SCH 4U Exam Review

Periodic Properties

Atomic radius:

- decreases across a period, increases down a group.
- increases down because more energy levels are being added
- decreases across because positive charge is increasing in the nucleus, but added electrons are the same distance away, so the electrons are pulled closer towards the nucleus

Effective nuclear charge:

- increases across a period, increases down a group
 - effective nuclear charge is the attraction felt by the valence electrons from the nucleus
- increases across because the number of protons is increasing in the nucleus, while the electrons being added are the same distance away
- increases down because more protons are being added. However the core electrons shield the valence electrons from the effect of the nucleus, hence decreasing effective nuclear charge down the group.

Ionization energy:

- increases across a period, decreases down a group
- Defined as the energy required to remove an electron from a gaseous atom in its ground state to from a gaseous cation.
- decreases down because effective nuclear charge is decreasing and atomic radius is increasing
- increases across with increasing nuclear charge and decreasing atomic radius.

Electron affinity:

increases across a period, decreases down a group

- Defined as the energy released when an electron is added to a gaseous atom in its ground state to form a gaseous anion
- increases across because elements go from metals to non-metals. Non-metals want electrons to bring them closer to their stable octet. Release energy because as atoms become more stable they have less energy.
- decreases down because metallic character is increasing, thus addition of an electron will destabilize the metallic atom, and is therefore not likely to be exothermic.

Metallic character: decreases across a period, increases down a group

Second electron affinity:

- to add another electron to a negative ion, one must add energy because the negative charge on the ion repels the electron you are trying to add, thus generally second electron affinities are endothermic.

Ionic radii:

a cation (+) has a smaller ionic radius than a neutral atom of the same element, because the nuclear charge which pulls in electrons is greater, making the radius smaller. In addition, an energy level may have been removed in forming the cation.

an anion (-) is always greater than a neutral atom of the same element, because when you add an electron, there is more repulsion in the electron cloud and it spreads out, increasing the ionic radius.

Compare electron – proton attraction and electron – electron repulsion, ex. Na⁺ and F⁻

<u>Electronegativity:</u> is a measure of the tendency of an atom to attract the electrons within a covalent bond (Recall: covalent bond = non metal + non metal)

- measures the polarity of a bond, electronegativity values are assigned in the range of 0 4
- if difference between electronegativities is:

less than 0.7 = purely covalent 0.7 - 1.7 = polar covalent

Greater than 1.7 = ionic

Bonding/Lewis Structure:

Ionic bonding:

happens between metals, because of low ionization energy and low electron affinity, (.:lose electrons) and non-metals because of high ionization energy and high electron affinity, (.:gain electrons), form ions, held by strong electrostatic forces of attraction in an ionic crystal lattice.

Drawing Lewis Structures:

- Choose a central atom. The central atom is the one that can make the most number of bonds to complete it. (Ex. C = 4, N = 3, O = 2, H = 1. Exception Be = 2, B = 3)
- 2) Count all valence electrons (note charges on ions). (Group number = # of valence electrons, cation: subtract electrons, anion: add electrons)
- 3) Arrange other atoms around central atom in a symmetrical skeleton, and place two electrons in each bond.
- 4) Complete the octets of the atom to the central atom by adding the electrons in pairs.
- 5) Place any remaining electrons on the central atom.
- 6) If the central atom does not have an octet, form double/triple bonds by moving electrons. The central atom must have an octet (except, Be, B).

Exceptions to the octet Rule:

- 1) Hydrogen can only hold one electron pair.
- 2) Lithium and family one can only hold one electron pair.
- 3) Beryllium can only hold 2 electron pairs.
- 4) Boron can only hold 3 electron pairs.
- 5) Elements of the 3rd and subsequent rows of the periodic table may form more than 4 bonds (due to the presence of the d-orbitals to accommodate electrons)
- Some atoms, ions and molecules have orbitals containing a single unpaired electron. These are called paramagnetic and they have an odd number of valence electrons so the Lewis structure will always show an unpaired electron eg: NO and NO₂

Resonance Structures

- when writing the Lewis structures for some molecules it is possible to write more than one correct structure.

for example SO₃

there are three possible structures, these are known as resonance hybrids. They are extreme forms of the true structure, which lies somewhere between the three.

Evidence for resonance comes from bond lengths, as the bond lengths between the sulphur and oxygen atoms in SO_3 are the same and are intermediate between single and double bonds.

Shapes of Molecules and Ions

VSEPR Theory:

- The shapes of simple molecules and ions can be determined by using valence shell electron pair repulsion (VSEPR) theory.
- this states that pairs of electrons arrange themselves around the central atom so that they are as far apart as possible from each other.
 - If you have bonding pairs on an atom and no lone pairs of the electrons, the bonding pairs repel each other equally, so the bond angles between them are all equal.
- Lone pairs repel greater than bonding pairs, so they occupy more space. The most space taken up is between two lone pairs. Second most between lone pair and bonding pair, and least by two bonding pairs.

Example: CH_4 NH_3 H_2O 109^0 107^0 104^0

Working out the Actual Shape

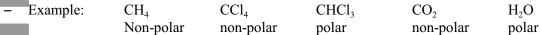
To work out the actual shape of a molecule calculate the number of pairs of electrons around the central atom, then work out how many are bonding pairs and how many are non-bonding pairs.

# bonding electron pairs on central atom	# lone electron pairs on central atom	VSEPR formulae	VSEPR shape	Bond Angle
2	0	AX_2	Linear	180^{0}
2	1	AX_2E	Non linear	<1200
2	2	AX_2E_2	Bent	<109°
3	0	AX_3	Triangular planar	1200
3	1	AX_3E	Trigonal Pyramidal	<109°
3	2	AX_3E_2	T-shape	<900
4	0	AX_4	Tetrahedral	109°
4	1	AX ₄ E	d istorted Pyramidal	1 <90°, <120°
4	2	AX ₄ E	square planar	90°
5	0	AX_5	Trigona Bypyramidal	1 90°, 120°
5	1	AX ₅ E	Square Pyramidal	90°
6	0	AX_6	Octahedral	900

Note: double bonds act as single charge center

Molecular Polarity:

- Whether a molecule is polar or not, depends both on the relative electronegativities of the atoms in the molecule and on its shape.
- if the individual bonds are polar then it does not necessarily follow that the molecule will be polar as the resultant dipole may cancel out all the individual dipoles.
- molecules are polar either when they have lone pairs on the central atom, or if the atoms attached to
 the central atom are not all identical, thus the bond dipoles do not cancel resulting in an unsymmetrical
 molecule.

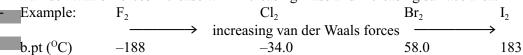


INTERMOLECULAR FORCES

- The covalent bonds between the atoms *within* a molecule are very strong. the forces of attraction *between* the molecules are much weaker.
- these intermolecular forces depend on the polarity of the molecule.

Van-der Waals' forces

- temporary instantaneous dipoles induces resulting in weak attractions between two non-polar molecules.
- Van-der Waals' forces increase with increasing mass and increasing surface area.



Dipole: dipole forces

- polar molecules are attracted to each other by electrostatic forces.
- Although still relatively weak the attraction is stronger than van der Waals' forces.
 - Example: butane propanone C_4H_{10} CH_3COCH_3 molar mass: 58 58 58 56.2

Hydrogen Bonding

- hydrogen bonding occurs when hydrogen is bonded directly to a small highly electronegative element, such as F, O or nitrogen.
- As the electron pair is drawn away from the hydrogen atom by the highly electronegative element, all that remains is the proton in the nucleus.
- The proton attracts the non-bonding pair of electrons from the F, N or O resulting in a much stronger dipole—dipole attraction.
 - The effect f hydrogen bonding is observed in the hydrides of Group V, Group VI and Group VII.
- Water has a much higher boiling point than the other Group VI hydrides as the hydrogen bonding between the water molecules is much stronger than the dipole—dipole attraction in the remaining hydrides.

Organic

<u>Valence bond theory</u>: covalent bonding is a bond formed between two overlapping or hybrid orbitals shown by the sharing of one pair of electrons

- Sigma bond, σ -bond: overlap across the bond nuclear axis, long strong bond.
- Pi bond, π bond: overlap perpendicular to the bond nuclear axis, weaker and shorter than a sigma bond

<u>Functional Group</u>: part of a molecule in an organic compound that enters into a characteristic set of reactions. Organic compounds that have the same functional group have the same chemical properties.

	Chemical Structure	Family Name	Suffix/Prefix	Example name	Example structure
				when methane is attached to a chain = methyl	
	alk	alkane eth	ethane wh	when ethane is attached to a chain = ethyl	
	alk	alkane p	Propane pp	when propane is wh attached to a chain by an end carbon = propyl	when propane is attached to a chain by its middle carbon = isopropyl
	alk	alkane Bu	butane, pentanead hexane, heptane, octane, nonane, decane		
_	alk	alkene -er	– ene eth	ethene	$H_2C = CH_2$
9	alk	alkyne -y	-yne eth	ethyne	HC ≡CH
+	F, Cl, Br, I	halogeno compound	fluoro-; chluoro-; iodo-; bromo-	chloromethane	
	ОН	alcohol	-ol	methanol	
5	C-C-C 0	ketone	-one	propanone	
U	С-С-Н О	aldehyde	-al	propanal	

		ether	alkoxy- alkane	methoxyethane	
	C – O - C			J	
	C – NH ₂	primary amine	-amine	ethylamine	
		secondary amine	amino-		
		tertiary amine	amino-		
		nitriles	-nitrile	ethannitrile	
	NO ₂	nitro compounds	nitro-	nitroethane	
	C - C - O-H	carboxylic acid	-oic acid	ethanoic acid	
9	2				
	-C-O -C	ester	Alkyl alkanoate	methyl ethanoate	
5	-C-NH ₂	amides	-amide	ethanamide	
±		Benzene rings	methyl benzene		
			phenol		
	5		benzoic acid		
	5		nitrobenzene		
			chlorobenzene, bromobenzene,		

<u>Benzene rings:</u> -relative to the first substituent: ortho -, meta- and para – positions.

Themochemistry — Enthalpy changes

-deals with the macroscopic property of temperature of a system

Enthalpy:

- H: the total amount of heat energy the system has. Any element under standard conditions has an enthalpy of formation of zero. Standard conditions are 1 atm pressure and 298K. the standard enthalpy change of a reaction is denoted by ΔH^0
- ΔH^0 of a reaction can be written on the side of the equation, or it can be written as part of the equation, but the sign (+ve or -ve) must be given.
 - When an equation is multiplied/divided by a factor so is the ΔH^0
 - Change in enthalpy is related to (i) the number of bonds being broken or formed.
 - (ii) the strengths of the bonds broken and formed

	EXOTHERMIC	ENDOTHERMIC
	heat energy is released = increase in	Heat energy is absorbed = decrease in
	Temperature	temperature
	ΔH is negative	ΔH is positive
	Potential energy of products is lower than	Potential energy of products is higher than
	potential energy of reactants.	potential energy of reactants.
	Bonds made in products are stronger than	Bonds made in products are weaker than those
	bonds broken in reactants.	broken in reactants.
	Products are more stable	Products are less stable
٦		
1	Reaction is self-sustaining, once activation	Reaction will stop once the energy source is
	energy is provided to start a reaction.	removed.
	POTENTIAL ENERGY GRAPH:	POTENTIAL ENERGY GRAPH:

Molar Enthalpy:

- Heat content of one mole of a substance; this is a characteristic property of the substance. The energy is stored in the substance during its' formation. Heat stored cannot be measured directly, only changes in heat content that occur during a chemical reaction can be measured.
- molecular enthalpy = K.E. + P.E. = all energy stored in molecule
- Kinetic energy refers to the energy of movement in a molecule and is associated with changes in temperature. Potential energy is related to the attractive forces in a substance and is associated with changes of state.
- chemical reactions tend towards products with minimum potential energy, as they are more stable

Standard enthalpy change of Formation, $\Delta H_{\rm f}^0$

The standard enthalpy change of formation of a compound is the enthalpy change when one mole of the compound is formed from its elements in their standard states at 298 k and 1 atm pressure.

From this it follows that ΔH_f^0 for an element in its standard state will be zero.

Heat Capacity:

- the amount of heat required to raise temperature of a given amount of substance by one degree
- units: J/ ⁰C or J/ ⁰Cmol

$$C = \underline{Q}$$
 ΔT

Specific Heat Capacity:

- The amount of heat required to raise the temperature of 1g of material by 1 degree.

Units: J/g ⁰C)

The specific heat capacity of water is $4.18 \text{ J/g}^{0}\text{C}$. That is, it requires 4.18 joules of energy to raise the temperature of one gram of water by on e degree Celsius.

$$c = C/m$$
 $Q = m c \Delta T$

Q = quantity of heat C = heat capacity c = specific heat capacity

The heat involved in changing the temperature of any substance can be calculated from the equation:

$$Q = m c \Delta T$$

Enthalpy changes are normally quoted in kJ/mol, for either a reactant or a product, so it is also necessary to work out the number of moles involved in the reaction which produces the heat change in the water.

Calorimetry:

The enthalpy change for a reaction can be measured experimentally by using a calorimeter

Bomb Calorimeter:

measures the amount of heat given off when something is burned in it

- insulated, air tight lid, filament to heat liquid
- amount of heat produced, $Q = \text{heat capacity of calorimeter } x \Delta T$

$$Q = C \Delta T$$

Hess's Law:

For any reaction that can be written in steps, the standard heat of reaction is the same as the difference between the sum of standard heat of the products minus the sum of the standard heat of reactants. Two ways of calculating the enthalpy change of a reaction which can not be measured directly:

- ■1. Manipulation of equations given to obtain the target equation.
- 2. Using Hess's Law of Summation:

$$\Delta H^0_{reaction} = \Sigma \Delta H^0_{f} (products) - \Sigma \Delta H^0_{f} (reactants)$$

Bond Enthalpies:

Enthalpy changes can also be calculated directly from bond enthalpies.

For a diatomic molecule the bond enthalpy is defined as the enthalpy change for the following process:

$$X - Y_{(g)} \longrightarrow X_{(g)} + Y_{(g)}$$

Average bond energy: bond enthalpies are obtained by considering a number of similar compounds. In practice the energy of a particular bond will vary slightly in different compounds, as the neighbouring atoms will affect it. So ΔH values obtained from using bond enthalpies will not necessarily be very accurate.

$$\Delta H^0_{reaction} = \Sigma Bonds broken (reactants) - \Sigma Bonds formed (products)$$

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If reaction is exothermic, then stronger bonds are made in products than those broken in reactants.

Rates of Reactions — Kinetics

Chemical kinetics is the study of the factors affecting the rate of a chemical reaction.

- is defined as the increase in concentration of one of the products per unit time or as the decrease in the concentration of one of the reactants per unit time.

Units: mol/L.s

Kinetically stable:

if thermodynamically a substance should be undergoing chemical change, but this reaction takes such a long time to happen that we can't see it happening.

Collision Theory:

if molecules are going to react, they must collide with enough energy to break their existing bonds, in order to form new bonds, forming a new product.

effective collisions are when there is enough energy to break the bonds and form products (1 out of 10^{11} collisions are effective)

<u>Activation energy</u> is the minimum amount of energy that molecules must bring into the collision for it to be an effective collision.

molecules must also have the correct spatial orientation in order to collide effectively

Activated complex (aka: transition state) is the peak of the activation energy, the species where old bonds are about to broken and new ones are about to be made, and has the highest potential energy. This does not increase if temperature is increased

Any factor that either increases the frequency of collisions or increases the energy with which they collide will make the reaction go faster.

Factors affecting the rate of Reaction:

- 1) Surface area: more = faster rate
 - increases rate because there is a higher surface to volume ratio
- 2) Concentration: more = faster rate
 - is the number of moles per volume, so increasing concentration increases # of molecules in a given amount of space (density)
- 3) Nature of Reactants: depends on IMFAs ability to lose and gain electrons, and if the acid is strong or weak (this changes percent dissociation)
- 4) Temperature: higher temperature = faster rate
 - 10 °C rise will double reaction rate
 - increasing temp increases the fraction of molecules which have the activation energy
 - ΔH does not increase if temperature is increased
- 5) Catalyst: provides an alternative reaction path with either a lower activation energy (for a negative catalyst that slows the speed of reaction, Ea is increased).
 - ΔH does not change when a catalyst is added
- a catalyst is used up in one step of a reaction with elementary steps, and regenerated in the next. This means that the catalyst provides an alternative mechanism for the reaction to take place by; it takes part in the mechanisms, but is not used up or altered throughout the entire reaction, the end reaction is the same but the mechanisms are different.

Kinetic Theory of Gases:

- all molecules in a system do not possess the same amount of energy
- most molecules possess the average amount of energy, but few have higher or lower energies. This is called their kinetic energy distribution: Maxwell – Boltzmann Distribution of Kinetic Energy (see temperature for example of distribution graph)

To find rates of reaction:

on graph: take tangents at the point in time you want the rate at, slope gives the instantaneous rate from equation: rate = concentration/time

Reaction Mechanism:

For reactions where there is more than two molecules involved, the reaction must take place over many steps. These are the elementary steps. Each step involves 2-3 molecules colliding, forming two new molecules. Each step has its own activated complex, activation energy and ΔH .

Rate Determining Step:

the elementary step with the highest activation energy

the slowest step, sometimes called the bottleneck

factors affecting only the rate determining step will increase or decrease the rate of the reaction

Rate Law:
$$A + B \longrightarrow C$$

Rate Law: Rate =
$$k[A]^m[B]^n$$

k =rate constant, units depend on rate law, higher the numerical value – faster the rate.

$$\frac{\text{Rate } \#1}{\text{Rate } \#2} = \frac{[\text{concentration } \#1(A)]^m}{[\text{concentration } \#2(A)]} = \frac{\text{Rate } \#1}{[\text{concentration } \#2(B)]} = \frac{[\text{concentration } \#1(B)]^m}{[\text{Rate } \#2]} = \frac{[\text{concentration } \#1(B)]^m}{[\text{concentration } \#2(B)]}$$

for a reaction with elementary steps, the exponents in the rate law of the rate determining step match the coefficients in front of the molecules in the balanced equation.

The exponents in the rate law of the rate determining step are the same as those in the overall reaction. This is because the rate of the overall reaction is dependant only on the rate of the rate determining step.

Overall order of a reaction: sum of the exponents in the rate law

Order with respect to: the exponent in the rate law on the concentration of what you are taking it

with respect to

Catalysis: homogeneous catalyst and heterogeneous catalysts

Equilibrium

- achieved when the rate of the forward reaction equals the rate of the reverse reaction

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Dynamic Equilibrium:

- reaction where molecular activity is continuous.
- <u>Macroscopic</u> properties (mass, pressure, temperature) are constant, microscopic are continuous

Microscopic properties:

- properties at a small molecular level, continuous-changing
- Equilibrium position: time it takes for the equilibrium system to be altered
- does not necessarily mean there are equal amounts of product and reactant, but that the rate of formation and decomposition are equal.

Steady state: a system which can never achieve equilibrium

Characteristics of Equilibrium:

- 1) it must be a closed system
- 2) macroscopic properties remain constant
- 3) microscopic properties are continuous
- 4) equilibrium can be established from any direction (forward to reverse, vice versa)

Le Châtelier's Principle:

- if a system in equilibrium is disturbed, the system will counter-act to oppose the change and to reattain equilibrium

Factors affecting equilibrium:

1) Concentration

- does not affect solids or liquids, but effects aqueous solutions and gases
- if the concentration of one component of the equilibrium is increased, the equilibrium will favor the reaction of this component, in order to decrease the component that was increased, and re-establish the equilibrium
- forward reaction is favored if the concentration of the products is decreased, or if the reactants concentration is increased
- reverse reaction is favored when product concentration is increased, or if the reactants concentration is decreased.

2) Pressure

- gases only
- related to the number of molecules in a certain volume
- count number of molecules on each side of equation
- if we increase pressure of the system, it will decrease it by favoring the side that has less molecules if we decrease pressure of the system, it will increase it by favoring the side that has the most molecules
- if the number of molecules on both sides of the equation is equal, pressure has no effect

3) Temperature

- if the temperature is increased, the equilibrium will oppose it by favoring the endothermic reaction in order to lower the temperature again
- if the temperature is decreased, the equilibrium will oppose it by favoring the exothermic reaction in order to increase the temperature again

4) Catalyst

- because a catalyst increases the rate of both the forward and reverse reaction, it has no effect on an established equilibrium, but it does allow equilibrium position to be obtained at a faster rate, because it will speed up whichever reaction is necessary to establish equilibrium
- a catalyst is specific to each reaction i.e.: one catalyst will not catalyze all reactions

5) Volume

- works the same way as pressure, if a one liter container containing a reaction, the concentrations will be increased and the pressure will be increased, as there are the same amount of molecules in half the amount of space:

6) Inert/ Noble GasNo effect

Equilibrium Constant:

$$Kc = \underline{[products]}^{exponent}$$

 $[reactants]^{exponent}$

- exponent of each concentration is equal to the coefficient of each molecule in the balanced equation
 only gases and aqueous solutions are considered in the equilibrium constant
- the equilibrium constant is ONLY dependant on temperature, ie: the numerical value of the equilibrium constant/rate constant can only be altered by temperature
- numerical value of the equilibrium indicates the extent of the reaction:

When the reaction goes nearly to completion then Kc >>> 1

If the reaction hardly proceeds then Kc <<< 1

If the value for Kc lies about 10^{-2} and 10^{2} then both reactants and products will be present in appreciable amounts.

- ICE CHARTS USED for equilibrium

<u>Reaction Quotient</u>: to determine if a system is at equilibrium using experimental concentrations and a known equilibrium constant (Kc value): do a trial equilibrium constant using the experimental data (called reaction quotient).

if the reaction quotient is too high/low TEMPERATURE must be altered for the system to establish equilibrium

Solubility Product, K_{sp}

when you have a solution in equilibrium that is saturated, so there is a constant mass of solid at the bottom,, the microscopic properties are continuous, which means molecules within the solution are constantly dissolving and solidifying.

Solubility constant (K_{sp}) :

each molecule has its own solubility constant; the higher the Ksp the greater the solubility

given:
$$A_x B_{y(s)} \Longrightarrow xA^+_{(aq)} + yB^-_{(aq)}$$

then, $K_{sp} = [A^+]^x [B^-]^y$

Solubility: the maximum amount of solute that can dissolve in 1L of solvent at a given temperature.

Precipitates:

- if trial K_{sp} is larger than given K_{sp} , precipitate will form
- if trial K_{sp} is smaller than given K_{sp} , no precipitate will form

Acids and Bases

Theories:

- Arrhenius: an acid produces H₃O⁺ in H₂O and a base produces OH⁻
- Bronsted-Lowry: an acid acts as a donor of protons (H₃O⁺) and a base acts as an acceptor of H₃O⁺
- Lewis: an acid is a lone electron pair acceptor, and a base is a lone electron pair donor

Acid: sour, corrosive, conducts, polar molecular, ionizes

- turns litmus=red, bromthymol blue=orange/yellow, methyl orange=red, phenolphthalein=clear
- reacts with Mg_(s) and NaHCO_{3(s)}

Base: bitter, slippery, conducts, ionic compound, dissociates

turns litmus=red, bromthymol blue=blue, methyl orange=orange, phenolphthalein=magenta

Electrolyte: substances that conduct electricity in water due to the movement of ions

Strong- substances that ionize/dissociate 100%

Weak- ionize only partially, set up weak equilibrium

Nonelectrolyte: does not ionize in H₂O (non polar covalent)

Dissociation: the separation of existing ions when an ionic substance melts or dissolves

Hydration: the process of ions in solution becoming surrounded by water molecules.

Once hydrated, these ions can move around within the solution, and behave independently. This ability to move allows the solution to conduct electricity.

Strong Acids: HCl, HBr, HI, HNO₃, H₂SO₄, HClO₄

Weak Acids: HF, CH₃COOH, H₃PO₄, HNO₂, anything with carbons

Strong Bases: NaOH, KOH, Ca(OH)₂, Ba(OH)₂

Weak Base: NH₃

Monoprotic Acid: only donates one H⁺ per molecule in solution

Diprotic Acid: donates two H⁺ per molecule in solution

Amphiprotic: a substance that can act as either a base or an acid, depending on which it is in solution with

Salt: any organic compound that doesn't contain OH or O². H part of acid is replaced by metal

Acid Salt: when an acid reacts and not all of the H⁺ions are neutralized by OH⁻, then the H⁺ions are present in the salt, making it acidic

Conjugate base: the product of an acid-base reaction that has few H⁺ions (left over from the acid). Strong acid-weak conjugate base

Conjugate acid: same as conjugate base but has more H⁺ions (left over from the base) strong base- weak conjugate acid

Types of acid/base reactions:

Acid + metal
$$\longrightarrow$$
 $H_{2(g)}$ + salt of acid

Acid + base
$$\longrightarrow$$
 salt + H₂O

Hydr ic acid ── hydrogen ion + anion Binary Acid:

Strength of binary acids:

- -increases down a group of the periodic table and across the periodic table
- increases down a group due to weaker overlap; increase across the periodic table due to an increase in electronegativity

Oxyacids: H + O + an element

- increases with electronegativity
- greater # of oxygens = more polar = more acidic

Auto-ionization of H_2O :

$$2H_2O_{(l)}$$
 \longrightarrow $H_3O^+_{(aq)} + OH^-_{(aq)}$

 $\Delta H = +ve \text{ (endo)}$

$$K_w = [H_3O^+][OH^-] = 1 \times 10^{-14} \text{ (at } 25^{\circ}C)$$

$$[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$$

$$pH = -log[H_3O^+]$$

$$[H_3O^+] = 10^{-pH}$$

$$pOH = -log[OH^-]$$

$$[OH^{-1}] = 10^{-pOH}$$

$$pH + pOH = 14$$

$$pH < 7 = acidic$$
 $pH > 7 = basic$

$$pH > 7 = basic$$

eak acids:

$$K_a = \underline{[H_3O^+][A^-]}$$
[HA]

$$HA + H_2O \iff H_3O^{+1} + A^{-1}$$

Veak bases

$$K_b = \underline{[OH^-][HB^+]}$$

$$B + H_2O \longrightarrow HB^{+1} + OH^{-1}$$

$$K_a \times K_b = [H_3O^+][OH^-] = K_w = 1 \times 10^{-14}$$

% ionization =
$$[\underline{H}^+]$$
 x 100% [acid]

$$pK_a = -\log K_a$$
 $pK_b = -\log K_b$ $pK_a \cdot pK_b = pK_w$

$$pK_b = -\log K_b$$

$$pK_a$$
, $pK_b = pK_{...}$

- the process of gradually neutralizing an acid or a base by adding its opposite dropwise an acid/base indicator is used to show the end-point
- these problems use stoichiometry

End-Point: point at which color indicator changes and titration is stopped Equivalence point: # moles H⁺= # moles OH⁻

Combinations of acid and bases:

- when acid is weak its conjugate base is strong and the solution is basic at equivalence point when base is weak, conjugate acid is strong and solution is acidic at equivalence point, therefore equivalence point does not equal endpoint
- when a salt dissolves, sometimes one of the products reacts with one of the parts of the H₂O's equilibrium, causing it to shift. $H_2O < --> OH^- + H^+$ (endothermic)
 - addition of heat to water causes ionization to increase and K_w to increase

Redox

- reactions consists of losses and gains of electrons
- something is oxidized when it loses electrons, and is a reducing agent (donates its electrons)
- something is reduced when it gains electrons, and is an oxidizing agent (takes electrons)

Balancing Redox Equations:

- 1. Determine the oxidation number of each species involved
- 2. Write a half-equation for the species that was oxidized (the one where the oxidation number increased)
- 3. Write the half-equation for the species that was reduced (the oxidation number decreased)
- 4. Add electron loss/gain to both sides of the half equations
- 5. Balance the number of electrons in each half-equation by a suitable factor so that the oxidation equals reduction
- 6. Place these coefficients in the given equation
- 7. For acid medium balance the equation using H⁺ and H₂O
- For basic medium balance the equation using H⁺ and H₂O, and then add an equal amount of OH⁻ ions as there are in the equation. Then simplify by making H₂O

<u>Half equations</u>: with every balanced redox equation, half equations must be given. These show the oxidization part and the reduction part separately.

Rules for writing Oxidation Numbers:

- 1) All elements have an oxidation number of zero
- 2) All ions of Group I have an oxidization number of +1
- 3) All ions of Group II have an oxidization number of 2+
- 4) Aluminum always has an oxidization number of 3+
- 5) Oxygen always has an oxidization number of 2-, except when it's in a peroxide, then its 1-
- 6) Hydrogen will always have an oxidization number of 1+, except when it's in a metal hydride, then it's 1-
- 7) All compounds have an oxidization number of zero
- 8) Polyatomic ions will always have their oxidization number equal to their charge

Electrode potential:

the measure of an atom/ion/molecule's ability to lose an electron. It is called electrode potential because it measure the difference in electron density using hydrogen as a reference point

- it is a force which pushes an electric current through a wire in a cell
- the larger the value, the greater its tendency to lose electrons (better reducing agent, weaker oxidizing agent)
 - electrode potential is used to predict if a reaction is spontaneous or not. If the value is positive- it is spontaneous. When the reaction is spontaneous, it can be used in a galvanic cell, to produce energy. If the value is positive, i.e.: non spontaneous, an electrolytic cell can be used to make it happen
- the sign on the electrode potential is reversed when the reaction is reversed; value of the electrode potential does not change, when the equation is multiplied, or divided by a factor
 - the electrode potential for an entire equation is given in VOLTS, so spontaneous reactions give off electricity
 - the maximum electric potential difference a cell can have is its cell potential (E). Cell potential is always measured at 25°C, at concentrations of 1M. This is standard cell potential, E°
 - To calculate standard cell potentials, write out the half reactions (*from given table) with their electrode potential, E⁰. Be sure one is reduction, and other is oxidation. Balance electron transfer, and add up two half reactions.

Electrolysis:

- electrochemical changes brought about by electricity. Reactions that happen by electrolysis are endothermic
- when electricity is passed through a molten ionic compound, or through a solution containing ions (an electrolyte), chemical reactions occur

Anode: the name of the electrode at which oxidization occurs (an ox) Cathode: the name of the electrode at which reduction occurs (red cat)

Electrolytic cells:

- these cells are used to make non spontaneous reactions occur. They do this by electrolysis. An electrolytic cell will not continue the electrolysis, if the electricity is turned off, because it is nonspontaneous, (ie: negative E). Because of this, electrolytic cells are entirely contained in one cell cathode, where reduction takes place, is the negative electrode; it is attached to the negative terminal of the power source
- anode, where oxidization occurs, is the positive electrode, it is attached to the positive terminal of the power source

In this diagram the electrolysis of NaCl is used as an example. Molten NaCl is in the cell. The negatively charged cathode attracts Na⁺ ions where they gain an electron from the energy source and become Na. The positively charged anode attracts Cl⁻ ions where they become $Cl_{2(g)}$ with the loss of an electron. Total reaction: $2Na_{(1)}^+ + 2Cl_{(1)}^- \longrightarrow 2Na_{(1)} + Cl_{2(g)}$ $E^{\circ} = -3.53 \text{ V}$

Total reaction: $2Na_{(1)}^+ + 2Cl_{(1)}^- \longrightarrow 2Na_{(1)} + Cl_{2(g)}$

Applications

- 1) Electroplating: the application by electrolysis of a thin, ornamental or protective coating of one metal over another
- used to improve appearance and durability of metal objects ie: metallic chromium applied over steel on automobile parts to make them attractive and prevent rusting of the steel; silver and gold plating on jewelry; silver plating on eating utensils
- metallic layers are generally 0.03-0.05 mm thick

diagram: a typical apparatus used for plating silver

- $Ag^{2+}_{(aq)}$ is reduced at cathode, where it is deposited as metallic silver on the object to be plated. At anode silver from metal bar is oxidized, replenishing the supply of Ag²⁺ (aq) in the solution
- The composition of electroplating baths varies depending on the metal to be deposited
- Silver plating: Ag(CN)₂; gold and cadmium are plated from cyanide baths; nickel from nickel sulphate solution; chromium plated from chromic acid solution H₂CrO₄

Production of Magnesium

magnesium has many structural uses because of its low density (light) ie: magnesium alloy ladder wire inside flash bulbs (produces flash of light when reacts with oxygen to give MgO)

Mg(OH)₂ is the creamy substance in milk of magnesia

Major source of magnesium is seawater, Mg²⁺ is the third most abundant ion in the ocean When seawater is made basic, it precipitates Mg(OH)₂. This is separated when dissolved in hydrochloric acid Mg(OH)₂ + 2HCl — \longrightarrow MgCl₂ + 2H₂O.

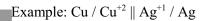
The solution of MgCl₂ is evaporated and resulting solid MgCl₂ is melted and electrolyzed

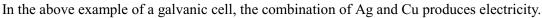
Free magnesium is deposited at the cathode, and chlorine gas is deposited at the anode.

$$MgCl_{2(l)}$$
 – electrolysis \longrightarrow $Mg_{(l)}$ + $Cl_{2(g)}$

Electrochemical Cell (galvanic):

- electrochemical cells produce electricity by spontaneous reactions. These spontaneous reactions give off electricity when they have $+E^0$.
 - This needs two half reactions taking place in two half cells.
 - It would take place spontaneously in a single cell, so with two half cells, a reaction can be turned on and off
- the cathode, where reduction takes place, is the positive electrode
 - the anode, where oxidation takes place, is the negative electrode



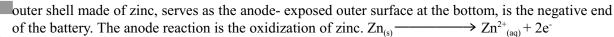


- The Ag in the container on the left gains electrons from the Cu in the container on the left.
- The electrons flow from the anode (produced as Cu loses 2 electrons) to the cathode, where Ag gains an electron.
- These two reactions are exothermic (positive E⁰), producing electricity.
- To complete the circuit, a salt bridge containing NaCl (or some other salt), is used. This stops a positive charge from building up on the anode side, as Cu²⁺ ions are produced. It does this by diffusing Cl⁻ ions into the solution. It also stops a negative charge from building up in the cathode, as Ag⁺ ions are used up in the reduction. Na⁺ ions flow from the salt bridge to replace this loss.

Total reaction:
$$2Ag^{+}_{(aq)} + Cu_{(s)} \longrightarrow 2Ag_{(s)} + Cu^{2+}_{(aq)}$$
 $E^{0} = +0.65 \text{ V}$

Applications

- Zinc-carbon dry Cell
- 1.5 V, relatively inexpensive. Used to power flashlights, tape recorders, etc. Normally works without leaking
 - One disadvantage is it loses its ability to function under heavy current drain, because products of reactions cannot diffuse away from the electrodes easily. It cannot be recharged, but can rejuvenate if left alone. Devices that claim to recharge, simply drive reaction products away from electrodes. This only works a few times until the zinc develops holes, and battery must be discarded.
 - diagram: cut away view of internal construction



- carbon (graphite) rod surrounded by a moist paste of graphite powder, manganese dioxide and ammonium chloride, is a cathode-serves as a positive terminal of the battery
 cathode half cell reaction is too complex to be written
 - Nickel- Cadmium storage cell

this is the nicad battery, that powers rechargeable electronic calculators, electric shavers, and power tools. It produces about 1.4 V.

Electrode reactions:
$$Cd_{(s)} + 2OH_{(aq)}^{-} \longrightarrow Cd(OH)_{2(s)} + 2e^{-}$$
 (anode) $2e^{-} + NiO_{2(s)} + 2H_2O \longrightarrow Ni(OH)_{2(s)} + 2OH_{(aq)}^{-}$ (cathode)

- rechargeable, and can be sealed to prevent leakage, which is important in electrical devices, however, it is much more expensive than other batteries