circ\text{C} = 4.2 \text{ kJ} / \text{kg}\cdot^\circ\text{C}$

Rate Processes in Chemical Reactions - Kinetics and Equilibrium

Reaction rates

- The reaction rate is defined as the rate of change in the concentration of reactants or products. ie. how fast a reactant gets used up, and how fast a product gets produced.
- $\text{Rate} = -\Delta\text{Reactant}/\Delta\text{Time}$ = how fast a reactant disappears.
- $\text{Rate} = \Delta\text{Product}/\Delta\text{Time}$ = how fast a product forms.
- The unit for rate is molarity per second, or M/s.

Dependence of reaction rate upon concentration of reactants; rate law

- The rate law is the equation that describes the rate = the product of reactants raised to some exponents.
- $aA + bB \rightarrow cC + dD$
 - If the above reaction is single-step, then $\text{rate} = k[A]^a[B]^b$
 - If the above reaction is the rate-determining step of a multi-step reaction, then the rate of the multi-step reaction = $k[A]^a[B]^b$
 - If the above reaction is a multi-step reaction, then $\text{rate} = k[A]^x[B]^y$, where x and y are unknowns that correspond to the rate-determining step.
- To determine the rate law, you refer to a table of rates vs reactant concentrations.

◦

[A] (M)	[B] (M)	[C] (M)	rate (M/s)
1	1	1	1
2	1	1	4
1	2	1	2

1	1	2	1
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- $r = k[A]^x[B]^y[C]^z$
- From this table, a 2x increase in [A] corresponds to a 4x increase in the rate. $2^x = 4$, so $x = 2$.
- A 2x increase in [B] corresponds to a 2x increase in the rate. $2^y = 2$, so $y = 1$.
- A 2x increase in [C] corresponds to 1x (no change) in rate. $2^z = 1$, so $z = 0$.
- $r = k[A]^2[B]^1[C]^0$
- $r = k[A]^2[B]$
- rate constant
 - The k in the rate law is the rate constant.
 - The rate constant is an empirically determined value that changes with different reactions and reaction conditions.
- reaction order
 - Reaction order = sum of all exponents of the concentration variables in the rate law.
 - Reaction order in A = the exponent of [A]
 -

Reaction Type	Reaction Order	Rate Law(s)
Unimolecular	1	$r = k[A]$
Bimolecular	2	$r = k[A]^2$, $r = k[A][B]$
Termolecular	3	$r = k[A]^3$, $r = k[A]^2[B]$, $r = k[A][B][C]$
Zero order reaction	0	$r = k$

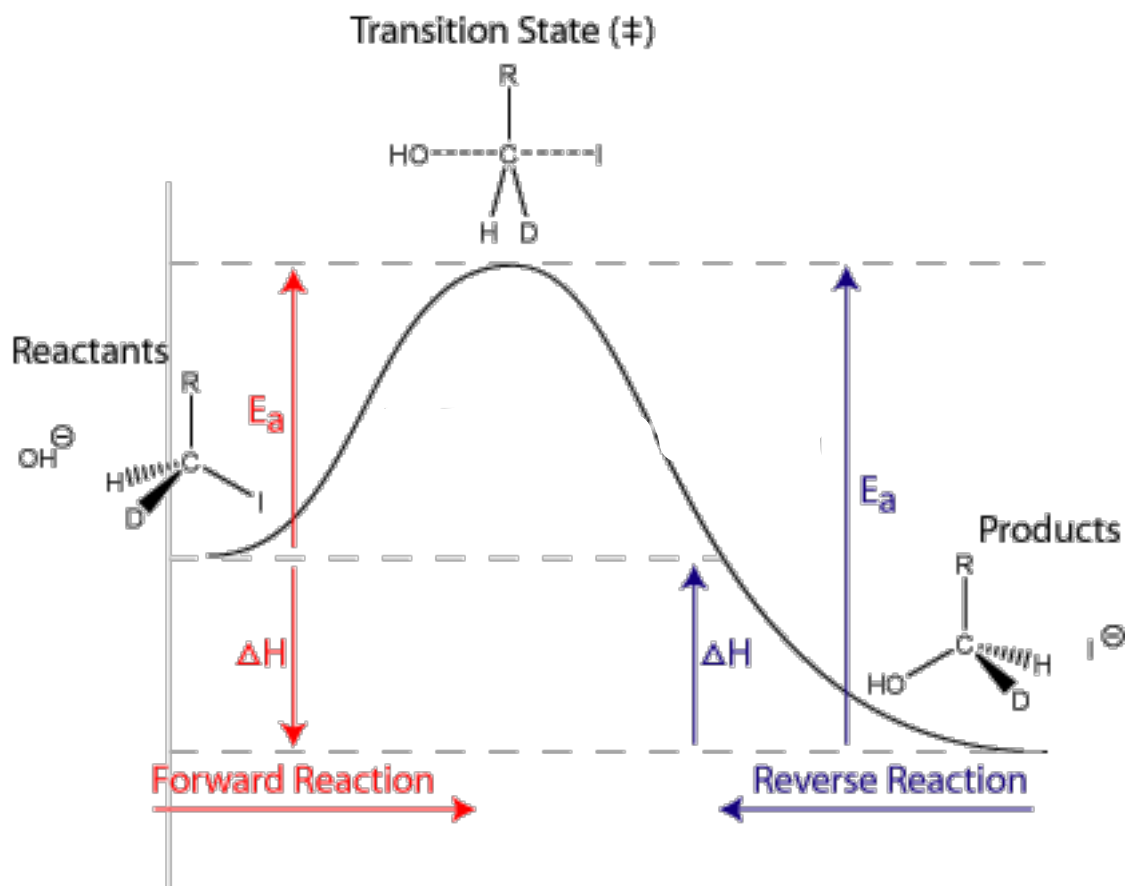
Rate determining step

- The slowest step of a multi-step reaction is the rate determining step.
- The rate of the whole reaction = the rate of the rate determining step.

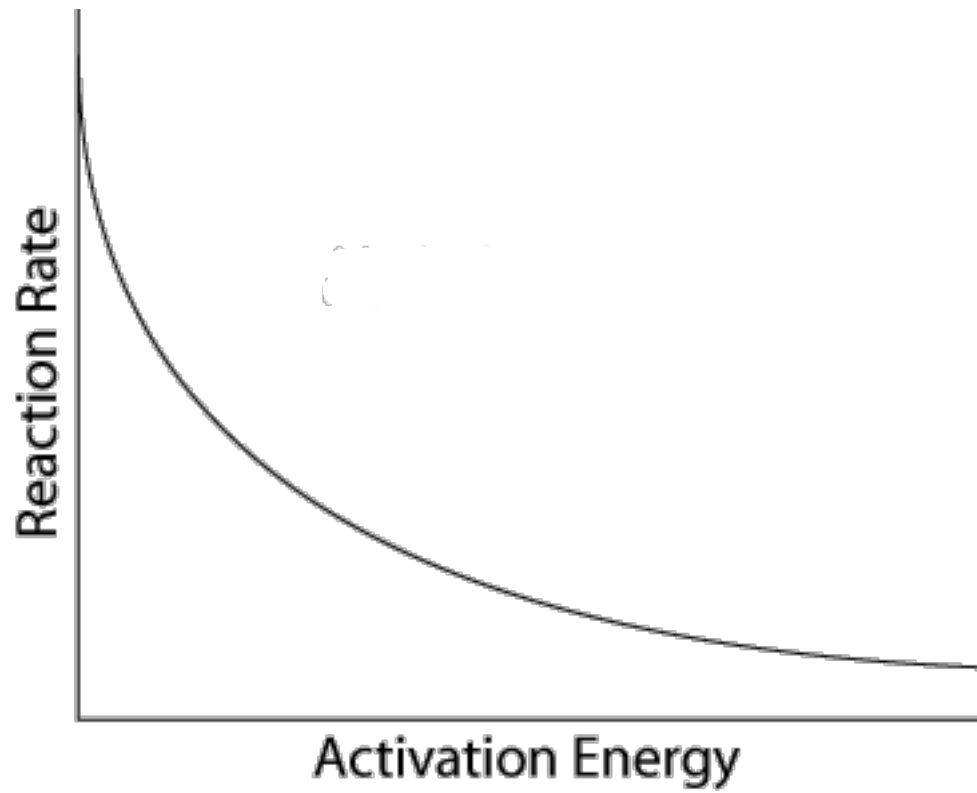
- The rate law corresponds to the components of the rate determining step.

Dependence of reaction rate on temperature

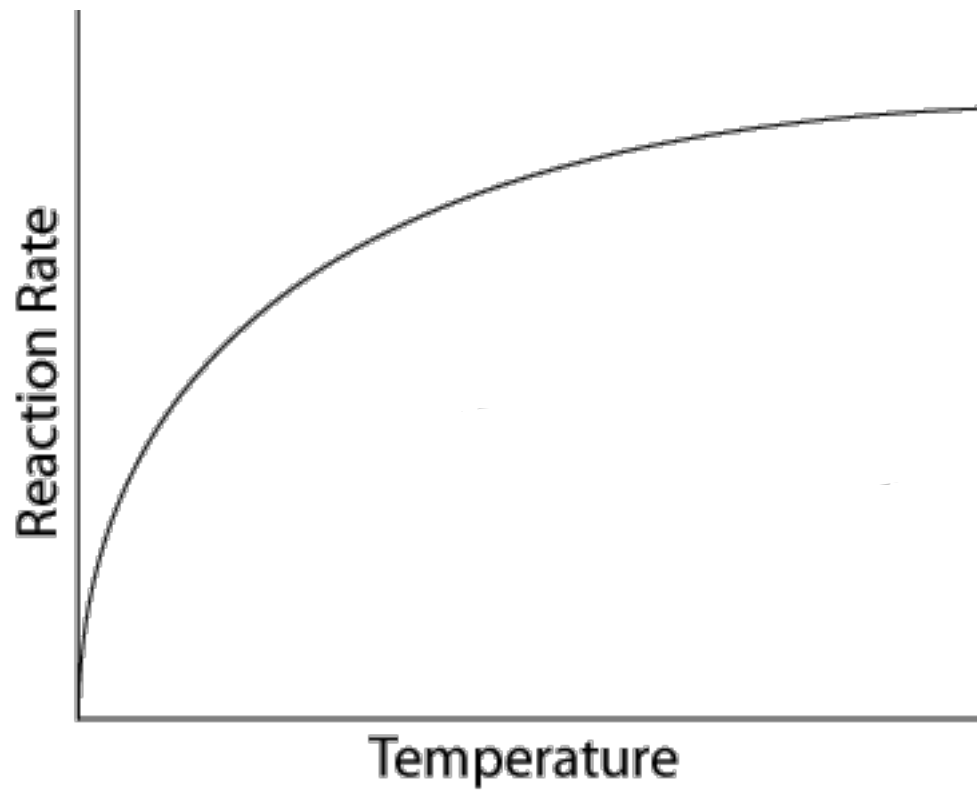
- Activation energy
 - Activated complex or transition state
 - Activated complex = what's present at the transition state.
 - In the transition state, bonds that are going to form are just beginning to form, and bonds that are going to break are just beginning to break.
 - The transition state is the peak of the energy profile.
 - The transition state can go either way, back to the reactants, or forward to form the products.
 - You can't isolate the transition state. Don't confuse the transition state with a reaction intermediate, which is one that you can isolate.
 - Interpretation of energy profiles showing energies of reactants and products, activation energy, ΔH for the reaction



- - The activation energy is the energy it takes to push the reactants up to the transition state.
 - ΔH is the difference between the reactant H and the product H (net change in H for the reaction).
 - H is heat of enthalpy.
 - Exothermic reaction = negative ΔH
 - Endothermic reaction = positive ΔH
- Arrhenius equation
 - $k = Ae^{-E_a/RT}$
 - k is rate constant, E_a is activation energy, T is temperature (in Kelvins), R is universal gas constant, A is a constant.
 - What this equation tells us: Low E_a , High T $\rightarrow$ large k $\rightarrow$ faster reaction.



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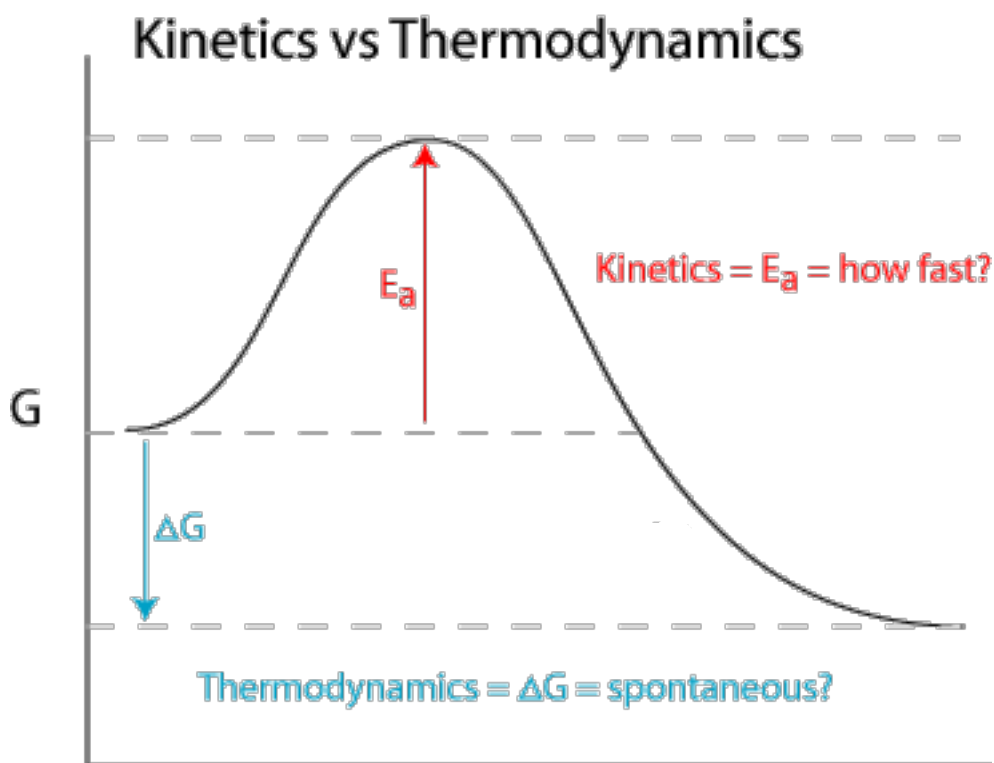
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- When activation energy approaches zero, the reaction proceeds as fast as the molecules can move and collide.

- When temperature approaches absolute zero, reaction rate approaches zero because molecular motion approaches zero.

Kinetic control versus thermodynamic control of a reaction

- A reaction can have 2 possible products: kinetic vs thermodynamic product.
 - Kinetic product = lower activation energy, formed preferentially at lower temperature.
 - Thermodynamic product = lower (more favorable/negative) ΔG , formed preferentially at higher temperature.



- Thermodynamics tells you whether a reaction will occur. In other words, whether it is spontaneous or not.
 - A reaction will occur if ΔG is negative.
 - $\Delta G = \Delta H - T\Delta S$

Factors favoring a reaction	Factors disfavoring a reaction
Being exothermic ($-\Delta H$)	Being endothermic ($+\Delta H$)
Increase in entropy (positive ΔS)	Decrease in entropy (negative ΔS)

Temperature is a double-edged sword. High temperatures amplify the effect of the ΔS term, whether that is favoring the reaction ($+\Delta S$) or disfavoring the reaction ($-\Delta S$)

- Kinetics tells you how fast a reaction will occur.
 - A reaction will occur faster if it has a lower activation energy.

Catalysts; the special case of enzyme catalysis

- Catalysts speed up a reaction without getting itself used up.
- Enzymes are biological catalysts.
- Catalysts/enzymes act by lowering the activation energy, which speeds up both the forward and the reverse reaction.
- Catalysts/enzymes alter kinetics, not thermodynamics.
- Catalysts/enzymes help a system to achieve its equilibrium faster, but does not alter the position of the equilibrium.
- Catalysts/enzymes increase k (rate constant, kinetics), but does not alter K_{eq} (equilibrium).

Equilibrium in reversible chemical reactions

- Law of Mass Action
 - The Law of Mass Action is the basis for the equilibrium constant.
 - What the Law of Mass Action says is basically, the rate of a reaction depends only on the concentration of the pertinent substances participating in the reaction.
 - Using the law of mass action, you can derive the equilibrium constant by setting the forward reaction rate = reverse reaction rate, which is what happens at equilibrium.
 - For the single-step reaction: $aA + bB \rightleftharpoons cC + dD$
 - $r_{\text{forward}} = r_{\text{reverse}}$
 - $k_{\text{forward}}[A]^a[B]^b = k_{\text{reverse}}[C]^c[D]^d$
 - $k_{\text{forward}}/k_{\text{reverse}} = [C]^c[D]^d/[A]^a[B]^b$

- $K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$
- This holds true for single and multi-step reactions, the exam will not ask you to prove why this is so.
- the equilibrium constant
 - There are 2 ways of getting K_{eq}
 - From an equation, $K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$
 - From thermodynamics, $\Delta G^\circ = -RT \ln (K_{eq})$
 - Derivation: $\Delta G = 0$ at equilibrium.
 - $\Delta G = \Delta G^\circ + RT \ln Q$
 - $0 = \Delta G^\circ + RT \ln Q_{at \text{ equilibrium}}$
 - $\Delta G^\circ = -RT \ln Q_{at \text{ equilibrium}}$
 - At equilibrium:
 - $\Delta G = 0$
 - $r_{forward} = r_{backward}$
 - $Q = K_{eq}$
 - K_{eq} is a ratio of $k_{forward}$ over $k_{backward}$
 - If K_{eq} is much greater than 1 (For example if $K_{eq} = 10^3$), then the position of equilibrium is to the right; more products are present at equilibrium.
 - If $K_{eq} = 1$, then the position of equilibrium is in the center, the amount of products is roughly equal to the amount of reactants at equilibrium.
 - If K_{eq} is much smaller than 1 (For example if $K_{eq} = 10^{-3}$), then the position of equilibrium is to the left; more reactants are present at equilibrium.
 - The reaction quotient, Q , is the same as K_{eq} except Q can be used for any point in the reaction, not just at the equilibrium.

- If $Q < K_{eq}$, then the reaction is at a point where it is still moving to the right in order to reach equilibrium.
- If $Q = K_{eq}$, the reaction is at equilibrium.
- If $Q > K_{eq}$, then the reaction is too far right, and is moving back left in order to reach equilibrium.
- The reaction naturally seeks to reach its equilibrium
- application of LeChatelier's principle
 - LeChatelier's principle: if you knock a system off its equilibrium, it will readjust itself to reach equilibrium.
 - A reaction at equilibrium doesn't move forward or backward, but the application of LeChatelier's principle means that you can disrupt a reaction at equilibrium so that it will proceed forward or backward in order to restore the equilibrium.
 -

Reaction at equilibrium	What will induce the reaction to move forward	What will induce the reaction to move backward
$A(aq) + B(aq) \rightleftharpoons C(aq) + D(aq)$	Add A or B. Remove C or D.	Remove A or B. Add C or D.
$A(s) + B(aq) \rightleftharpoons C(l) + D(aq)$	Add B. Remove D. Adding or removing solids or liquids to a reaction at equilibrium doesn't do anything that will knock the system off its equilibrium. So, altering A and C won't make a difference.	Remove B. Add D.
$A(s) + B(aq) \rightleftharpoons C(l) + D(g)$	Add B. Remove D. Remove (decrease) pressure.	Remove B. Add D. Add (increase) pressure.
$A(s) + B(g) \rightleftharpoons C(l) + D(g)$	Add B. Remove D. Since both side of the balanced equation contains the same mols of gas products, modifying pressure is of no use.	Remove B. Add D.
$A(s) + B(aq) \rightleftharpoons C(l) + D(aq)$ $\Delta H < 0$	Add B. Remove D. Removing heat by cooling the reaction.	Remove B. Add D. Add heat by

		heating the reaction.
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Relationship of the equilibrium constant and standard free energy change

- $\Delta G = \Delta G^\circ + RT \ln Q$
 - Set $\Delta G = 0$ at equilibrium.
 - Q becomes K_{eq} at equilibrium.
- $0 = \Delta G^\circ + RT \ln (K_{eq})$
- $\Delta G^\circ = -RT \ln (K_{eq})$

Solution Chemistry

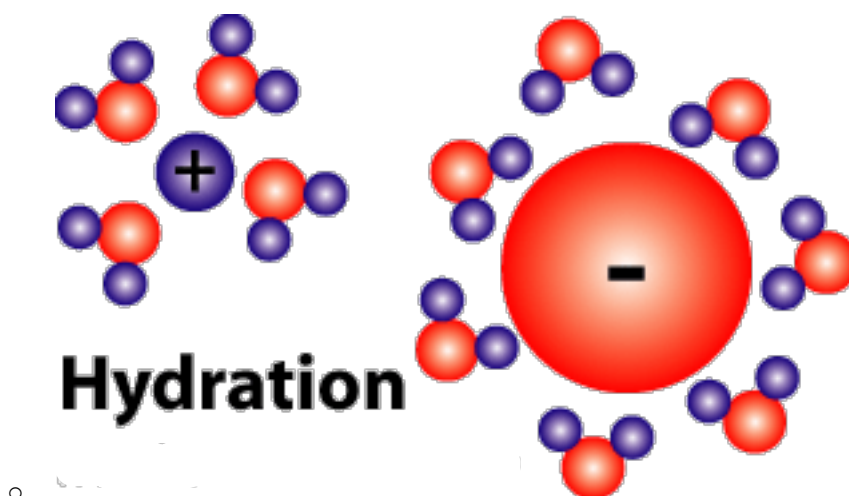
Ions in solution

- Anion, cation (common names, formulas and charges for familiar ions; e.g., NH_4^+ , ammonium; PO_4^{3-} , phosphate; SO_4^{2-} , sulfate)

Common name	Formula
Anion	
Hydroxide	OH^-
Chloride	Cl^-
Hypochlorite	ClO^-
Chlorite	ClO_2^-
Chlorate	ClO_3^-
Perchlorate	ClO_4^-
Halide, hypohalide, etc	X^- , XO^- , etc
Carbonate	CO_3^{2-}
Hydrogen Carbonate (Bicarbonate)	HCO_3^-
Sulfate	SO_4^{2-}
Hydrogen Sulfate (Bisulfate)	HSO_4^-
Sulfite	SO_3^{2-}
Thiosulfate	$\text{S}_2\text{O}_3^{2-}$
Nitrate	NO_3^-
Nitrite	NO_2^-
Phosphate	PO_4^{3-}
Hydrogen Phosphate	HPO_4^{2-}
Dihydrogen Phosphate	H_2PO_4^-
Phosphite	PO_3^{3-}
Cyanide	CN^-
Thiocyanate	SCN^-
Peroxide	O_2^{2-}
Oxalate	$\text{C}_2\text{O}_4^{2-}$
Acetate	$\text{C}_2\text{H}_3\text{O}_2^-$
Chromate	CrO_4^{2-}

Dichromate	$\text{Cr}_2\text{O}_7^{2-}$
Permanganate	MnO_4^-
Cation	
Hydronium	H_3O^+
Ammonium	NH_4^+
Metal	M^{n+}

- Hydration, the hydronium ion



- Another name for hydration is solvation.
- Hydration is where water forms a shell around ions in solution.
- The oxygen atom on water is partially negative, so it surrounds cations.
- The hydrogen atoms on water is partially positive, so they surround anions.
- Hydronium ion = H_3O^+
- H^+ never exist as a proton in water, it always exists as the hydronium ion.

Solubility

- Units of concentration (e.g., molarity)
 - Molarity = $M = \text{mol solute/L solution}$

- Molality = $m = \text{mol solute/kg solvent}$
- Normality = $N = \text{Molarity of the species that matter.}$
 - $1 \text{ M HCl} = 1 \text{ N HCl}$
 - $1 \text{ M H}_2\text{SO}_4 = 2 \text{ N H}_2\text{SO}_4$
 - $1 \text{ M H}_3\text{PO}_4 = 3 \text{ N H}_3\text{PO}_4$
- $x \% = x \text{ g} / 100 \text{ g} = x \text{ g} / 100 \text{ mL}$
- $x \text{ ppm} = x \text{ parts per million} = x \text{ mg} / \text{kg} = x \text{ mg} / \text{L}$
- Solubility product constant, the equilibrium expression
 - Solubility product constant = K_{sp}
 - $\text{AgCl (s)} \rightleftharpoons \text{Ag}^+ \text{ (aq)} + \text{Cl}^- \text{ (aq)}$
 - $K_{sp} \text{ for AgCl} = [\text{Ag}^+][\text{Cl}^-]$
 - $\text{Ag}_2\text{SO}_4 \text{ (s)} \rightleftharpoons 2\text{Ag}^+ \text{ (aq)} + \text{SO}_4^{2-} \text{ (aq)}$
 - $K_{sp} \text{ for Ag}_2\text{SO}_4 = [\text{Ag}^+]^2[\text{SO}_4^{2-}]$
 - K_{sp} values are found in a table:
 - $K_{sp} \text{ for AgCl} = 1.8 \times 10^{-10}$
 - $K_{sp} \text{ for Ag}_2\text{SO}_4 = 1.2 \times 10^{-5}$
 - K_{sp} is simply K_{eq} for dissolutions.
 - The higher the K_{sp} , the more the reaction products dominate in a saturated solution (at equilibrium).
 - What is the solubility of MX_2 if given K_{sp} ?
 1. $\text{MX}_2 \rightleftharpoons \text{M}^{2+} + 2\text{X}^-$
 2. $K_{sp} = [\text{M}^{2+}][\text{X}^-]^2$
 3. $K_{sp} = [\text{M}^{2+}][2\text{M}^{2+}]^2$ (because for every M^{2+} , there's two times as much X^-)
 4. $K_{sp} = 4[\text{M}^{2+}]^3$

5. Solve for $[M^{2+}]$. Solubility is the same thing as $[M^{2+}]$ because you used $Q = K_{sp}$ for a saturated solution.
 6. If you solved for $[X^-]$ instead, divide your results by 2.
 7. If you were given solubility and asked to solve K_{sp} , then know that $\text{solubility} = [M^{2+}] = [X^-]/2$
- Common-ion effect, its use in laboratory separations
 - The common-ion effect is simply Le Chatelier's principle applied to K_{sp} reactions.
 - $\text{AgCl (s)} \rightleftharpoons \text{Ag}^+ \text{ (aq)} + \text{Cl}^- \text{ (aq)}$
 - The common-ion effect says that if you add Cl^- to the solution above, then less AgCl would dissolve.
 - For example, if you add NaCl to a saturated solution of AgCl , then some AgCl will crash out of solution.
 - Another example: more AgCl can dissolve in pure water than in water containing Cl^- ions.
 - In laboratory separations, you can use the common ion effect to selectively crashing out one component in a mixture.
 - For example, if you want to separate AgCl from a mixture of AgCl and Ag_2SO_4 , then you can do so by adding NaCl . This will selectively crash out AgCl by the common ion effect (Cl^- being the common ion).
 - Complex ion formation
 - $\text{Metal}^+ + \text{Lewis base} \rightarrow \text{Complex ion}$
 - $M^+ + L \rightarrow M-L_n^+$
 - The Lewis base can be charged or uncharged.
 - The K_{eq} for this reaction is called K_f , or the formation constant.
 - Complex ions and solubility
 - The "complex ion effect" is the opposite of the common ion effect.

- $\text{AgCl (s)} \rightleftharpoons \text{Ag}^+ \text{ (aq)} + \text{Cl}^- \text{ (aq)}$; $\text{M}^+ + \text{Cl}^- \rightleftharpoons \text{M-Cl}_n \text{ complex ion}$.
- When complex ion forms, the Cl^- ion is taken out, so more of the AgCl will dissolve.
- Alternatively: $\text{AgCl (s)} \rightleftharpoons \text{Ag}^+ \text{ (aq)} + \text{Cl}^- \text{ (aq)}$; $\text{NH}_3 + \text{Ag}^+ \rightleftharpoons \text{Ag-(NH}_3)_n \text{ complex ion}$.
- Here, the complex ion formation takes out Ag^+ , again causing more AgCl to dissolve.
- Solubility and pH
 - Acids are more soluble in bases.
 - $\text{HA} \rightarrow \text{H}^+ + \text{A}^-$
 - Putting the above in a base will take out the H^+ , thus, more HA will dissolve according to Le Chatelier's principle.
 - Bases are more soluble in acids.
 - $\text{B} + \text{H}^+ \rightarrow \text{BH}^+$
 - Putting the above in an acid will add more H^+ , and thus, drive more B to dissolve according to Le Chatelier's principle.

Acids/Bases

Acid / base equilibria

- Bronsted definition of acid, base
 - $\text{H-Acid} + \text{Base}^- \rightleftharpoons \text{Acid}^- + \text{H-Base}$.
 - From left to right:
 - Acid: proton donor.
 - Base: proton acceptor.
 - Conjugate base: acid after losing its proton.
 - Conjugate acid: base after gaining its proton.
- Ionization of water
 - K_w , its approximate value ($K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$ at 25°C)
 - $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$
 - At standard conditions, pure water dissociates to achieve $[\text{H}^+] = 10^{-7} \text{ M}$ and $[\text{OH}^-] = 10^{-7} \text{ M}$.
 - $K_w = [\text{H}^+] \times [\text{OH}^-] = 10^{-7} \times 10^{-7} = 10^{-14}$
 - definition of pH; pH of pure water
 - $\text{pH} = -\log[\text{H}^+]$
 - For pure water, $\text{pH} = -\log[10^{-7}] = 7$.
 - Acidic: pH lower than 7.
 - Neutral: pH = 7.
 - Basic: pH higher than 7.
 - $\text{pOH} = -\log[\text{OH}^-]$.
 - $\text{pH} + \text{pOH} = 14$.

- Conjugate acids and bases (e.g., amino acids)

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Acid	Base	↔	Conjugate base	Conjugate acid
H ₂ O	H ₂ O	↔	OH ⁻	H ₃ O ⁺
R-COOH	H ₂ O	↔	R-COO ⁻	H ₃ O ⁺
H ₂ O	R-NH ₂	↔	OH ⁻	R-NH ₃ ⁺

- More acidic ← ⁺H₃N-CH₂-COOH ⇌ ⁺H₃N-CH₂-COO⁻ ⇌ H₂N-CH₂-COO⁻ → more basic

- Strong acids and bases (common examples, e.g., nitric, sulfuric)

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Strong acid	Formula
Perchloric acid	HClO ₄
Hydroiodic acid	HI
Hydrobromic acid	HBr
Sulfuric acid	H ₂ SO ₄
Hydrochloric acid	HCl
Nitric acid	HNO ₃
Hydronium ion	H ₃ O ⁺ or H ⁺

- Strong acids completely dissociate in solution.
- Complete dissociation occurs because the conjugate base anion is highly stable.

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Strong bases	Formula
Lithium hydroxide	LiOH
Sodium hydroxide	NaOH
Potassium hydroxide	KOH
Rubidium hydroxide	RbOH
Cesium hydroxide	CsOH
Calcium Hydroxide	Ca(OH) ₂

Strontium hydroxide	$\text{Sr}(\text{OH})_2$
Barium hydroxide	$\text{Ba}(\text{OH})_2$

- Strong bases completely dissociate in solution.
- Complete dissociation occurs because the conjugate acid cation is highly stable.
- Weak acids and bases (common examples, e.g. acetic, benzoic)

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Weak acid	Formula
Formic acid	HCOOH
Acetic acid	CH_3COOH
Hydrofluoric acid	HF
Hydrocyanic acid	HCN
Hydrogen sulfide	H_2S
Water	H_2O

- Weak acids partially dissociate in solution.
- Partial dissociation occurs because the conjugate base is fairly stable.

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Weak base	Formula
Ammonia	NH_3
Amine	NR_3
Pyridine	$\text{C}_5\text{H}_5\text{N}$
Ammonium hydroxide	NH_4OH
Water	H_2O

- Weak bases partially dissociate in solution.
- Partial dissociation occurs because the conjugate acid is fairly stable.
- dissociation of weak acids and bases with or without added salt

- CH_3COOH will dissociate less in a solution containing CH_3COONa salt.
 - NH_4OH will dissociate less in a solution containing NH_4Cl salt.
 - This is due to Le Chatelier's principle: the hydrolysis of salts of weak acids will produce their conjugate bases, which reduces dissociation. Likewise, hydrolysis of salts of weak bases will produce conjugate acids.
- hydrolysis of salts of weak acids or bases
- Salt of weak acid:
 $\text{CH}_3\text{COONa} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{Na}^+$
 $\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-$
 - Salt of weak base:
 $\text{NH}_4\text{Cl} \rightleftharpoons \text{NH}_4^+ + \text{Cl}^-$
 $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$
- calculation of pH of solutions of salts of weak acids or bases
- **Salt of weak acid:**
 - Let's say a solution contains M molar of CH_3COONa .
 - $\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-$
 - As M molar of CH_3COO^- start to abstract protons from the solvent:
 - $[\text{CH}_3\text{COO}^-] = M - x$
 - $[\text{CH}_3\text{COOH}] = x$
 - $[\text{OH}^-] = x$
 - $K_b = K_w/K_a = [\text{CH}_3\text{COOH}][\text{OH}^-] / [\text{CH}_3\text{COO}^-] = x^2/(M - x)$
 - Because x is very small, $K_w/K_a = x^2/M \rightarrow$ solve for x.
 - $\text{pOH} = -\log[\text{OH}^-] = -\log(x)$
 - $\text{pH} = 14 - \text{pOH}$.
 - **Salt of weak base:**

- Let's say a solution contains M molar of NH_4Cl .
- $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$.
- As M molar of NH_4^+ dissociates:
 - $[\text{NH}_4^+] = M - x$
 - $[\text{NH}_3] = x$
 - $[\text{H}^+] = x$
 - $K_a = K_w/K_b = [\text{NH}_3][\text{H}^+] / [\text{NH}_4^+] = x^2/(M - x)$
 - Because x is very small, $K_w/K_b = x^2/M \rightarrow$ solve for x.
 - $\text{pH} = -\log[\text{H}^+] = -\log(x)$.
- Equilibrium constants K_a and K_b : pK_a , pK_b
 - $\text{H-Acid} \rightleftharpoons \text{H}^+ + \text{Acid}^-$

$$K_a = \frac{[\text{H}^+][\text{Acid}^-]}{[\text{HAcid}]}$$
 - $\text{Base} + \text{H}_2\text{O} \rightleftharpoons \text{H-Base}^+ + \text{OH}^-$

$$K_b = \frac{[\text{HBase}^+][\text{OH}^-]}{[\text{Base}]}$$

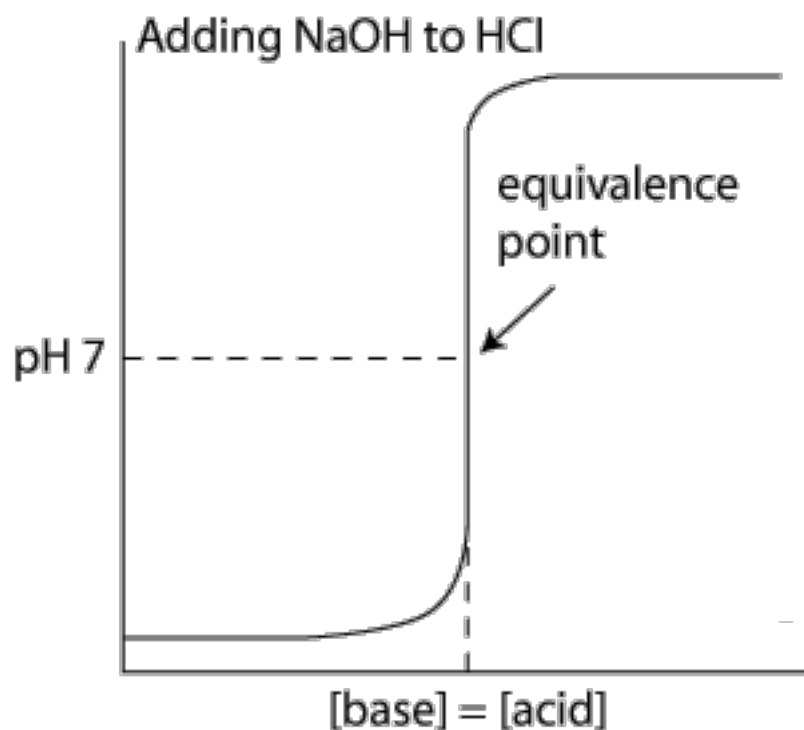
note: water is not included in the formula because it is not a solute.
 - $K_a \times K_b = K_w = 10^{-14}$
 - $\text{pK}_a = -\log K_a$
 - $\text{pK}_b = -\log K_b$
 - $\text{pK}_a + \text{pK}_b = 14$
- Buffers
 - definition and concepts (common buffer systems)
 - Buffers = Solutions that resist changes in pH.
 - Salts of weak acids and bases form buffer systems.

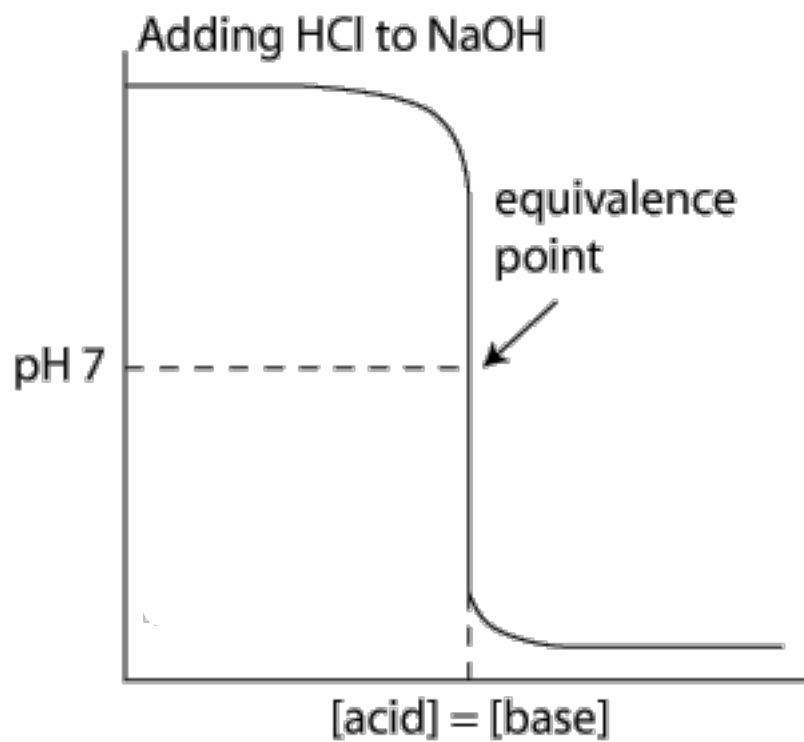
- A buffer system consists of an equilibrium between an acidic species and a basic species. Note the "equilibrium", you can't just dump HCl and NaOH together and expect buffering, because neutralization will occur and the acidic species and the basic species won't be at an equilibrium.
- The concept is that acidic species of the buffer system will donate protons to resist increases in pH, while the basic species of the buffer system will accept protons to resist decreases in pH.
- Buffer systems formed by weak acids have maximum buffering capacity at the $\text{pH} = \text{pK}_a$ of the acid.
- When $[\text{acid}] = [\text{conjugate base}]$, the system is buffered at $\text{pH} = \text{pK}_a$ of the acid.
- Buffer systems formed by weak bases have maximum buffering capacity at the $\text{pH} = 14 - \text{pK}_b$ of the base.
- When $[\text{base}] = [\text{conjugate acid}]$, the system is buffered at $\text{pH} = 14 - \text{pK}_b$ of the base.
- influence on titration curves
 - Buffers make the titration curve "flat" at the region where buffering occurs. On a titration curve, this is the point of inflection.
 - The point of inflection is at $\text{pH} = \text{pK}_a$ (or $14 - \text{pK}_b$) of the buffer.
 - The area around the point of inflection is the region where the solution has buffering capacity. The pH of this buffering region is typically $\text{pK}_a \pm 1$ (or $14 - \text{pK}_b \pm 1$).

Titration

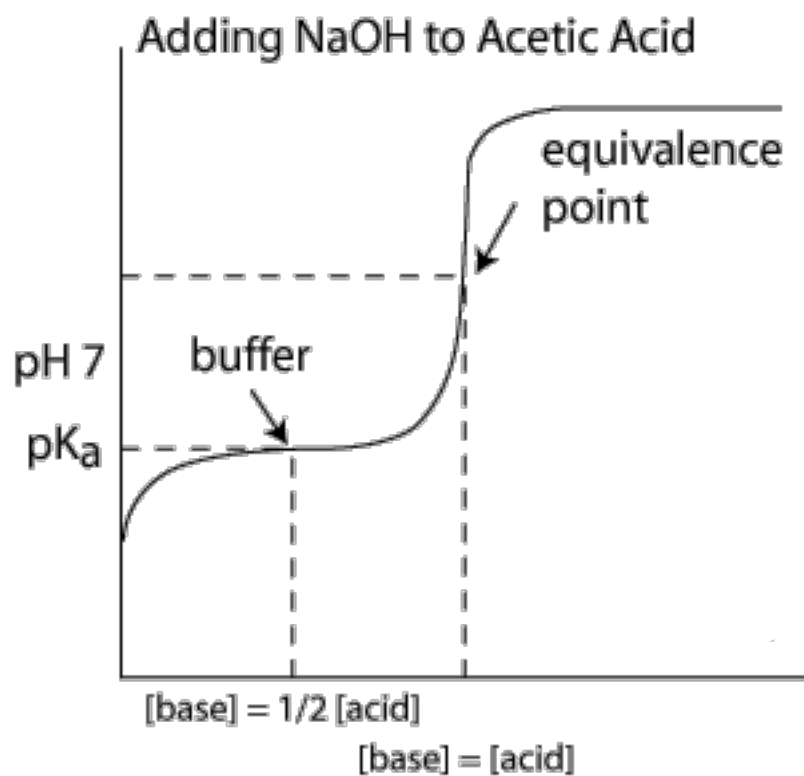
- Indicators
 - $\text{H-In} \rightleftharpoons \text{H}^+ + \text{In}^-$
 - $K_a = [\text{H}^+][\text{In}^-] / [\text{H-In}]$
 - Indicators behave just like weak acids/bases.

- The indicator is present in such a small amount that it doesn't affect the solution's pH.
- When the solution has a low pH (high $[H^+]$), the indicator is mostly in the H-In form, which is of one color.
- When the solution has a high pH (low $[H^+]$), the indicator is mostly in the In^- form, which is of another color.
- Neutralization: Acid + Base = Salt + Water.
- Interpretation of titration curves

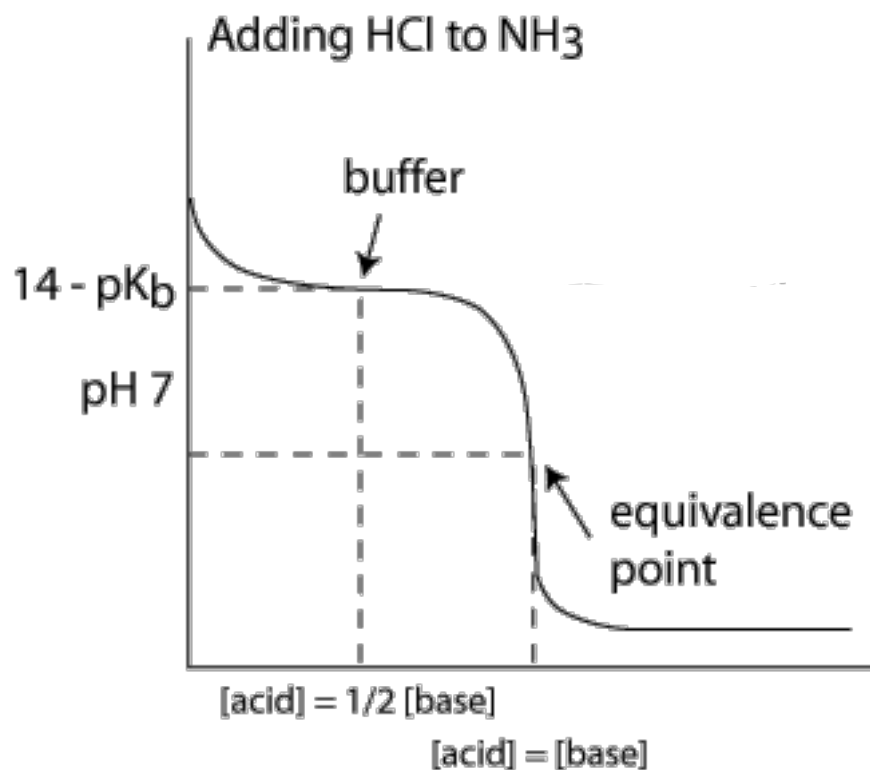




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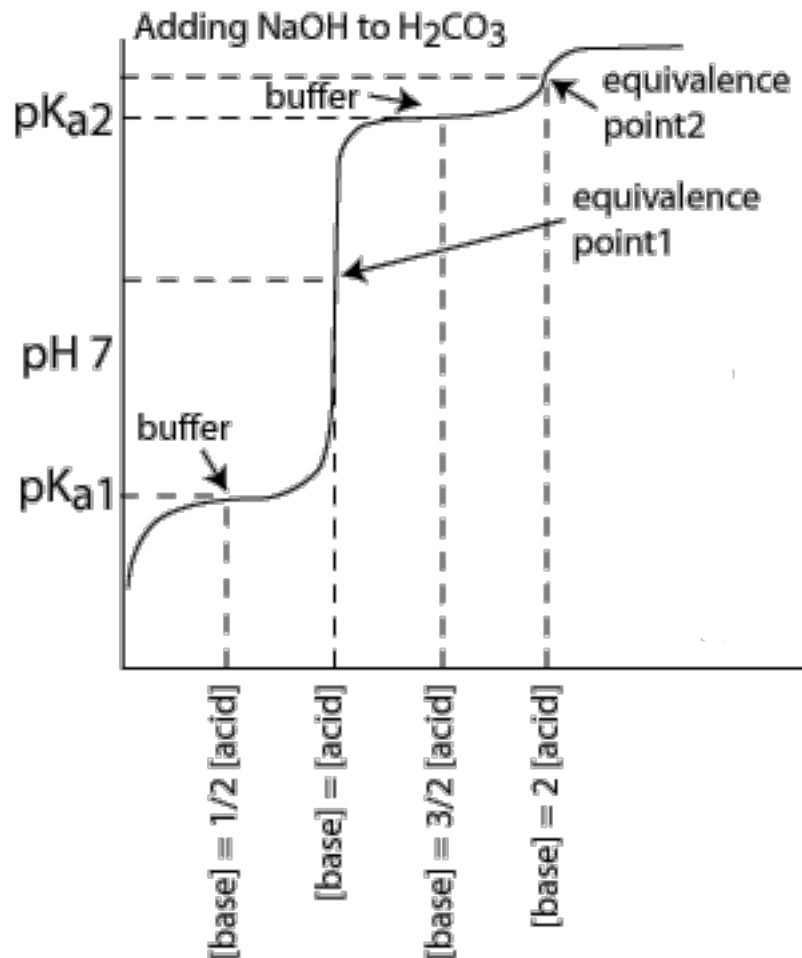


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- At the point of inflection (buffer arrow), the $[\text{acid}] = [\text{conjugate base}]$ or $[\text{base}] = [\text{conjugate acid}]$, $\text{pH} = \text{pK}_a$, and $[\text{titrant}] = 1/2 [\text{weak acid/base}]$
- The buffer region has pH values of $\text{pK}_a \pm 1$.

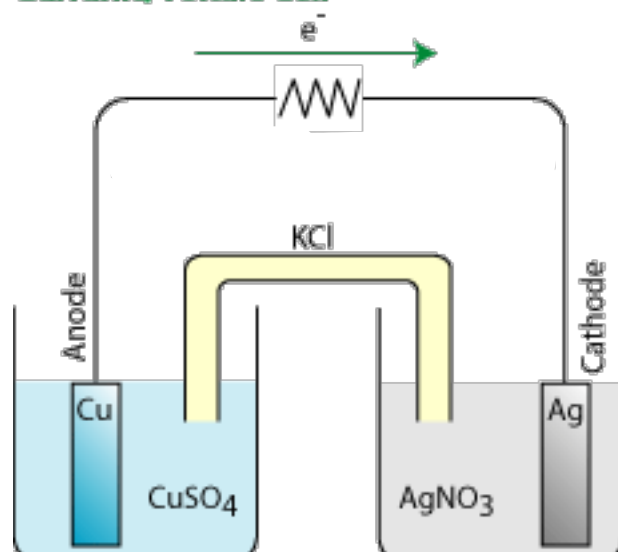


- - Polyprotic acids have multiple pK_a, points of inflection, and equivalence points.
 - Like monoprotic acids, each point of inflection corresponds to the pK_a for the acidic species.
 - At each pK_a, [acidic species] = [conjugate base of the acidic species].
 - For H₂CO₃:
 - pK_{a1}: [H₂CO₃] = [HCO₃⁻]
 - Equivalence point 1: almost everything is HCO₃⁻
 - pK_{a2}: [HCO₃⁻] = [CO₃²⁻]
 - Equivalence point 2: almost everything is CO₃²⁻
- Redox titration

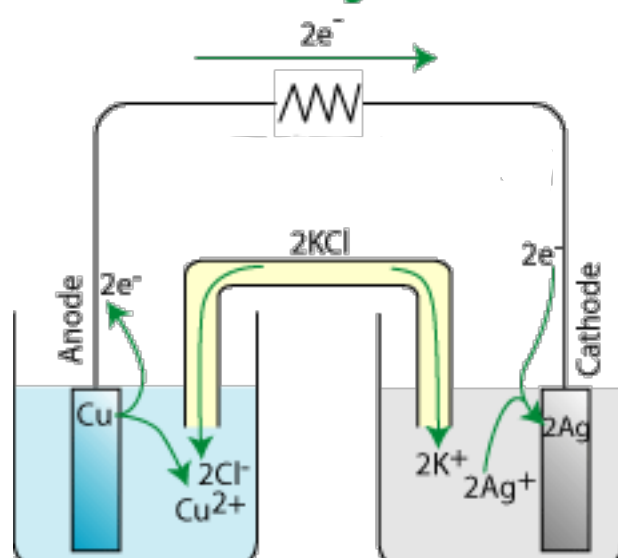
- While Bronsted acid-base titrations involve proton transfers, redox titrations involve electron transfers.
- Redox = reduction + oxidation = species A gains electrons + species B lose electrons.
- Reduction = reduction in charge = decreased oxidation number = gaining electrons.
- Oxidation = increase in charge = increased oxidation number = losing electrons.
- $5\text{H}_2\text{O}_2 + 2\text{MnO}_4^- + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{O}_2 + 8\text{H}_2\text{O}$
 - Normally oxygen has an oxidation state of -2, but in peroxides, it is -1. The reactants here include a peroxide.
 - Oxygen, and anything else in its elemental state has an oxidation number of 0. The product O_2 is one such case.
 - Hydrogen is always +1 unless it is a hydride, in which case it's negative 1. For this reaction, all hydrogens are +1.
 - Doing some math, we find that the reactant Mn has an oxidation number of +7.
 - The half reactions (reactions that depict electron transfer only) are as follows:
 - Reduction: $\text{Mn}^{7+} + 5\text{e}^- \rightarrow \text{Mn}^{2+}$
 - Oxidation: $\text{O}^- \rightarrow \text{O}^0 + \text{e}^-$

Electrochemistry

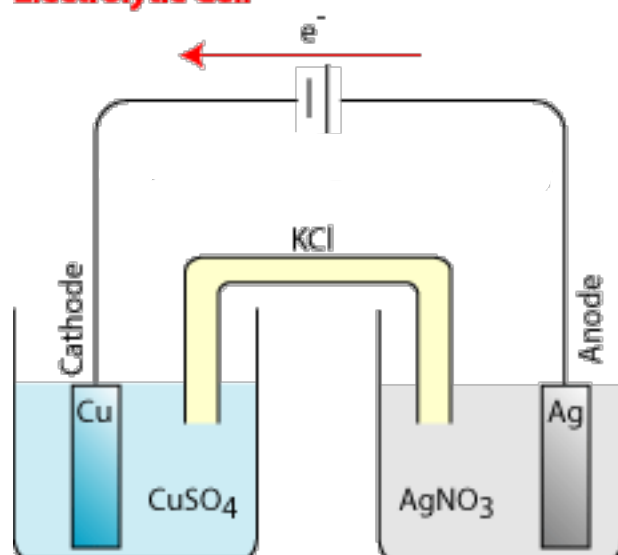
Galvanic/Voltaic Cell



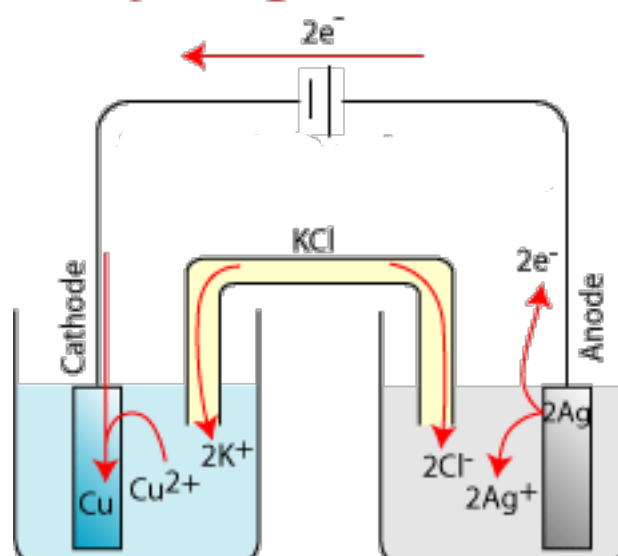
Galvanic/Voltaic Charge Flow



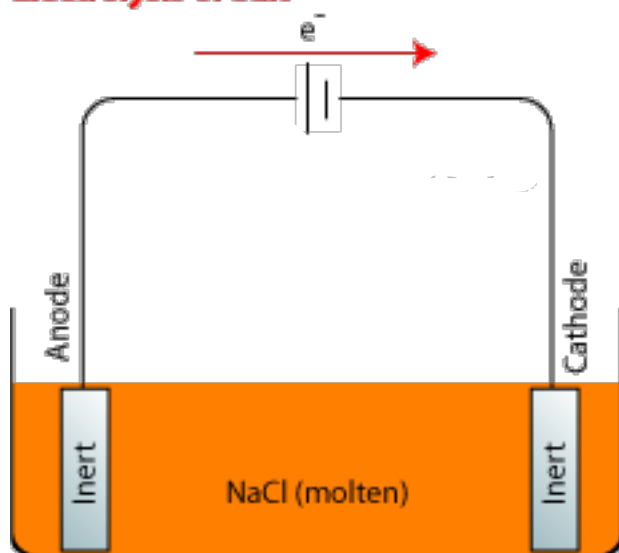
Electrolytic Cell



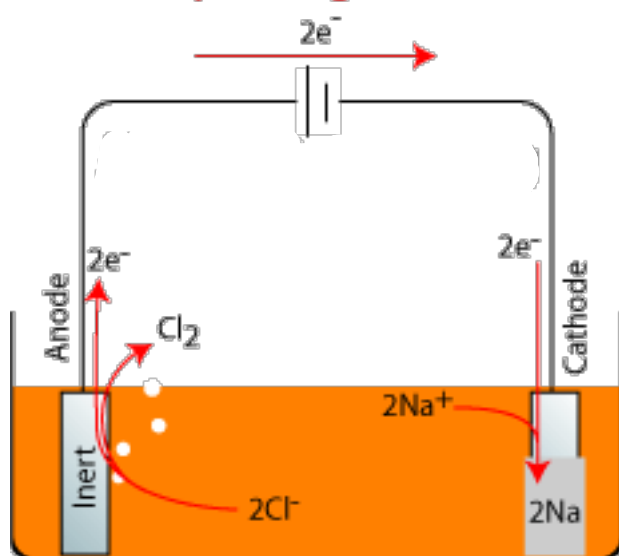
Electrolytic Charge Flow



Electrolysis of Salt



Salt Electrolysis Charge Flow



Electrolytic cell

- electrolysis
 - Requires potential/voltage input. On the diagram, this is represented by a battery in the circuit. In contrast, a galvanic cell has in its place either a resistor, or a Voltmeter.
 - The potential/voltage input + the cell potential must be > 0 for the reactions to occur.

- For electrolytic cells, the cell potential is negative, so a potential input greater than the magnitude of the cell potential must be present for electrolysis to occur.
- In contrast, galvanic/voltaic cells already have a positive cell potential. Thus, no input is required for galvanic/voltaic cells.
- In the diagram above, arrows are shown in red because the battery is forcing the flow of electrons. Normally, the electrons would want to flow the other way (or not flow at all).
- anode, cathode
 - The following rules hold true for both electrolytic and galvanic/voltaic cells.
 - Anode is always the place where oxidation happens.
 - Cathode is always the place where reduction happens.
 - Mnemonic:
 - An Ox = ANode OXidation
 - Red Cat = REDuction CAThode
 - Anode shoots out electrons, Cathode takes in electrons.
- electrolyte
 - Ions = electrolyte.
 - Electrolytes conduct electricity by the motion of ions.
 - Without electrolytes, there won't be a circuit because electricity won't be able to travel.
- Faraday's law relating amount of elements deposited (or gas liberated) at an electrode to current
 - Current = coulombs of charge per second. $I = q/t$
 - Faraday's constant = coulombs of charge per mol of electron = total charge over total mols of electrons. $F = q/n$.
 - $q = It$ and $q = nF$, thus we get:
 - $It = nF$
 - Current x time = mols of e^- x Faraday's constant.

- Using this equation, you can solve for n, mols of electrons. Then using the half equation stoichiometry, you can find out how many mols of element is made for every e^- transferred. For example, 1 mol of Cu is deposited for every 2 mols of electrons for the following half reaction: $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$.
- electron flow; oxidation, and reduction at the electrodes
 - Electrons shoot out of the anode because oxidation occurs there to lose electrons. $\text{M} \rightarrow \text{M}^+ + e^-$.
 - Electrons travel into the cathode, where it crashes into the cations on the surface of the cathode. This is because reduction occurs at the cathode to receive electrons. $\text{M}^+ + e^- \rightarrow \text{M}$.
 - Mnemonic:
 - Oil Rig : Oxidation Is Losing e^- Reduction Is Gaining e^- .
 - Oxidation is an increase in charge, Reduction is a decrease in charge.

Galvanic or voltaic cell

- half reactions
 - Oxidation half reaction describes the species that loses electrons (increases in charge). For example, $\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^-$
 - Reduction half reaction describes the species that gains electrons (decreases in charge). For example, $2\text{Ag}^+ + 2e^- \rightarrow 2\text{Ag}$
- reduction potentials; cell potential
 - You find reduction potentials in a table:

▪

Half reactions	Reduction potential (V)	comments
$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$	+1.359	Chlorine has high electron affinity, it loves to gain electrons and being reduced. Thus, it has a high reduction potential. Similarly, species like oxygen, halogens, and nonreactive metals have positive reduction potentials.
$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	0.000	Hydrogen is set to have a standard reduction potential of zero

$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.714	Sodium hates its electron, it gets rid of it to obtain a full outer shell and be stable as a cation. It is very hard to force electrons onto the stable cation to reduce it. Thus, it has a very negative reduction potential. Similarly, species like potassium and other reactive metals have negative reduction potentials.
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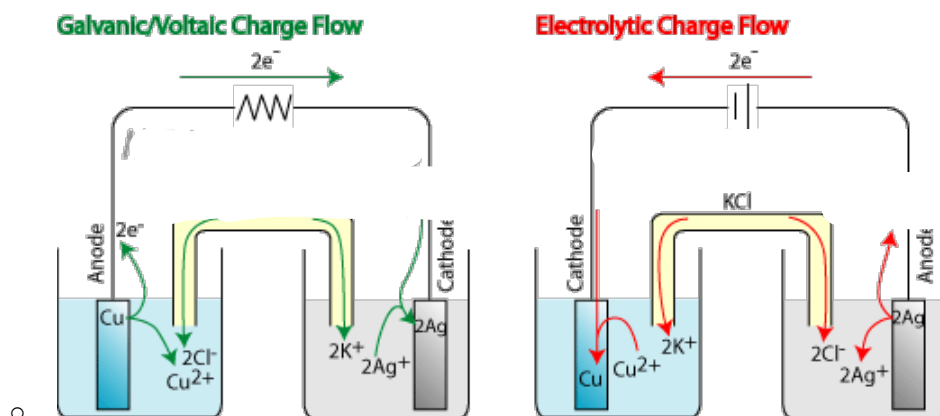
- Reduction potential = potential of the reduction half reaction.
- Oxidation potential = potential of the oxidation half reaction = reverse the sign of the reduction potential.
- Cell potential = Reduction potential + Oxidation potential.
- For example, the cell potential for the galvanic cell shown in the diagram is:

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Reduction potential table	
Species	Reduction Potential (V)
Ag(I)	+0.799
Cu(II)	+0.337

- Reduction half reaction: $2\text{Ag}^+ + 2\text{e}^- \rightarrow 2\text{Ag}$
- Reduction potential = +0.799
- Oxidation half reaction: $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$
- Oxidation potential = $+0.337 \times -1 = -0.337$
- Cell potential = $0.799 - 0.337 = 0.462 \text{ V}$
- The cell potential for all galvanic/voltaic cells is positive, because the voltaic cell generates potential.
- Another example, the cell potential for the electrolytic cell shown in the diagram is:
 - Reduction half reaction: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
 - Reduction potential = +0.337
 - Oxidation half reaction: $2\text{Ag} \rightarrow 2\text{Ag}^+ + 2\text{e}^-$

- Oxidation potential = $+0.799 \times -1$
 - Cell potential = $0.337 - 0.799 = -0.462 \text{ V}$
 - The cell potential for all electrolytic cells is negative, because the electrolytic cell requires potential input.
- direction of electron flow



- Electrons always flow from the Anode to the Cathode. Mnemonic: A to C in alphabetical order. Or, think about AC power - the A comes first and stands for anode)
 - Oxidation (at the anode) produces electrons (and cations), and shoots out the electrons toward the cathode. The cathode receives those electrons and uses them for reduction.
 - Naturally, the species with the highest oxidation potential (lowest reduction potential) will be the anode, and the species with the highest reduction potential will be the cathode.
 - In the diagram above, the Galvanic/Voltaic cell shows a natural flow because Cu (higher oxidation potential/lower reduction potential) is the anode, and Ag (higher reduction potential) is the cathode.
 - However, the electrolytic cell shows exactly the opposite. In order to force the Cu to be the cathode and Ag to be the anode, a battery is used to drive the reaction.
 - Electrons flow in wires and electrodes, while ions flow in the electrolyte solution, thus creating a completed circuit.