← back to Study Materials for Various APs

Note: If you are planning to use this document AFTER Spring 2023, please make a copy of it before then; I can't guarantee that it won't be deleted after that point.

italicized = not sure if needed
🟨 = important (should be well-understood)
🟩 = especially important for AP (and/or should be memorized)
General preparation tip: These concepts may seem difficult to understand at first, but doing practice problems, checking them, and then reviewing these notes can greatly help your understanding.

General Test-Taking Tips

- Check the given units and the requested units.
- Distinguish between physical (e.g. evaporation) and chemical (rxn) processes/equations.
- MC: check for similar answers and sigfigs
- FRQ: RSQ! Read thoroughly.
  - What is the question asking for? What do you need to know? What is given? Always check units, balance, and phases.
  - "justify": math alone sufficient
  - "explain": physical reasons needed
- Reasonability: Use known laws to check if your answer is reasonable
  - e.g. if gas pressure increases, gas temperature should increase (PV=nRT)
- Memorize: (Quizlet Folder)
  - Diatomic elements mnemonic: Have No Fear Of Ice (Cl)old (Br)eer (nonpolar, since identical atoms)
  - 3 Key Experiments
  - Lab Tools
  - Ions
  - Solubility
  - Redox rxns
  - Types of Spectroscopy

  - Molecular Geometry (Diagrams)
  - Acids & Bases
- Given formulas (AP; aka stuff you don't have to memorize but should know how to use)
  - **green-highlighted formulas below this point are NOT on the formula sheet**

Miscellaneous

- Diatomic elements mnemonic: Have No Fear Of Ice (Cl)old (Br)eer (nonpolar, since identical atoms)
- 3 Key Experiments
- solutions are homogeneous mixtures: solvent dissolves solute (we usually use water as solvent)
  - aqueous solution = solution of substance(s) dissolved in water
  - dissolved substances are denoted in chemical equations with phase (aq)
- Distillation: use different boiling points to separate miscible liquids in a solution
- Impurities can mess up experimental melting point (too low or broad range)
- rxn work-up: isolation/purification — pull out the extract, discard the wash
  - immiscible organic solvent and aqueous solution
  - use differing solubilities: neutral organic substances prefer organic solvent, charged/inorganic prefer aqueous solution
  - layers form based on density differences
- Gravimetry Overview
  - mix solutions → dry precipitate (binary compound) → use molar mass + knowledge of one of the elements in the compound to guess identity of unknown other element
- Lab tools

Unit 1: Stoichiometry and Redox Rxns

- Prefixes: mega (6), kilo, deci (-1), centi, milli, micro (-6), nano (-9)
- Sigfigs
    - 0.00010 and 0.010 both have two sigfigs
    - 10000 has 1 sigfig, 10000. and 10001 have 5 sigfigs
    - i.e. just think of scientific notation
    - multiply/divide: least sigfigs
    - add/subtract: least precise (least decimal digits)
- C + 273.15 = K
- 1 mole = $6.022 * 10^{23}$ particles (Avogadro constant)
    - molar mass: g/mol
- Redox rxns (rules on Quizlet) show electrons transferred
    - reduction = oxidation number decreases (is reduced)
        - oxidizing agent = reduced
    - oxidation = oxidation number increases (is oxidized)
        - reducing agent = oxidized
- When ionic compounds dissolve in water, they dissociate (vs. molecular solids do not dissociate)
- Foolproof method of balancing rxns (really only needed when complex): systems of equations (treat elements as distinct objects, subscripts as known coefficients and unknown coefficients as variables)
- limiting reactant
    - calculate possible product from each reactant; least is limiting
    - alternative: Before-Change-After chart
- percent yield: actual/theoretical
- dilution equation: $M_1V_1=M_2V_2$ (constant mols)
- neutralization: mols H^+ = mols OH^-
    - $M_aV_an_a=M_bV_bn_b$ (n is mols H^+or OH^- per mol acid or base)
- Net ionic reactions: memorize ions and solubility rules!
    - only (aq) compounds dissociate (cancel out aqueous ions on both sides)
    - write weak acids/bases as full aqueous compounds (not entirely dissociated)

  - Diatomic elements mnemonic: Have No Fear Of Ice (Cl)old (Br)eer

Unit 2: Gases

- all energy is potential or kinetic
  - $KE = \frac{1}{2}mv^2$ (just use for comparisons)
- Pressure units: 1 atm = 101.325 kPa = 14.7 psi = 760 mm Hg (or torr)
- Ideal gas equation: PV=nRT
  - T must be in Kelvin (absolute temperature)
  - R: ideal gas constant $= 0.08206\ \frac{atm \cdot L}{mol \cdot K}$ (conversions are on the sheet)
  - Constant T and P: pressure directly proportional to moles
  - given same gas, different conditions:
    - $\frac{P_1V_1}{n_1RT_1} = \frac{P_2V_2}{n_2RT_2} = \frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$ (cancel equivalent values, then plug in & solve for unknown)
- STP: 273 K (0 °C) and 1 atm
  - At STP, 1 mol of any gas takes up 22.414 L (=0.08206*273.15)
- DRT equation:
  - derivation (if you forget):
    - $PV = nRT$
    - $n = \frac{PV}{RT}$
    - $m \div n = m \div \frac{PV}{RT}$
    - $M = \frac{mRT}{PV}$
    - $M = \frac{dRT}{P}$
  - M: molar mass in g/mol
  - d: density in g/L
- gas vocabulary
  - evacuated: vacuum
  - flushed: 1 gas

    - rigid: constant volume
    - volatile: high vapor pressure
- Partial Pressures: each gas exerts unique pressure even when combined
    - calculate partial pressure via mole fraction
- vapor pressure: pressure of vapor (not gas at room temp) during dynamic equilibrium of evaporation/condensation
    - total pressure = gas pressure + vapor pressure
- KMT of (Ideal) Gases
    1. Particles are very far apart w/ negligible volume
    2. Particles are in constant, random motion, with elastic collisions
    3. Particles do not exert attractive/repulsive forces on each other
    4. Avg kinetic energy of particles is directly proportional to absolute temperature (Kelvin)
    - most ideal at HIGH TEMPERATURE and LOW PRESSURE
        - real gases: particle volume increases pressure (subtracts from container's volume), IMFs decrease pressure (compared to ideal gas law)
- Maxwell-Boltzmann Distribution for gases: higher speeds (flatten) with higher temperature and lower molar mass
- Graham's Law (diffusion/effusion): $\frac{Rate_A}{Rate_B} = \sqrt{\frac{M_B}{M_A}}$
    - rates are inversely proportional to molar mass
        - lighter particles are faster on avg (and vice versa)

Unit 3: Thermochemistry Pt. 1

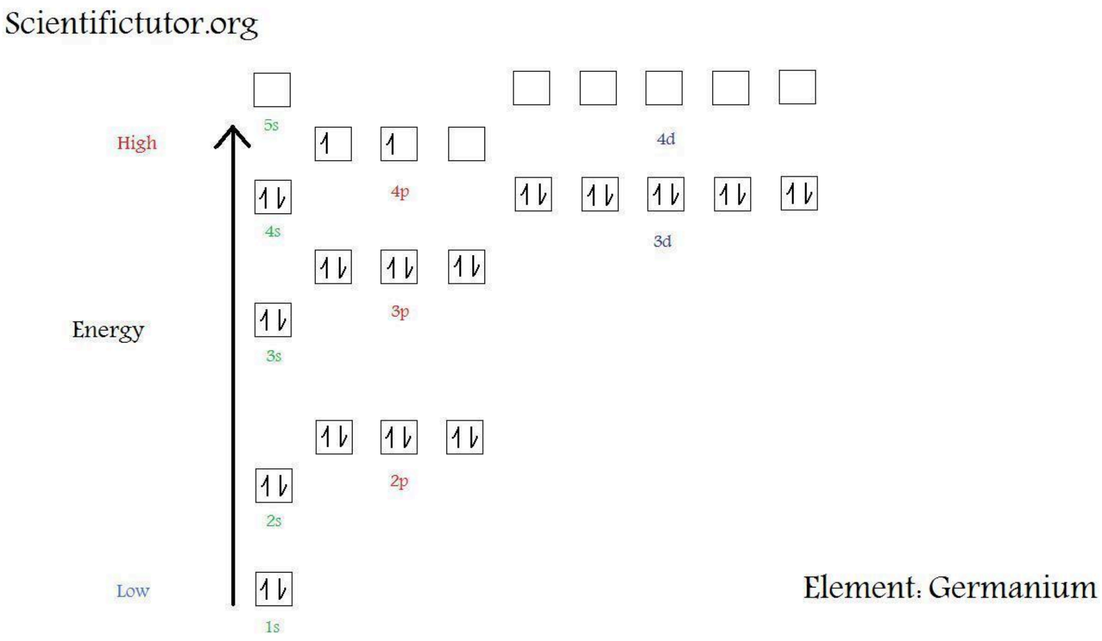
- $\Delta H_{rxn}^{o} = \sum \Delta H_f^{o}(products) - \sum \Delta H_f^{o}(reactants)$
- freezing is an exothermic physical process because heat is transferred from system to surroundings (particles lose and release energy when they slow down)
    - q (heat) <0 (system loses energy)

- melting is an endothermic physical process because heat is transferred from surroundings to system (needs energy to break bonds or overcome forces)
  - q >0 (system gains energy)
- specific heat (c): heat needed to raise temp of 1 g of substance by 1°C
  - $\frac{J}{g\cdot°C}$ (may use different units)
  - $c_{H_2O} = 4.184\ \frac{J}{g\cdot°C}$
  - $q = mc\Delta T$
- heat capacity (C): heat needed to raise temp of entire sample by 1°C
  - $\frac{J}{°C}$ (may use different units)
  - $q = C\Delta T$
- calorimetry: $q = mc\Delta T$
  - $\Delta T = T_{final} - T_{initial}$ (use sigfigs of ΔT)
  - solution increases temperature: exothermic (energy from chemical bonds released into solution mixture)
  - $-q_{hot} = q_{cold}$ (assuming constant P)
    - Do NOT forget the negative sign!
  - chemical reaction: $q_{sys} = q_{rxn\ mixture} + q_{cal} + q_{rxn} = 0$ (assuming no interaction with surroundings)
    - $q_{rxn} = -(q_{rxn\ mixture} + q_{cal})$
    - rxn mixture is usually just water
    - usually will just be told to ignore the rest of the calorimeter (q_{cal})
    - $q_{rxn} = \Delta H$ (constant P)
  - bomb calorimetry: $q_{sys} = q_{water} + q_{bomb\ cal} + q_{rxn} = 0$
    - $q_{rxn} = -(q_{water} + q_{bomb\ cal})$
    - notice that the formulas are essentially the same
    - $q_{rxn} = \Delta H$ (constant P)
- enthalpy (H): heat flow in/out of system (constant P)

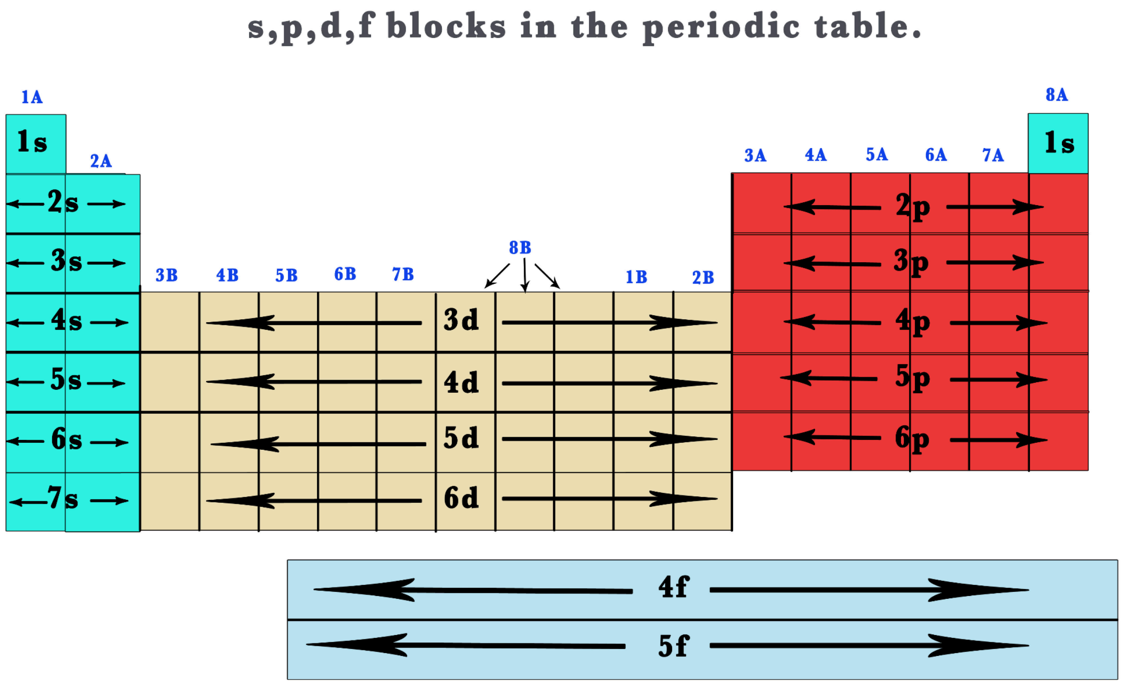
- $\Delta H = \sum \Delta H_{products} - \Delta H_{reactants}$
  - each ΔH multiplied by respective coefficients
- $\Delta H < 0$: exothermic (and vice versa; same as q)
- units (usually): $\frac{kJ}{mol_{rxn}}$ (specific to the reaction)
- Hess's Law: when particular set of reactants is converted to a particular set of products, ΔH is the same regardless of steps (state function)
- reverse rxn: ΔH changes sign
- scale rxn: ΔH is scaled
- ΔH^{o}_{comb} (heat of combustion) is per 1 mol fuel
  - reacts with oxygen and produces CO_2 and H_2O
- ΔH^{o}_{f} (standard heat of formation): heat change when 1 mol of compounds is formed from its elements at 1 atm
  - ΔH^{o}_{f} of any element at most stable form is 0
    - $\Delta H^{o}_{f}(O_2) = \Delta H^{o}_{f}(C, graphite) = 0$
    - Diatomic elements mnemonic: Have No Fear Of Ice (Cl)old (Br)eer
    - may have fractional coefficients
- ΔH^{o}_{rxn} (standard heat of rxn) is heat of rxn w/ standard states
  - standard states (standard conditions)
    - gas: 1 atm
    - solution: 1 M
    - element: form at 1 atm, 25°C (room temp)
  - $\Delta H^{o}_{rxn} = \sum \Delta H^{o}_{f}(products) - \sum \Delta H^{o}_{f}(reactants)$ (given by AP; also essentially the same as the prior equation)

Unit 4: Atomic Structure

- speed of EM radiation (in vacuum) = speed of light (c) = $2.998*10^8$ m/s
  - $c = \lambda\nu$ (wavelength [m] *frequency [hz=s^{-1}])
    - $v = \frac{c}{\lambda}$ (plug into below)
  - $E = hv$ where $h = 6.626 \cdot 10^{-34} J \cdot s$
    - calculates per one photon; may have to multiply by Avogadro's number
- Heisenberg Uncertainty Principle: cannot know both position & momentum of an electron
- principal quantum number n: main energy levels/shells
  - higher level: on average, electrons further from nucleus
  - contains sublevels/subshells: s, p, d, f, (g, h)
    - n determines # sublevels
      - n=1 → s
      - n=2 → s,p
      - ...
    - sublevels contain orbitals: spaces with high probability of being occupied by pair of electrons (at max)
    - sublevel type determines # orbitals
      - max # electrons in sublevel = 2*number of orbitals
      - s → 1 orbital (2 electrons max)
      - p → 3 orbitals (6 electrons max)
      - d → 5 orbitals (10 electrons max)
      - f → 7 orbitals (12 electrons max)
      - ...
    - real world: more electron → more repulsion → sublevel energy is offset (order of filling → periodic table)
  - max # electrons in energy level: $2n^2$

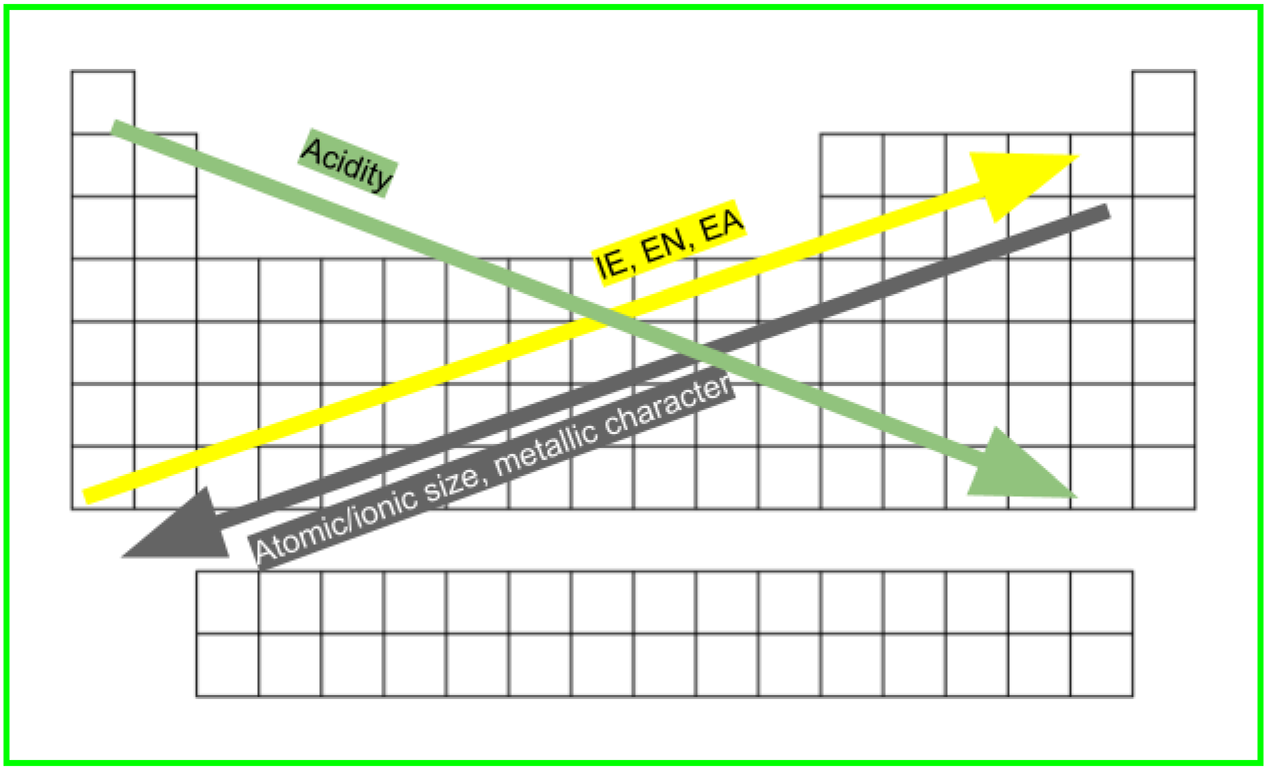


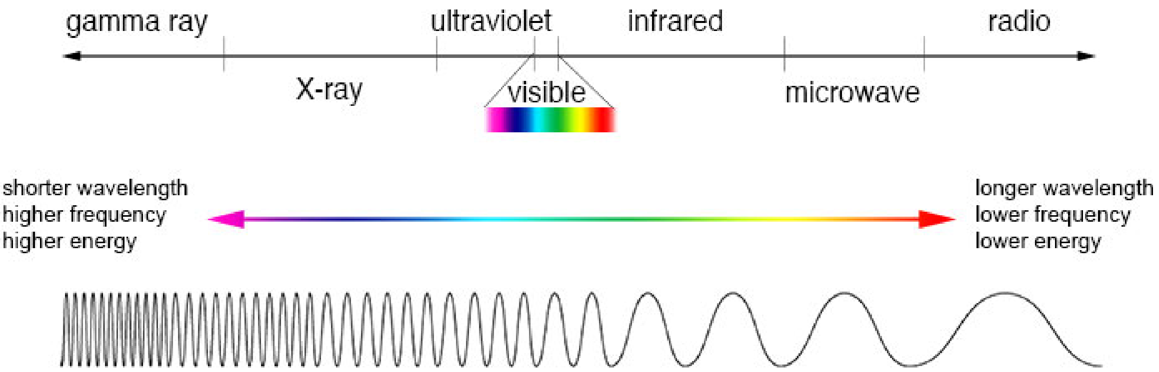
- How to build electron configuration
    - (Aufbau principle): electrons occupy lower energy orbitals first
        - ground state: all electrons obey
        - excited state: at least 1 does not
    - (Pauli Exclusion principle): orbital can only hold 2 electrons of opposite spin
    - (Hund's rule): electrons fill orbitals such that number of parallel signs (unpaired electrons) is maximized
- periodic table: period is energy lvl, except d is (period-1) and f is (period-2)



- standard notation vs. noble gas notation:
  - e.g. fluorine: $1s^2 2s^2 2p^5$ vs. $[He]2s^2 2p^5$
- Valence always s & p
- core electrons = non-valence
- Exceptions: half-filled orbitals are more stable (e.g. $Cr=[Ar]4s^1 3d^5$)
- Coulomb's Law for force of attraction between an electron and the nucleus: $F = k\frac{q_1 q_2}{r^2}$ where q_1 is nuclear charge, q_2 is the electron, and r is radius (no calculation, just comparison)
  - Exceptions: more stable requires more energy (half-filled orbitals)
  - $Z_{eff} = \# p^{+} - \# core\ e^{-}$ (noble gases have 0 core e^-)
    - all elements in group have same Z_{eff}
    - (this is an approximated calculation for the sole purpose of comparisons)
  - Valence electrons of elements in same period have same distance from nucleus (same energy level)

  - Valence electrons down group are further from nucleus (higher energy levels)
- Ionization energy (endothermic, forms cations, opposite of electron affinity): energy needed to remove electron from ground state gas
  - Turning neutral atoms to ions: lose highest LEVEL electrons first (energy of electron ≠ energy needed to remove)
    - e.g. Ti^{2+} is $[Ar]3d^2$, NOT $[Ar]4s^2$
  - across period: IE_1 increase because greater effective nuclear charge w/ roughly same distance
  - down group: IE_1 decrease because electrons further away w/ roughly same effective nuclear charge
  - lower energy level in the same element: takes significantly more energy
- Electronegativity: tendency to attract electrons from other elements
  - “increase” electron affinity → higher electronegativity
  - across period: increase because more protons → more attraction
  - *down group: decrease because of shielding*
  - noble gases generally have no EN
- Electron affinity (exothermic, forms anions, opposite of IE): energy change from adding electron to ground state gas
  - same justification as IE
  - “increase” = more negative (increase in magnitude)
- atomic size
  - across period: more protons → stronger attraction → decrease
  - down group: more energy levels → increase
- ionic size
  - cations: atom loses electrons → smaller
  - anions: atom gains electrons → bigger
  - same pattern as atomic size EXCEPT anions>cations in a period
  - comparing isoelectronic ions (same electron config): more protons → smaller



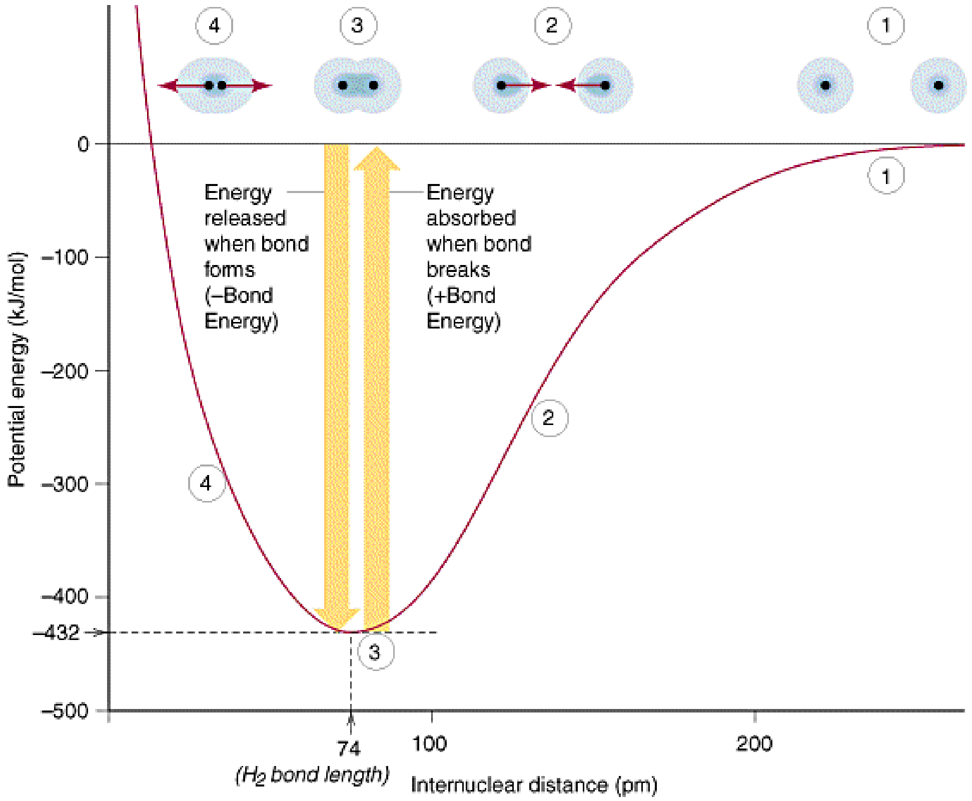


- Types of spectroscopy ([Quizlet](#))
    - UV (high energy → electron jump): electron transitions
    - IR (low energy bends): covalent bonds bend (molecular vibration)
    - MW ("rotate in the microwave"): chemical composition via molecular rotation
    - NMR (magnetism is a property): identify properties via magnetic nuclei
    - Photoelectron (PES): energy needed to remove electrons

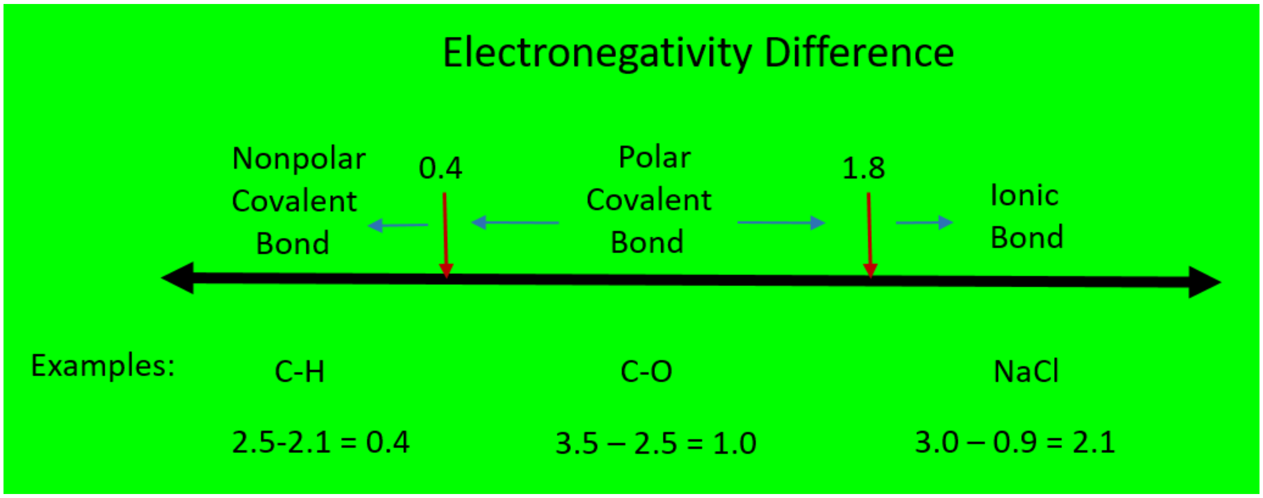
        - peaks correspond to # electrons in the orbital, highest energy should be 1s
    - mass spectrometry: isotopes by mass
        - relative size of peaks = relative # particles (like PES)
        - just match to weighted atomic mass on periodic table
    - spectrophotometry (see Beer's law): determine concentration by measuring optical properties

Unit 5: Bonding

- Coulomb's Law for lattice energy (ionic bonding): $E = k\frac{Q_1 Q_2}{r}$ where Q_1, Q_2 are ionic charges and d is distance between nuclei (charge usually overrides size)
- ionic bond: cations/anions attract (interionic forces)
    - ions do NOT form molecules!
- covalent bonding: share pairs (below)



- bond energy: involved in forming (exothermic; stable) and breaking (endothermic) bonds
- bond order (strength) is inversely proportional to bond length
    - single bond has bond order 1, double bond has bond order 2, triple bond has bond order 3
    - resonance: each bond has bond order equal to sum of bond orders of each of the resonance bonds divided number of resonance bonds (see resonance below)
- bond order for molecule: sum of individual bond orders divided by number of bonds

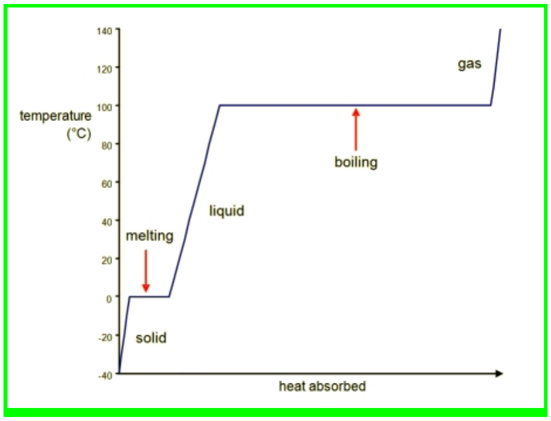


- nonmetal + nonmetal: generally covalent
- nonmetal + metal: generally ionic (metal becomes cation by transferring electrons to nonmetal, which becomes anion)
    - *Be is an exception: small radius & high ionization energy → forms covalent instead of ionic compounds*
- $\Delta H^{o}_{rxn} = \sum \text{energy needed to break reactant bonds} - \sum \text{energy needed to form product bond}$
    - switched order compared to prior enthalpy equations, so if you forget just use your intuition
- Lewis structures
    1. sum valence
    2. least EN = central (always C, never H)
    3. single bonds (all hydrogen should be filled)
    4. add rest until octets filled
        - exceptions
            - B: 6
            - Be: 4
            - exceed (period 3+): add leftover to central
    - polyatomic ions: factor in added/removed electrons
        - brackets and charge on outside
    - resonant structures: more than one equivalent position to place a higher order bond
        - bond lengths are actually equal; see bond order above

        - resonance stabilizes the molecule (e.g. HClO3 is a stronger acid than HClO2 because the additional oxygen stabilizes the conjugate base)
    - formal charge (only if asked): FC_{atom} = # valence e^- - # assigned e^-
        - maximize FCs of 0
        - assigned electrons come from half of bond electrons + lone electrons
        - any negative FC must be on MOST electronegative (not central)
- steric number = # electron domains = # bonds & lone pairs attached to **central atom**
- VSEPR: electrons arranged around central atom to minimize repulsion
- Electron geometry treats lone pairs as undistinguished domains, while molecular geometry does not
    - Treat all bonds same
    - All diatomic are linear
    - Most bent molecules are polar
        - NO_2: single electron makes it bent
    - diagrams are never to scale: use molecular geometry to determine bond angles
- hybridization: (sum of exponents of s, p, & d) = (steric number-1)
    - lone pairs contribute to steric number! Can't just tell from formula
- single bond has 1 sigma bond, double bond has 1 sigma and 1 pi bond, triple bond has 1 sigma and 2 pi bonds
- dipole moments (in polar molecules)
    - any diatomic molecule w/ polar bond
    - asymmetrical polar bonds or lone pairs (use molecular geometry for shape, electronegativity differences (>0.4) for directions (low to high), and vectors for net dipole)

Unit 6: IMFs, Phases, and Solutions

- for similar size: LDF < dipole-dipole < hydrogen bonding (< ion-dipole < interionic)
    - LDF: more electrons (“larger” molecule) → more polarizable
        - e.g. “Both molecules are nonpolar. Cl_2 has more electrons than F_2, thus making Cl_2 more polarizable, with stronger London dispersion forces. Thus, Cl_2 has a higher boiling point than F_2.”
    - dipole-dipole: dipole moments
    - hydrogen bonding: H must be bonded to N/O/F within the molecule in order for intermolecular hydrogen “bonding”
- viscosity and surface tension increase with IMFs
- vapor pressure decreases as IMF increases
- Draw heating/cooling curve
    - Phase changes are flat (heat absorbed is used to overcome IMFs, so temperature does not change)
        - $q = \pm n\Delta H_{fus}^{o}$ (melting or freezing)
        - $q = \pm n\Delta H_{vap}^{o}$ (boiling or condensing)
        - boiling takes longer than melting because IMFs have to be completely overcome (aka specific heat of gas phase is higher than specific heat of liquid phase of same substance)
    - Heating/cooling is sloped
        - $q = mc\Delta T$



- types of crystalline solids

    - covalent-network: highest melting points (diamond, graphite, SiO_2, SiC)
    - ionic: anions and cations form lattice
    - metallic
        - delocalized electrons enable conductivity
        - alloy: mixture (same conductivity)
            - interstitial: smaller atom in holes
            - substitutional: similar size atoms replace
        - doping: can improve conductivity
            - n-type doping: negative mobile charge (electron)
            - p-type doping: positive mobile charge (hole)
    - molecular solids (IMF): lowest melting points
- steps of dissolution of ionic compound
    1. solvent's positive side attracts negative ions, vice versa
    2. ions are solvated (surrounded)
    3. energy changes for bonds broken/formed
- more disorder → more entropy (mixing is favored)
- saturated: know by undissolved solute
- gas solubility in water increases with mass and pressure, decreases with temperature
- solubility of solid in liquid increases with temperature
- mass%, volume%, ppm, ppb, and mole fractions are all out of TOTAL mass/volume/mols
    - ppm and ppb are $\frac{mass\ of\ A}{total\ mass}$ times 10^6 or 10^9

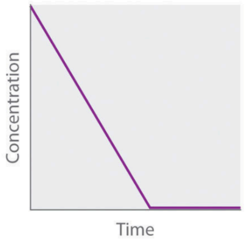
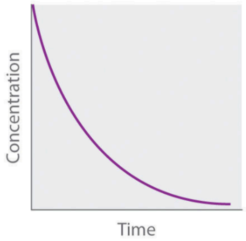
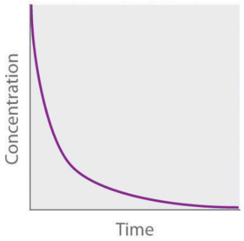
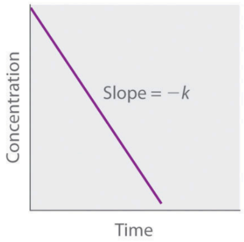
Chromatography

- high affinity to mobile phase → move further
- high affinity to stationary phase → don't move as far
- *when comparing chromatograms, compare proportional distance, not absolute (if chromatograms are different sizes)*

Unit 7: Kinetics

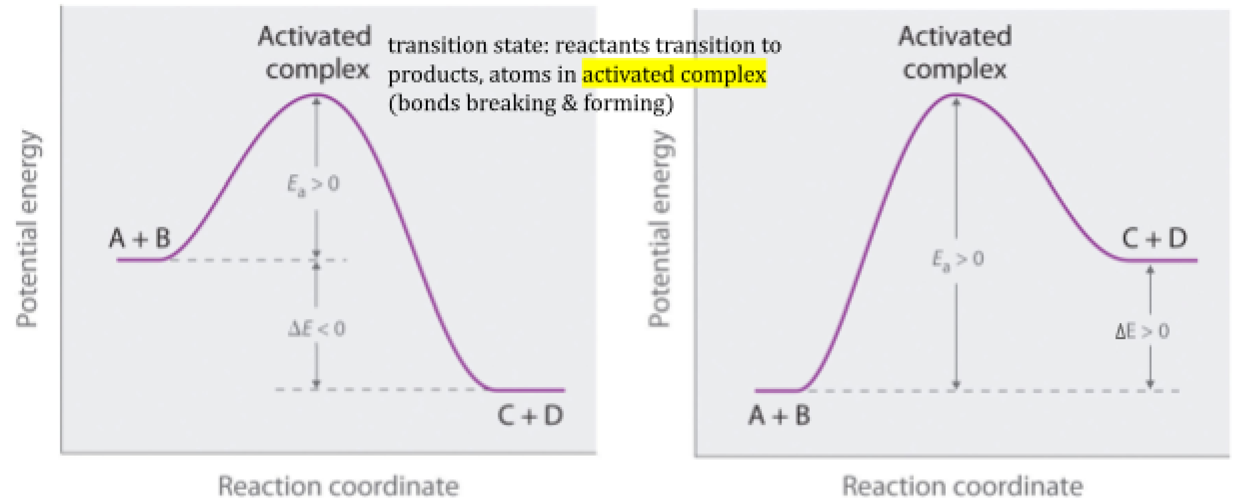
- kinetics: study of reaction rate
- collision theory: in order to react, particles need to collide in the correct orientation with enough energy to break bonds
    - frequency of effective collisions ∝ reaction rate
    - reaction rate ∝ concentration, homogeneity (surface area), temperature, catalyst, pressure (for gases)
- reaction rate = $\frac{\Delta concentration}{\Delta time}$ (M/s)
    - rxn proceeds → concentration decreases → rxn rate decreases
        - use t=0 as baseline (initial rate w/ initial concentrations)
    - aka instantaneous rate of change of concentration vs. time curve
    - can use one rate (or amount of particular species consumed/produced) to find another via stoichiometry (switch signs between reactants/products)
        - aA + bB → cC + dD
        - $-\frac{1}{a}\cdot\frac{\Delta[A]}{t} = -\frac{1}{b}\cdot\frac{\Delta[B]}{t} = \frac{1}{c}\cdot\frac{\Delta[C]}{t} = \frac{1}{d}\cdot\frac{\Delta[D]}{t}$
- **RATE LAW**: rate (M/s) = $k[A]^m[B]^n$ (reactants only)
    - exponents (order $m, n \in N_{\geq 0}$) are determined from experimental data (tables/plots)
        - if asked to find order given concentration over time, plot data according to different orders until linear
        - 2 ways to justify order of reactant:
            - Comparing experiment 1 versus experiment 2, [A] was constant while [B] tripled, and the rate tripled. Thus, the reaction is 1st order in respect to B.
            - $\frac{rate_{exp.\,2}}{rate_{exp.\,1}} = \frac{k(\ldots}{k(\ldots}$ (plug in values)
    - stoichiometric coefficients ≠ orders (except in elementary rxns)
    - overall order of rxn = sum of orders
    - units of k depend on overall order ($\frac{1}{s}$,$\frac{1}{M\cdot s}$,etc.)
        - check units, also write $\frac{1}{M}$ as $\frac{L}{mol}$

- **INTEGRATED RATE LAWS** (calculus, depend on order)
  - derived from AROC = rate law in respect to one species
    - e.g. $\frac{[A]_t - [A]_0}{t} = k[A]_t$ for 1st order
  - 0th order: $[A]_t = -kt + [A]_0$
    - plot of $[A]_t$ vs. t is linear (slope $= -k$)
      - think u-substitution or linearizing transformations
  - 1st order: $\ln[A]_t = -kt + \ln[A]_0$ or $\ln(\frac{[A]_t}{[A]_0}) = -kt$
    - plot of $\ln[A]_t$ vs. t is linear (slope $= -k$)
      - think u-substitution or linearizing transformations
    - Note that 0th and 1st order integrated rate laws are the same except 1st order has natural logarithm
  - 2nd order: $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$
    - plot of $\frac{1}{[A]_t}$ vs. t is linear (slope $= k$)
      - think u-substitution or linearizing transformations

	Zeroth Order	**First Order**	**Second Order**
Differential rate law	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$
Concentration vs. time			
Integrated rate law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$ or $\ln[A] = \ln[A]_0 - kt$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
Straight-line plot to determine rate constant			
Relative rate vs. concentration	[A], *M* / Rate, M/s 1 / 1 2 / 1 3 / 1	[A], *M* / Rate, M/s 1 / 1 2 / 2 3 / 3	[A], *M* / Rate, M/s 1 / 1 2 / 4 3 / 9
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$
Units of *k*, rate constant	M/s	1/s	$M^{-1} \cdot s^{-1}$

- Pseudo-1st Order: higher order rxn appears 1st order due to excess of one reactant
    - If A is in high excess, $[A]$ is effectively constant → treat rxn as 0 order in respect to A
    - Let $k_{eff} = k[A]_0$. Then, $rate_{eff} = k_{eff} \cdot [B]$
        - *rate law would still be rate* $= k[A][B]$
- half-life ($t_{1/2}$): time for half of reactant to react

  - can be derived from integrated rate laws (don't need to memorize half-life formulas; just plug stuff into integrated rate laws)
  - 1st order: $\frac{0.693}{k} = t_{1/2}$ (initial concentration does not matter)
  - initial concentration matters for 0th and 2nd orders
- collision model (activated complex at transition state at peak):



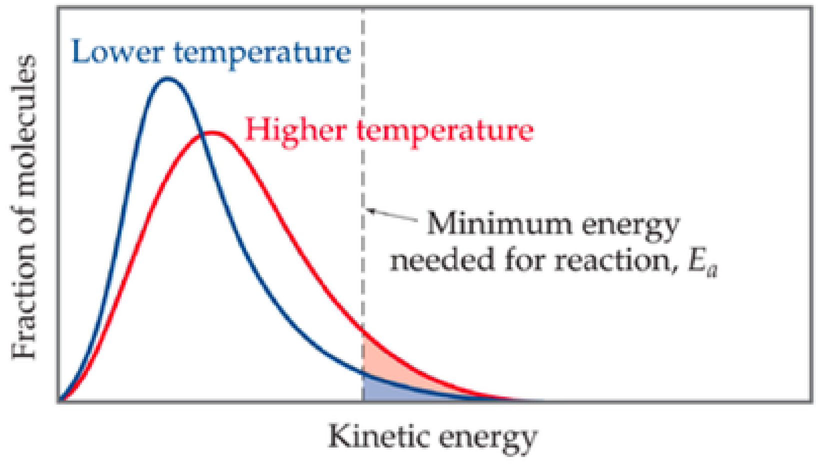
transition state: reactants transition to products, atoms in activated complex (bonds breaking & forming)

Exothermic

Endothermic

Note: E_a denotes activation energy

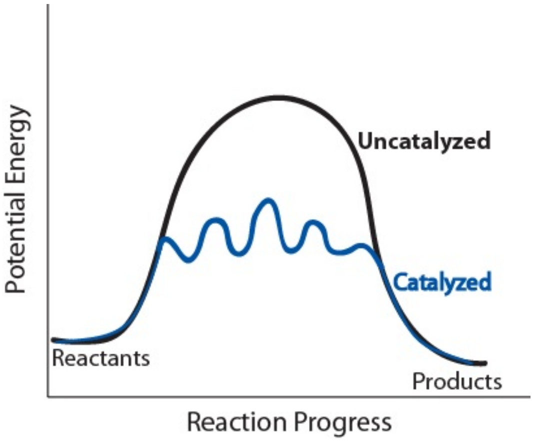
- Maxwell-Boltzmann Distribution for rxns



  - higher temperature → more molecules can overcome activation energy barrier
  - catalyst lowers activation energy (moves it leftward)

        - heterogeneous catalyst may adsorb (hold/bind to) reactant molecules for correct orientation, lowering activation energy
- (AP) Derived from Arrhenius equation: a graph of $\ln(k)$ vs. $\frac{1}{T}$ has slope $= E_a$
- rxn mechanisms can consist of discrete steps (elementary rxns), e.g.
    - $A + A \rightarrow X$
    - $X + B \rightarrow C + D$
    - $A + B \rightarrow C + D$ (rxn mechanism; not elementary)
    - molecularity of rxn: how many molecules involved (e.g. unimolecular, bimolecular, termolecular)
        - don't forget to look at coefficients
    - all reactants in elementary rxn are 1st order
        - if overall mechanism is multistep: one step is slowest, which overall rxn cannot be faster than → rate-determining step
            - species absent from rate-determining step are absent from rate law
            - intermediate: produced in one step, consumed COMPLETELY in later step (if not completely consumed, the leftover is a product)
                - concentration low throughout the rxn
            - fast equilibriums are never rate-determining step
            - intermediates are never in the rate law: use equilibrium step to substitute out intermediate (this affects molecularity)
            - catalyst: consumed in one step, produced in later step (opposite of intermediate; can appear in rate law)
            - *can also look at bonds broken/formed to determine which elementary step has largest activation energy (slowest)*
- catalysts increase rxn rate by changing rxn mechanism & decreasing activation energy
    - heterogeneous catalyst (see above)

    - enzymes are biological catalysts and help orient



Beer's Law (Spectrophotometry; see Spectroscopy Quizlet)

- $A = abc = -\log(T)$
    - A: absorbance
    - a: molar absorptivity
    - b: path length (through solution)
    - c: concentration (spectrophotometry can be used to find this)
    - T: transmittance

Unit 8: Equilibrium

- for a reversible rxn, system is at equilibrium when $\text{rate}_{\text{foward}} = \text{rate}_{\text{reverse}}$
    - NOT to be confused with concentration over time graph
- $K_c = \frac{\prod[products]^{coefficients}}{\prod[reactants]^{coefficients}}$ (based on balanced equation; solid/liquid not included)
    - no units, but make sure factors' units are molarity when calculating (to account for volume)
    - changes with temperature
    - equilibrium position: concentrations at equilibrium (experimentally determined)
    - large K (>10): product-favored rxn (consume most of reactants)

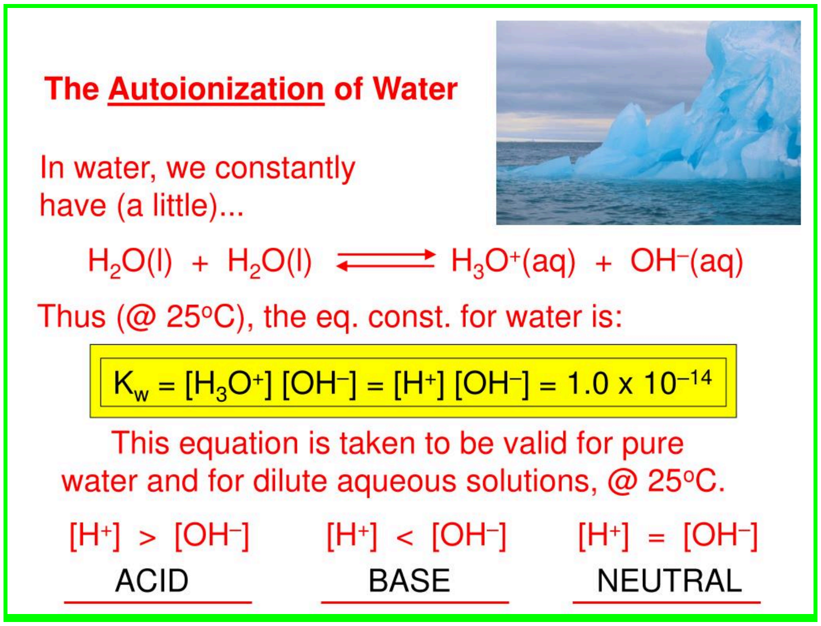
  - small K (<0.1) reactant-favored rxn (very little of reactants converted)
  - reverse equation: K becomes its reciprocal
  - scale equation by n: raise K to the nth power
  - add equations together: multiply K values
  - for gases, K_p is essentially the same but with partial pressures
- heterogeneous equilibrium position does NOT depend on amt of pure solids/liquids, as long as there is enough solid/liquid to reach equilibrium (at least bare minimum by stoichiometry)
  - adding more liquid/solid does NOT change equilibrium UNLESS volume changes, which changes aqueous concentration or partial pressure, AND these changes are not canceled out (not the same number of factors in the numerator and denominator of the equilibrium expression)
- reaction quotient: same as K formula, but not necessarily at equilibrium
  - Q=K: equilibrium
  - Q>K: system will shift left (products to reactants; Q will decrease in order to reach equilibrium)
  - Q<K: system will shift right (reactants to products; Q will increase)
    - if the system has not yet reached equilibrium, use "proceeds" instead of "shifts"
    - Q vs. K comparison is sufficient for AP FRQs
  - If there is not only one way for the rxn to proceed (all species are present) then compare Q & K to determine which way the system will go
    - if one species on a side is absent, that side's reaction cannot progress initially
  - ICE (Initial, Change, Equilibrium) table beneath chemical equation
    - if K is very small, x is very small, so you can "assume x is negligible" (can check work with 5% rule; x is less than 5% of whatever it is being added to/subtracted from)
    - also look for canceling out terms

        - if you have to use the quadratic formula or graphing (you probably won't), avoid intermediate rounding as much as possible
        - there can be extraneous solutions (e.g. x can be too large)
- Le Chatelier's Principle: if system subjected to stress, system may respond to relieve stress
    - shift right or left: [products] or [reactants] are higher at new equilibrium than at previous equilibrium
        - exception: manually added species will be greater than previous concentration
    - increase concentration → shift to opposite side
    - more volume → all partial pressures/concentrations decrease → toward side that produces more gaseous/aqueous mols (this side decreases more in the equilibrium expression, so the system shifts towards it to counter the decrease)
    - when cthermic/exothermic rxns and changes in temperature, add heat as species
        - endothermic: reactants + heat ⇌ products
        - exothermic: reactants ⇌ products + heat
        - increase temperature → system shifts towards opposite direction
            - e.g. increasing temperature decreases K (more reactants; more products convert to reactants): heat must be on product side (forward rxn is exothermic)
    - changes in rxn rates (e.g. catalysts, increasing liquid/solid amt) do NOT change equilibrium position

Unit 9: Acids and Bases

- 3 definitions of acid
    - Arrhenius: increases H^+
    - Bronsted-Lowry: proton (aka H^+) donor (class default)
    - Lewis: electron-pair acceptor (only definition that does not need H^+)

- Bronsted-Lowry definition requires acid-base pair
    - acid must have ionizable H (usually in front)
    - base must have lone pair
    - amphoteric: can be acid or base
    - acid loses proton to become conjugate base
    - base gains proton to become conjugate acid



The Autoionization of Water

In water, we constantly have (a little)...

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

Thus (@ 25°C), the eq. const. for water is:

$$\boxed{K_w = [H_3O^+]\,[OH^-] = [H^+]\,[OH^-] = 1.0 \times 10^{-14}}$$

This equation is taken to be valid for pure water and for dilute aqueous solutions, @ 25°C.

$[H^+] > [OH^-]$	$[H^+] < [OH^-]$	$[H^+] = [OH^-]$
ACID	BASE	NEUTRAL

- note H^+ and H_3O^+ are interchangeable because we often deal with water
- $K_w=K_aK_b=[H^+][OH^-]=1.00 \times 10^{-14}$ at 25°C
- pH = -log(H^+)
    - no units
    - at 25°C, pH=7 is neutral
    - for $[H^+]=A \times 10^{-B}$, pH has same significant figures as A to the RIGHT of the decimal point (everything to the left is unlimited)
    - think of "p" as log function: pH + pOH = pK_w=14 at 25°C
    - if concentration of added acid/base to water is very low, its effect on pH is negligible and remains neutral (if you try to calculate, you will get a contradictory result)
    - use indicators or pH meters to estimate/measure pH
- general acid dissociation: $HA(aq)+H_2O(l) \rightleftharpoons A^-(aq)+H_3O^+(aq)$, $K_c=K_a$
    - aka $HA \rightleftharpoons A^-+H^+$, $K_c=K_a$
    - strong acid: very high K_a, completely dissociated in water

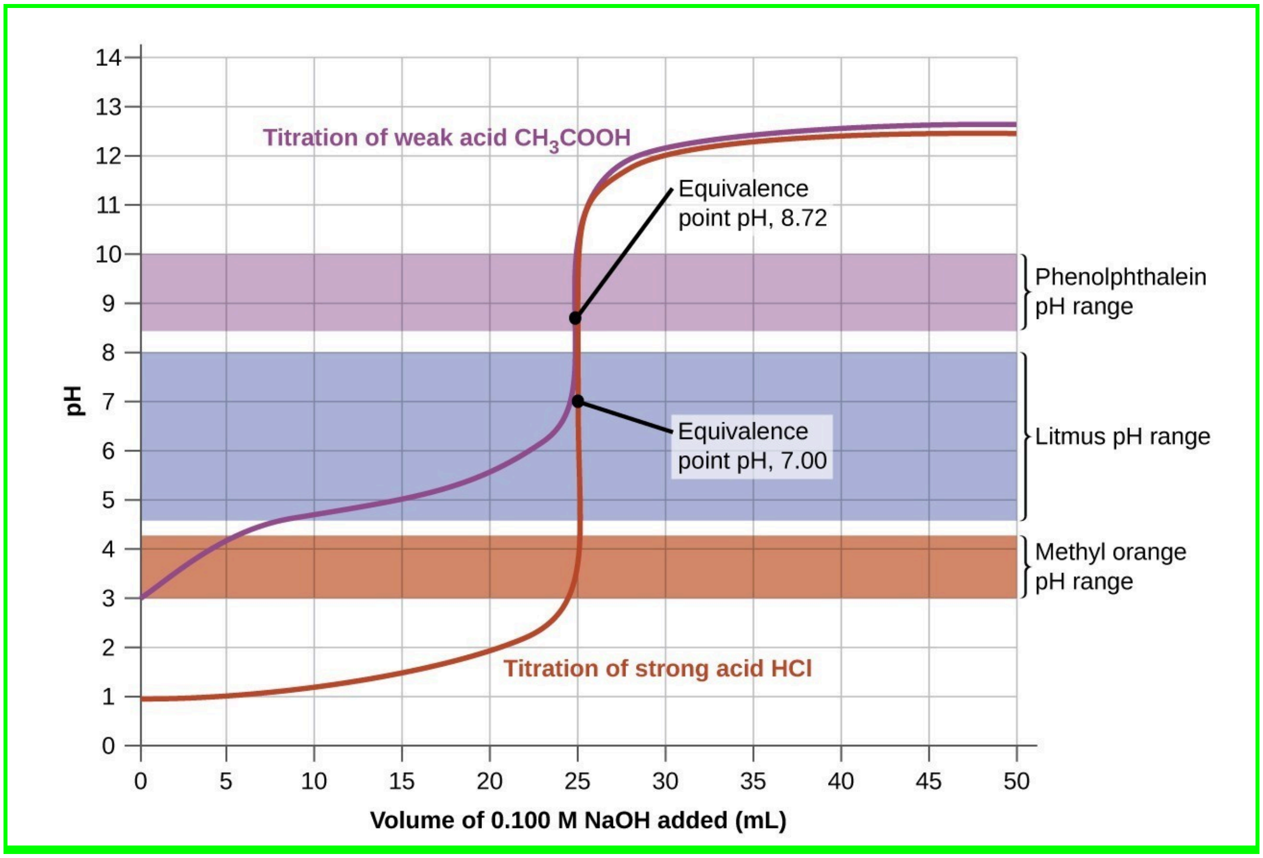
    - conjugate base is very weak with negligible effect on pH (effectively one-way rxn)
  - moderately weak acid: partially dissociated in water (calculate with K)
    - moderately weak conjugate base
    - weak acids written as complete aqueous compound in net ionic equation
  - do NOT confuse strength (K_a) with concentration, or dissociation with solubility
  - equilibrium favors reaction that moves proton to stronger base (that side will have greater K_a value; stronger acid dissociates more)
  - percent ionization: $\frac{amount\ ionized}{total\ amount\ in\ solution} \cdot 100\% = \frac{[A^-]}{[HA]_{initial}}$
    - (for acid) increases when adding water (product), decreases when adding dissolved/dissociated acid (reactants)
  - polyprotic acids: more than 1 ionizable hydrogen
    - if K_{a_1} and subsequent K values are 10^3 apart, pH essentially only depends on 1st dissociation
      - *MC: if that doesn't work and all K values are given, try adding up all the equations and multiplying their K values*
- strong base dissociation: $MOH(s) \rightarrow M^+(aq)+OH^-(aq)$, $K_c=K_b$
- weak base equation: $B(aq)+H_2O(l) \rightleftharpoons HB^+(aq)+OH^-(aq)$, $K_c=K_b$
  - weak bases are also written as full aqueous compounds in net ionic equations
- Acids/Bases to Memorize
- salts: ionic compounds that are products of acid-base neutralization
  - dissolved: dissociate and release conjugate acid/conjugate base
- acidity increases right/down on periodic table (more polar H-X bond or weaker H-X bond = more acidic)

  - shorter bond (like HF): stronger bond, less dissociation, weaker acid
  - longer bond: weaker bond, more dissociation, stronger acid
  - more electronegativity difference: more polar bond, hydrogen bonding with water, stronger acid
  - resonance → less dissociation
- Lewis acids do NOT need H^+ and can have empty valence orbitals
  - any Bronsted-Lowry base is a Lewis base, but not the other way around

Unit 10: Aqueous Equilibria

- Common Ion Effect: if ion in solution equilibrium is already dissolved in solution (before adding the salt), equilibrium shifts left (opposite to ion), making salt less soluble
  - basically just Le Chatelier extension to solubility
  - change ion's initial concentration (order doesn't matter since equilibrium is established the same way)
- when $[H^+]$ is negligible compared to $[HA]$ & $[A^-]$, $K_a \cdot \frac{[HA]}{[A^-]} = [H^+]$
- buffer: solution of moderately weak acid-base pair (same moles of each)
  - resistant to pH changes
    - add strong base to equimolar solution of $[HA]$ & $[A^-]$ (aka buffer): $HA + OH^- \rightarrow H_2O + A^-$ (assume all the strong base dissolves and assume this rxn goes to completion; ALL of the OH^- is consumed)
    - add strong acid to equimolar solution of $[HA]$ & $[A^-]$ (aka buffer): $A^- + H^+ \rightarrow HA$ (assume all the strong acid dissolves and assume this rxn goes to completion; ALL of the H^+ is consumed)
      - these reactions are also used for titration
  - $pH = pK_a + \log\frac{[A^-]}{[HA]}$ (Henderson-Hasselbalch)
  - $pOH = pK_b + \log\frac{[BH^+]}{[B]}$

    - use these for adding strong acid/base assuming in effective range; also used for target pH calculations
  - ideal buffer: $[HA]=[A^-]$, $K_a=H^+$, pH=pKa
    - but in reality, usually want buffer of specific pH
    - to get close, choose acid with pKa close to target pH
    - effective range in pH: about ± 1 pH
    - ratio $\frac{[A^-]}{[HA]}$ influences pH, but actual concentrations influence effectiveness range (higher concentrations → more buffering capacity)
  - 2 ways to make ideal buffer
    - equal mols of weak acid HA and its salt (contains conjugate)
    - react half of the weak acid with strong base (to end up with equal moles of conjugate base and weak acid)
- titration: known acid/base concentration (titrant) added to solution of unknown concentration of acid/base (analyte)
  - use pH meters or indicators to determine equivalence point: mols acidic H^+=mols basic OH^-
    - point of color change is endpoint; ideally near equivalence point
    - since volumes are changing, use mols in calculations UNTIL you can calculate a final volume



- types:
  - strong + strong (tells how much acid/base in unknown)
    - conjugates do not affect pH, pH=7 at equivalence point
  - weak + strong (finding K_a values, since pH=pKa halfway to equivalence point)
    - weak acid and strong base: conjugate base affects pH so that pH>7 at equivalence point
    - weak base and strong acid: likewise, pH<7 at equivalence point
    - see above for equations used for calculation
      - same chemical equations as those used for adding strong acid/base to buffer
      - Henderson-Hasselbalch for target pH
      - when in doubt, use equilibrium expression

- indicator: weak acid/base where conjugate has different color (amount is small enough to not affect environment's pH)

    - $pKa_{indicator} = pH_{environment} - \log\frac{[In^-]}{[HIn]}$ (rearranged Henderson-Hasselbalch; don't have to memorize)
        - halfway color change (e.g. green between blue/yellow; midpoint of indicator range): $[In^-]=[HIn]$, thus pKa=pH
        - e.g. $[In^-] = 10 \times [HIn]$ (yellow masks blue) → $\log\frac{[In^-]}{[HIn]} = 1$, so at 1 pH higher and above, solution appears blue (indicator color change occurs around $pKa \pm 1$)
- solubility (review solubility rules!)
    - "insoluble" really means very low solubility
    - $K_c=K_{sp}$ (solubility product)
    - e.g. $Cu(IO_3)_3(s) \rightleftharpoons Cu^{2+}(aq)+2IO_3^-(aq)$, $K_{sp}=[Cu^{2+}][IO_3^-]^2$
        - ICE: molar solubility = x (but they may ask for g/L)
    - if compounds break into same # ions (e.g. NaCl & KF), K_{sp} can be used to compare solubility; bigger K_{sp} = more soluble
    - if compounds don't break into same # ions, manually calculate solubilities
    - recall Common Ion Effect (or Le Chatelier)
        - acidic solution: basic ion (conjugate base) will attract H^+ → higher solubility (consume product)
        - basic solution: acidic cation (conjugate acid) will attract OH^- → higher solubility (consume product)
        - think percent ionization
    - Will precipitate form?
        - if dealing with double replacement (products are two salts), first determine which salt could possibly precipitate (very soluble products are unlikely to; recall solubility rules) → proceed with that salt's dissociation equation
        - if both products in the salt dissociation equation have nonzero concentrations, it becomes precipitation question (compare Q and Ksp first)
        - Q=Ksp: at equilibrium (saturated)
        - Q<Ksp: can still dissolve more solid
        - Q>Ksp: salt precipitates until Q=Ksp

        - if the salt contains hydronium (H_3O^+) or hydroxide (OH^-) ions, then the autoionization of water is not necessarily negligible (unless there is already additional amounts of those ions)
    - selective precipitation: using solubility differences to separate ions in a mixture

Unit 11: Thermochemistry Pt. 2

- Review Units 3 & 5!!!
- spontaneous process = thermodynamically favored (naturally proceeds under certain conditions; does not need continuous energy input)
    - spontaneous forward reaction = product-favored (useful for next unit)
    - opposite direction is non-spontaneous, not thermodynamically favored
    - even if spontaneous, may not occur due to high activation energy (conditions not met)
- reversible process: system changes such that universe (system & surroundings) can be put back into original state by exactly reversing the process
- irreversible process: system changes such that universe cannot be put back into original state by exactly reversing process
    - spontaneous → irreversible
    - real → irreversible (often assume reversible contrary to reality)
- entropy change measures how much or how widely energy is dispersed at a particular T ($\Delta S = S_{final} - S_{initial},$; state function)
    - *for isothermal process:* $\Delta S_{sys} = \frac{q_{reverse}}{T}$
    - 2nd law of thermodynamics: entropy of universe does not change for reversible processes & increases for spontaneous processes
        - reversible (ideal): $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = 0$

- irreversible (real/spontaneous):
  $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$

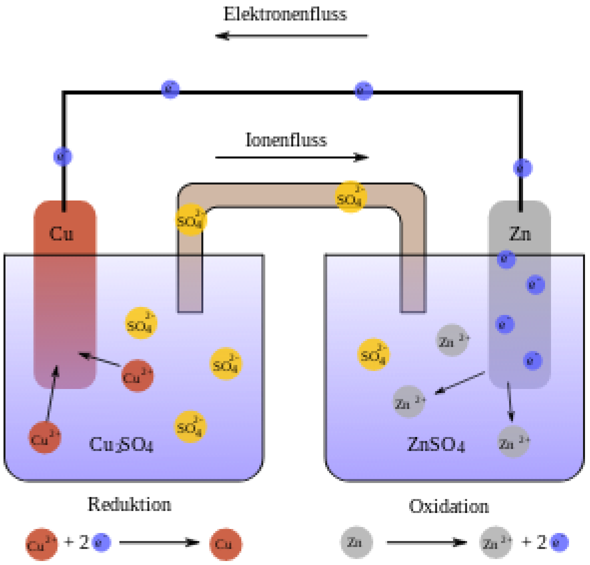
- Boltzmann’s microstate: snapshot of a molecule in a thermodynamic system at a point in time
  - more particles → more microstates
    - matters more than molar masses
  - higher T → more microstates (more energy states)
  - less structure (e.g. gas vs. solid) → more microstates (usually dominant over change in T)
    - predicting sign of ΔS using this alone does not always work
  - more gas volume → more microstates (freedom of motion)
    - more microstates → entropy increases
- dissolution of solid: ions increase in entropy, but some water decreases in entropy due to attraction to ions: usually increase entropy overall unless very high charge
- ΔS^o: standard molar entropy (units: $\frac{J}{mol\cdot K}$, standard conditions: 1 atm, 1 M solutions, typically 25°C)
  - 3rd law of thermodynamics: entropy of pure crystalline substance at absolute zero is 0
  - tend to increase with molar mass (but firstly, more atoms matters more)
- $\Delta S^o_{rxn} = \Sigma S^o(products) - \Sigma S^o(reactants)$ (multiply by respective coefficients)
  - pure elements: $\Delta H^o = 0, S^o \neq 0$
- *at constant T & P:* $\Delta S_{surr} = \frac{-q_{sys}}{T} = \frac{-\Delta H^o_{sys}}{T}$
- Gibbs free energy: $\Delta G^o =- T\Delta S_{univ} = \Delta H^o_{sys} - T\Delta S^o_{sys} =- RT\ln K_{eq}$ (rxn=sys, units: $\frac{kJ}{mol}$, standard conditions, $R = 8.314\ \frac{J}{mol\cdot K} = 0.008314\ \frac{kJ}{mol\cdot K}$)
  - $\Delta G < 0$: forward spontaneous (K>1 aka product-favored; Q<K)

  - $\Delta G = 0$: equilibrium (K=1; Q=K; for phase changes, melting/boiling pts)
  - $\Delta G > 0$: reverse spontaneous (K<1; Q>K)
  - watch signs and always convert ΔS^o & R to $\frac{kJ}{mol \cdot K}$
- Gibbs free energy in NON-STANDARD conditions: $\Delta G = \Delta G^o + RT \ln Q$

Unit 12: Electrochemistry

- Review Unit 1 (redox)
- electrochemical cell (galvanic/voltaic: external circuit): energy from spontaneous redox rxn used to perform electrical work (battery is 2+ cells)
  - solid metal electrodes (each corresponds to a solution of respective ion):
    - anode: oxidation (lower reduction/higher oxidation potential)
    - cathode: reduction (higher reduction/lower oxidation potential)
    - mnemonic: (an ox and a red cat)
    - electrons flow from anode to cathode (oxidation to reduction; losing electrons to gaining electrons)
      - note: anode is actually the negative electrode (negative electrode oxidizes), and cathode is the positive electrode (positive electrode reduces), which makes sense because electrons are attracted to positive charges, thus they flow to the cathode
  - salt bridge completes circuit by connecting half-cells: prevents mixing & charge buildup (electrolytes conduct electricity and balance out charges)
  - shorthand notation: anode | soln || soln | cathode (anode to cathode)
    - || = salt bridge
    - e.g. Zn(s) | Zn^{2+}(aq) || Cu^{2+}(aq) || Cu(s)

            - rxn: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ (cation produced from solid anode, solid produced at cathode from dissolved cations)



- coulomb (C): SI unit of electron charge
- electromotive force: E_{cell} has units Volts
  $(emf = E_{cell} = potential\ difference = V = \frac{J}{C} = \frac{work}{charge})$
    - standard conditions: $E^0_{cell} = E^0_{red} + E^0_{ox} = E^0_{red}(cathode) - E^0_{red}(anode)$
        - $E^0_{red}(anode) < E^0_{red}(cathode)$
        - Be cautious of sign errors; make sure you are using unchanged reduction potentials when using the 2nd formula (if you flip stuff such that one half-rxn is reduction and the other is oxidation and you change the signs of the potentials accordingly, you have to use the 1st formula)
        - standard reduction potentials (E^0_{red}) are measured in relation to standard hydrogen electrode (set as the 0 case)
        - standard electrode potential is an INTENSIVE property; DON'T multiply by coefficients; balancing does NOT matter
        - $\Delta G^0 = -\ nFE^0_{cell}$
            - n is mol electrons and Faraday's constant is $96,485\ \frac{C}{mol\ e^-}$

      - $E^0_{cell}>0$, $\Delta G^0<0$, K>1: forward spontaneous (product-favored)
      - $E^0_{cell}=0$, $\Delta G^0=0$, K=1: at equilibrium
      - $E^0_{cell}<0$, $\Delta G^0>0$, K<1: forward nonspontaneous; reverse is spontaneous (reactant-favored)
        - derived from equation above + previous unit
  - if NOT standard conditions, $E_{cell}\neq E^0_{cell}$
    - Q=K: $E_{cell}=0$ (equilibrium)
    - Q<1: $E_{cell}>E^0_{cell}$
    - Q=1: $E_{cell} = E^0_{cell}$
    - Q>1: $E_{cell}<E^0_{cell}$
      - can use Nernst Equation instead of memorizing
    - FRQ Explanation (NOT Le Chatelier's): "When Q<1, a relatively large [reactant] and relatively small [product] increase the driving force for the rxn, thus $E_{cell}>E^0_{cell}$"
      - "When Q>1, a relatively small [reactant] and relatively large [product] decrease the driving force for the rxn, thus $E_{cell}<E^0_{cell}$"
    - Nernst Equation: $E_{cell} = E^0_{cell} - \frac{RT}{nF}\ln Q$, where $R = 8.314\ \frac{J}{mol\cdot K}$, n is mol electrons, F is Faraday's constant
      - increase in Q (relatively more product of oxidation) leads to decrease in E_{cell}
      - decrease in Q (relatively more reactant of reduction) leads to increase in E_{cell}
- electricity is like a hose
  - voltage (volts, V) is like pressure
  - current (amps, A or I) is like diameter
  - resistance (ohms, R or Ω) is like sand build-up blocking the water
- concentration cell: same element, different concentrations
  - anode to cathode: lower to higher (increasing the difference in concentrations leads to higher voltage)
  - $E^0_{cell}=0$, calculate E_{cell} via Nernst

        - $Q = \frac{[cation]_{anode}}{[cation]_{cathode}} = \frac{products\ of\ oxidation\ at\ anode}{reactants\ of\ reduction\ at\ cathode}$
- *corrosion (e.g. iron oxidized in humid/water): cathode rxn is* $2H_2O + O_2 + 4e^- \rightarrow 4OH^-$
    - *anti-corrosive protection:*
        - *galvanize: coat iron with steel*
        - *alloy: other metals form oxide coating (e.g. nickel in stainless steel)*
        - *cathodic protection: connect & sacrifice active metal to oxidize first*
- electrolytic cell: force nonspontaneous rxn to occur by using electric current to trigger chemical change with negative cell potential
    - requires voltage > E_{cell}(spontaneous reverse)
        - opposite of electrochemical: for example,
            - electrochemical (spontaneous): $2Na(s) + Cl_2(g) \Leftrightarrow 2NaCl(l),\ E_{cell}(spont.)$
            - electrolytic (nonspontaneous):
            - $2NaCl(l) \Leftrightarrow 2Na(s) + Cl_2(g),\ E_{cell}(nonspont.) = -E_{cell}(spont.)$
    - electrolysis of aqueous solution: water undergoes redox
        1. $O_2(g) + 4H^+(aq) + 4e^- \Leftrightarrow 2H_2O(l),\ E_{red} = 1.23\ V$
            - anions must have lower reduction potential than above in order to oxidize (like an ox*; water will then reduce according to rxn 2*)
                - *otherwise (i.e. anion's reduction potential is not lower), anion will not oxidize and water will oxidize according to rxn 1 (but reversed)*
            - *Be careful! Given a reduction potential table, if you flip the reaction (or just memorize 1 & 2 and avoid this precaution), it becomes the following:*
                - $2H_2O(l) \Leftrightarrow O_2(g) + 4H^+(aq) + 4e^-,$ $E_{ox} = -1.23\ V$

          - *anions must have greater oxidation potential (more negative reduction potential) in order to oxidize (water will then reduce according to rxn 2)*
            - *otherwise, (i.e. anion's oxidation potential is not greater), anion will not oxidize and water will oxidize according to rxn 1 (but reversed)*

    2. $2H_2O(l) + 2e^- \Leftrightarrow H_2(g) + 2OH^-(aq),\ E_{red} = -0.83\ V$
        - cations must have greater reduction potential than above in order to reduce (like red cat*; water will then oxidize according to rxn 1 (but reversed)*)
          - *otherwise (i.e. cation's reduction potential is not greater), cation will not reduce and water will reduce according to rxn 2*
    - aqueous solution will have cation & anion from binary compound, but it is not necessary that either of them will actually react; you have to check
- electroplating: deposit metal onto metal
    - Faraday's laws: charge = current * time = mol e^- * F
        - Q=It=nF (C = amp * sec = mol e^- * 96,485 $\frac{C}{mol\ e^-}$)
          - convert time to seconds
          - not mol of element, mol of e^-; need stoichiometry to convert between the two using charge of the cation