TRINITY
COLLEGE SCHOOL

Advanced Placement Chemistry, SCH4UAP

EXAMINATION REVIEW

Memorization!

Table of Ionic Charges

CATIONS (positive ions)			
+1	**+2**	**+3**	**+4**
GROUP IA ELEMENTS (*Alkali Metals*): Li^+, Na^+, K^+, etc. SILVER, Ag^+ AMMONIUM, NH_4^+	GROUP IIA ELEMENTS (*Alkaline Earth Metals*): Mg^{2+}, Ca^{2+}, etc. MOST TRANSITION METALS FORM IONS WITH +2 CHARGES LEAD(II), Pb^{2+} TIN(II), Sn^{2+}	IONS OF CERTAIN GROUP IIIA ELEMENTS, including Al^{3+} & B^{3+} IRON(III), Fe^{3+}	TIN(IV), Sn^{4+} LEAD(IV), Pb^{4+}

ANIONS (negative ions)			
-1	**-2**	**-3**	**-4**
GROUP VIIA ELEMENTS (the *Halogens*): F^-, Cl^-, Br^-, I^- ACETATE, CH_3COO^- BICARBONATE, HCO_3^- (*hydrogen carbonate*) BISULPHATE, HSO_4^- (*hydrogen sulphate*) CHLORATE, ClO_3^- CYANIDE, CN^- CYANATE, OCN^- HYDROXIDE, OH^- NITRATE, NO_3^- PERCHLORATE, ClO_4^- PERMANGANATE, MnO_4^- THIOCYANATE, SCN^-	GROUP VIA ELEMENTS: O^{2-}, S^{2-}, etc. CARBONATE, CO_3^{2-} CHROMATE, CrO_4^{2-} DICHROMATE, $Cr_2O_7^{2-}$ OXALATE, $(COO)_2^{2-}$ PEROXIDE, O_2^{2-} SULPHATE, SO_4^{2-} SULPHITE, SO_3^{2-} THIOSULPHATE, $S_2O_3^{2-}$	GROUP VA ELEMENTS, including N^{3-} PHOSPHATE, PO_4^{3-}	

Nonmetals

- You should know that the following nonmetals are diatomic: $H_2, N_2, O_2, F_2, Cl_2, Br_2$ & I_2.
- Phosphorus exists as P_4; phosphorus oxide can exist either as P_4O_{10} (most likely) or as P_4O_6.
- Sulphur normally exists as S_8 molecules.

Atomic Structure

SUMMARY OF THE THREE MAIN SUBATOMIC PARTICLES			
	SYMBOL	RELATIVE CHARGE	MASS (u)
ELECTRON	e^-	-1	$1/2000$
PROTON	p	+1	1.00
NEUTRON	n	0	1.00

In any (uncharged) atom:

THE NUMBER OF PROTONS = THE ATOMIC NUMBER OF THE ATOM

THE NUMBER OF ELECTRONS = THE NUMBER OF PROTONS

THE NUMBER OF NEUTRONS = THE MASS NUMBER - THE ATOMIC NUMBER

Isotopes are atoms of the same element containing different numbers of neutrons and therefore having different masses.

Gases

Volume is always measured in *litres (L), millilitres (mL)* or *cubic centimetres (cm^3)*.
$$1 \text{ L} = 1000 \text{ mL} = 1000 \text{ cm}^3$$

DENSITY OF A GAS	=	MOLAR MASS OF THE GAS (g/mol)
(g/L)		MOLAR VOLUME OF THE GAS (L/mol)

The five principal assumptions of the **kinetic molecular theory of gases** are as follows:

☑   Gases consist of molecules whose volumes are <u>negligible</u> compared with the volume occupied by the gas.

☑   Since the molecules of a gas are far apart, the forces of attraction between them are negligible.

☑   The molecules of a gas are in continual, random, and rapid motion.

☑   The average kinetic energy of gas molecules depends only on the gas temperature, and can be expressed by $E_K \, \alpha \, T$.

☑   Gas molecules collide with each other and with the walls of their container, but they do so without loss of energy (The collisions are said, by scientists, to be "perfectly elastic").

Real Gases versus Ideal Gases

The Gas Laws work for "Ideal Gases". However, there is no such thing as an Ideal Gas!

- **Real Gases** deviate most from ideal behaviour at high pressures.

- **Real Gases** deviate most from ideal behaviour at low temperatures.

- At a given temperature and pressure, the greater the intermolecular forces, the greater will be the deviation from ideal behaviour.

- At high pressures and low temperatures, the greater the size of the gas molecules, the greater will be the deviation from ideal behaviour.

Quantum Numbers

Quantum Number	Symbol	Allowable Values	What the quantum number is responsible for
Principal	**n**	1, 2, 3, 4, 5, 6, 7, ..	determining the energy of the electron and the size of the orbital.
Secondary (Azimuthal)	**ℓ**	0 to (n-1)	determining the shape of the orbital.
Magnetic	**m$_\ell$**	+ℓ to -ℓ	determining the spatial orientation of the orbital relative to the other orbitals in the atom.
Spin	**m$_s$**	+½ or -½	determining the spin of the electron within the orbital.

Electron Configurations

The following "rules" govern the electron configuration of atoms:

The Aufbau Principle: This simply states that the lowest energy level orbitals are filled first.

The Pauli Exclusion Principle: This states that *no two electrons in an atom can have the same set of four quantum numbers*.

Hund's Rule: This states that *the most stable arrangement of electrons is that with the maximum number of unpaired electrons, all with the same spin direction.*

The maximum number of electrons in the various subshells is:

| subshell	maximum number of electrons
s	2
p	6
d	10
f	14

QUANTUM NUMBERS AND THE PERIODIC TABLE

You can use the periodic table to tell the first two quantum numbers of the valence electrons of any element.

1s						1s
2s					2p	
3s					3p	
4s		3d			4p	
5s		4d			5p	
6s	4f▷	5d			6p	
7s	5f▷	6d				

4f
5f

You can also tell the order in which shells and subshells are filled by following the table from left to right across each period.

You should note that after the third period, the filling of subshells becomes more complicated. Notice, for instance, that the 4s subshell fills before the 3d subshell.

Here's a simple tool that many people use to keep track of the order in which orbitals are filled.

1s
2s 2p
3s 3p 3d
4s 4p 4d 4f
5s 5p 5d 5f
6s 6p
7s
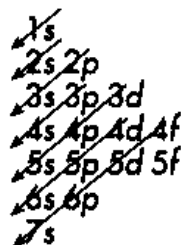
1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s 5f

Filled subshells, particularly in the valence shell, lead to stable, unreactive, elements. Additionally, there is stability associated with **half-filled valence subshells**.

The **Noble Gases** are, of course, the most stable of all the elements.

Nitrogen, phosphorus and **arsenic** have unusually stable properties due to the fact that their valence shells consists of filled *s* orbitals and half-filled *p* orbitals.

Periodic Trends: Sizes of Atoms, Ionization Energies, Electronegativity

1) Within each column (group), the **atomic radius** tends to increase as we proceed from top to bottom.

2) Within each row (period), the **atomic radius** tends to decrease as we move from left to right.

The **ionization energy** of an atom or ion is the minimum energy required to remove an electron from the ground state of the isolated gaseous atom or ion. The *first ionization energy, I_1*, is the energy needed to remove the first electron from a neutral atom. For example, the first ionization energy for the sodium atom is the energy required for the process, $Na(g) \rightarrow Na^+(g) + e^-$

The *second ionization energy, I_2*, is the energy needed to remove the second electron, and so forth, for successive removals of additional electrons.

1. Within each group, **ionization energy** generally decreases with increasing atomic number as you proceed down the group.

2. Within each row, **ionization energy** generally increases with increasing atomic number as you proceed from left to right. There are slight irregularities in this trend, however.

Electronegativity is the ability of an atom in a molecule to attract electrons to itself. Electronegativities generally decrease as you proceed down a group and increase as you proceed from left to right across a period. **Fluorine is the most electronegative element.**

Ionic Bonding & Ions

An **ionic bond** is formed when one electron, or more, is/are transferred from one atom to another.

Positive ions are referred to as *cations*; **negative ions** are referred to as anions.

Lattice energy is governed by the formula, $E \propto \dfrac{Q_1 Q_2}{d}$

(where Q_1 and Q_2 are the charges and d is the distance between them).

The most common ionic charge of the **fourth row transition elements**, from *scandium* to *zinc*, is 2+ (e.g. Ti^{2+} & Fe^{2+}). When such ions are formed, the transition metal atom loses its two 4s electrons (3d electrons are <u>not</u> lost). (In fact, whenever a positive ion is formed from an atom, electrons are always lost first from the subshell having the largest value of *n*). Thus, *in forming ions, transition metals lose the valence-shell s electrons first, then as many d electrons as are required to reach the charge of the ion.*

Relative Sizes of Ions

- For the Representative (*s-block* and *p-block*) Elements that form positive ions (cations), the **radius of the positive ion** will always be smaller than the radius of the corresponding atom. This is due primarily to the fact that when these elements form ions the outermost shell (highest value of n) is lost in its entirety.

- For the Representative Elements that form negative ions (anions), the **radius of the negative ion** will always be larger than the radius of the corresponding atom.

- For all of the Representative Elements, as you go down a group the **radii of ions of equal charge** increase. This is due primarily to the fact that as you go down the group the outermost electrons have a larger value of n.

Lewis Structures for Covalent Molecules

☑ **Ensure that each atom ends up with the "correct" number of valence electrons**.
- Most elements end up with **eight** valence electrons (the "octet rule").
- Hydrogen ends up with **two** valence electrons.
- Boron and beryllium usually end up with **fewer than eight** valence electrons.
- Some elements from periods 3, and higher, end up with **more than eight** valence electrons. These elements include **sulphur**, **phosphorus**, **arsenic**, **selenium** and **xenon**. They are said to form "expanded octets".

The **formal charge** of an atom equals *the number of valence electrons in the isolated atom, minus the number of electrons assigned to the atom in the Lewis structure:* the most likely Lewis structure is one in which the formal charges on the atoms are a minimum.

How to calculate formal charges
① For each atom count all the nonbonding electrons (i.e. "lone pairs" of electrons).
② Count exactly half of the electrons that the atoms uses to bond with other atoms.
③ Add steps ① and ② to obtain the electrons assigned to that atom.
④ Subtract the assigned electrons from the atom's valence electrons to obtain the formal charge of the atom.

BOND LENGTH IS THE DISTANCE BETWEEN THE NUCLEI OF THE BONDED ATOMS, AND **BOND ENERGY** IS THE ENERGY REQUIRED TO SEPARATE THE BONDED ATOMS TO GIVE NEUTRAL PARTICLES.
A **DOUBLE BOND** IS BOTH SHORTER AND STRONGER THAN A SINGLE BOND. Similarly, a **triple bond** is both shorter and stronger than a double bond.

Enthalpy

Exothermic reactions have negative ΔH values; endothermic reactions have positive ΔH values.

ΔH^o represents an enthalpy change occurring at standard conditions, which are 25 ^{o}C and 101.3 kPa.

ΔH_f° represents the enthalpy change for a special type of reaction known as a formation reaction. A formation reaction is one in which one mole of a compound is made (or "formed") from its elements, with all the chemicals in their standard states.

ΔH_c represents the enthalpy change for a special type of reaction known as a combustion reaction. It is also sometimes referred to as the heat of combustion.

Rate Laws

For the general (hypothetical) rate determining step,

$$a\,A \ + \ b\,B \rightarrow products$$
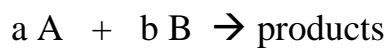
the *Rate Law (Expression)* is,

$$r \ \alpha \ [A]^a\,[B]^b \quad or \quad r \ = \ k\,[A]^a\,[B]^b$$

Units of Rate Constants

Overall Reaction Order	Units of Rate Constant, k
0	$M.s^{-1}$
1	s^{-1}
2	$M^{-1}.s^{-1}$
3	$M^{-2}.s^{-1}$

Integrated Rate Laws

For **First Order Reactions**, $\ln \dfrac{[A]_t}{[A]_0} = -kt \quad or \quad \ln[A]_t - \ln[A]_0 = -kt$

(The second equation is given on the data sheet but you need to know that it works for First Order Reactions)

✱ Thus, for a **first order reaction**,

- ✚ **A graph of ln[A]$_t$ versus time gives a straight line**.
- ✚ The slope of the line is equal to -k .
- ✚ The y-intercept is equal to ln[A]$_0$.

Half-life, $t_{1/2}$**,** is the time required for a reactant to reach exactly half of its original concentration.

$$t_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{0.693}{k}$$ (This formula is **not** given on the data sheet!)

For **Second Order Reactions**, $\dfrac{1}{[A]_t} - \dfrac{1}{[A]_0} = kt$

(This equation is given on the data sheet but you need to know that it works for Second Order Reactions)

✱ Thus, for a **second order reaction**,

- ✚ **A graph of 1/[A]$_t$ versus time gives a straight line**.
- ✚ The slope of the line is equal to +k .
- ✚ The y-intercept is equal to 1/[A]$_0$.

✱ Thus, for a **zero order reaction**,

- ✚ **A graph of [A]$_t$ versus time gives a straight line**.
- ✚ The slope of the line is equal to -k .
- ✚ The y-intercept is equal to [A]$_0$.

Activation Energy & Catalysis

The minimum energy required to initiate a chemical reaction is called the **activation energy**, E_a.

A **catalyst** is a substance which increases the rate of a chemical reaction without undergoing a permanent chemical change itself in the process.

Homogeneous catalysts are in the same phase as the reactants; **heterogeneous catalysts** are in a different phase from that of the reactants.

Nuclear Reactions

The most common **isotope of hydrogen**, ^1_1H, has a nucleus consisting of a single proton. This isotope comprises 99.9844 percent (but don't memorize the actual percentage!) of naturally occurring hydrogen. Two other isotopes are known: ^2_1H, whose nucleus contains a proton and a neutron, and ^3_1H, whose nucleus contains a proton and two neutrons. The ^2_1H isotope, called **deuterium** whereas the third isotope, ^3_1H, is known as **tritium.**

TYPES OF RADIOACTIVE DECAY		
	ATOMIC NUMBER	*MASS NUMBER*
alpha decay	decreases by 2	decreases by 4
beta decay	increases by 1	remains unchanged
positron emission	decreases by 1	remains unchanged
electron capture	decreases by 1	remains unchanged

Particle	Symbol	Charge	Mass (u)	Approx. speed (x speed of light)	Penetrating ability
alpha	^4_2He	+2	4	0.1	Low
beta	β or $^0_{-1}e$	-1	$\frac{1}{2000}$	0.9	Higher
gamma radiation	γ	0	0	speed of light	Very high
proton	^1_1P	+1			
neutron	^1_0n	0			
positron	$^0_{+1}e$	+1			

Radioactive Decay

Radioactive decay is a first-order kinetics process.

The **half-life** of a radioactive isotope (radioisotope) is defined as the time it takes for exactly one-half of the nuclei in a given sample of the isotope to decay.

$$N_t = N_o \times 2^{-\frac{t}{h}}$$

where......

N_t = the amount of radioisotope at time = t
N_0 = the amount of radioisotope present initially (time, t = 0)
h = half-life
t = time during which the radioisotope has decayed

Also, for **radioactive decay**:

$$\ln \frac{N_t}{N_0} = -kt$$

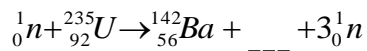where......

N_t = the amount of radioisotope at time = t
N_0 = the amount of radioisotope present initially (time, t = 0)
k = the rate constant
t = the time during which the radioisotope has decayed

Nuclear Fission

- ***nuclear fission*** is the splitting of a large nucleus into two, or more, smaller nuclei

- a typical fission reaction is:

$$_{0}^{1}n + _{92}^{235}U \rightarrow _{56}^{142}Ba + \underline{\quad} + 3_{0}^{1}n$$

- $_{92}^{235}U$ is the *fissionable* isotope of uranium

- less than 1% of the atoms present in naturally-occurring uranium are $_{92}^{235}U$ atoms and that the vast majority are $_{92}^{238}U$

- a nuclear fission reaction is a ***chain reaction*** since one neutron or more are produced

- that the ***critical mass*** of $_{92}^{235}U$ is approx. 1 kg

- that the ***moderator*** in a nuclear reactor slows down the fast moving neutrons so that they can be more readily captured by the $_{92}^{235}U$ atoms

Nuclear Fusion

- nuclear fusion is the joining together of two, or more, lighter nuclei to form a heavier one

- a typical fusion reactions are:

$$_{1}^{1}H + _{1}^{1}H \rightarrow _{1}^{2}H + \underline{\quad} \qquad \& \qquad _{1}^{1}H + _{1}^{2}H \rightarrow \underline{\quad}$$

- nuclear fusion usually involved hydrogen and helium isotopes

- nuclear fusion reactions occurs in stars, including our Sun

- nuclear fusion reactions take large amounts of energy, and temperatures of around 40,000,000 K, to initiate.

Molecular Shapes Summary

NUMBER OF ELECTRON PAIRS AROUND CENTRAL ATOM	NUMBER OF *LONE PAIRS* AROUND CENTRAL ATOM	EXAMPLE	MOLECULAR SHAPE		IS THE MOLECULE SYMMETR-ICAL?	WILL THE MOLECULE BE POLAR IF IT CONTAINS POLAR BONDS?	TYPE OF HYBRI-DIZATION
			BOND ANGLES	NAME OF SHAPE			
2	0	$BeCl_2$		LINEAR			
3	0	BCl_3		TRIGONAL PLANAR			
4	0	CH_4		TETRAHEDRAL			
4	1	NH_3		TRIGONAL PYRAMIDAL			
4	2	H_2O		BENT			
5	0	PCl_5		TRIGONAL BIPYRAMIDAL			
5	1	SF_4		SEESAW			
5	2	ClF_3		T-SHAPED			
5	3	XeF_2		LINEAR			
6	0	SF_6		OCTAHEDRAL			
6	1	BrF_5		SQUARE PYRAMIDAL			
6	2	XeF_4		SQUARE PLANAR			

Sigma and Pi Covalent Bonds

The first bond between any two atoms is a strong **sigma** (σ) bond.

To describe multiple (double and triple) bonding we must consider a second kind of bond that results from the overlap between two *p* orbitals oriented perpendicular to the inter-nuclear axis, as illustrated below:
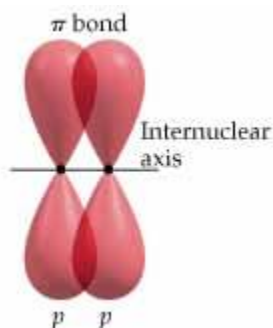
This sideways overlap of *p* orbitals produces a **pi (π) bond.** π bonds are generally weaker than *σ* bonds.

Bonding in Alkanes, Alkenes, Alkynes and Aromatic Hydrocarbons

ALKANES ARE *SATURATED* HYDROCARBONS IN WHICH THE CARBON ATOMS ARE JOINED BY SINGLE COVALENT BONDS ONLY. ALL ALKANES HAVE 109.5° BOND ANGLES AND EXHIBIT sp^3 HYBRIDIZATION. ALL OF THE COVALENT BONDS PRESENT IN ALKANES ARE STRONG SIGMA (σ) BONDS.

ALKENES ARE *UNSATURATED* HYDROCARBONS CONTAINING AT LEAST ONE DOUBLE C=C BOND. ALL ALKANES HAVE 120° BOND ANGLES AND sp^2 HYBRIDIZATION AROUND THE CARBON ATOMS JOINED BY THE DOUBLE BOND. THE DOUBLE BOND CONSISTS OF ONE STRONG SIGMA (σ) BOND AND ONE WEAKER PI (π) BOND.

ALKYENES ARE *UNSATURATED* HYDROCARBONS CONTAINING AT LEAST ONE TRIPLE C≡C BOND. ALL ALKYNES HAVE 180° BOND ANGLES AND sp HYBRIDIZATION AROUND THE CARBON ATOMS JOINED BY THE TRIPLE BOND. THE TRIPLE BOND CONSISTS OF ONE STRONG SIGMA (σ) BOND AND TWO WEAKER PI (π) BONDS.

BENZENE IS AN AROMATIC HYDROCARBON WITH THE FORMULA C_6H_6 AND WITH THE SIX CARBON ATOMS IN A RING STRUCTURE. It is often represented as follows:
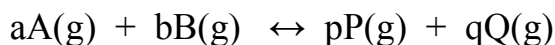
Equilibrium Constants

For the general reaction,

$$aA(g) + bB(g) \leftrightarrow pP(g) + qQ(g) ,$$
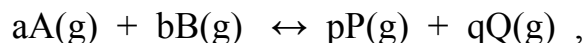
$$K_c = \frac{[P]^p [Q]^q}{[A]^a [B]^b}$$

This relationship is called the **equilibrium law (expression)** for the reaction. The subscript c indicates that <u>concentrations</u> (measured in mol/L, *molarity)* are used.

When the reactants and products in a chemical equation are gases, we can formulate the equilibrium law expression in terms of partial pressures instead of molar concentrations. When partial pressures in **<u>atmospheres</u>** are used in the equilibrium-constant expression, we denote the equilibrium constant as K_p . So, for the general reaction:

$$aA(g) + bB(g) \leftrightarrow pP(g) + qQ(g)$$

$$K_P = \frac{(P_P)^p (P_Q)^q}{(P_A)^a (P_B)^b}$$

SINCE THE CONCENTRATIONS OF **PURE SOLIDS** AND **PURE LIQUIDS** CANNOT EASILY BE ALTERED, THEY ARE ALWAYS <u>OMITTED</u> FROM EQUILIBRIUM LAW EXPRESSIONS.

Reversing a chemical equation will cause the value of the equilibrium constant to *become the reciprocal*, **doubling** an equation will cause the value of an equilibrium constant to *square*, **halving** an equation will cause the value of the equilibrium constant to *become the square root*, etc.

If two equations (with equilibrium constants K_1 and K_2) are added together, then the equilibrium constant for the overall equation, $K_{overall}$, is given by:

$$K_{overall} = K_1 \times K_2$$

Le Châtelier's Principle

WHEN A STRESS IS APPLIED TO A SYSTEM AT EQUILIBRIUM, THE EQUILIBRIUM WILL READJUST SO AS TO RELIEVE THE STRESS.

WHEN A SYSTEM "SHIFTS" TO RELIEVE A STRESS, THE SYSTEM NEVER TOTALLY COMPENSATES.

Solubility & Solubility Product

Solubility is the maximum amount of solute which will dissolve in a given amount of solvent to form a saturated solution at a given temperature. Solubility is normally measured in g/L, although molar solubility is, obviously, measured in mol/L. The equation for the saturated solution is written with the solid on the left – e.g.:

$$MgF_2(s) \; \leftrightarrows \; Mg^{2+}(aq) \; + \; 2\, F^-(aq)$$
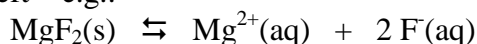
The equilibrium constant for an equilibrium of this sort is referred to as the **solubility product**, and it is given the symbol K_{SP}. In this example:

$$K_{SP} \; = \; [Mg^{2+}]\,[F^-]^2$$

It should be noted that the K_{SP} of a salt increases as its solubility   .

SOLUBILITY (g/L)	$\div\ ^g/_{mol}$ → ← $\times\ ^g/_{mol}$	SOLUBILITY (mol/L)	→ *use equilibrium law* ←	SOLUBILITY PRODUCT, K_{SP}
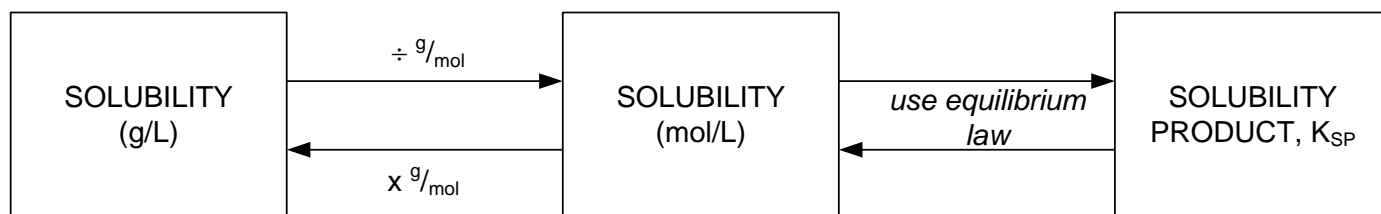
Intermolecular Forces

In general, as the strength of the inter-molecular forces increases,

- Melting points increase.
- Boiling points increase.
- Solubility decreases.
- Viscosity increases.

MR HEDNEY'S BONDING CHART

SOME NOTES ON BOND STRENGTHS

- COVALENT BONDS ($\equiv$ > = > −)
- IONIC BONDS
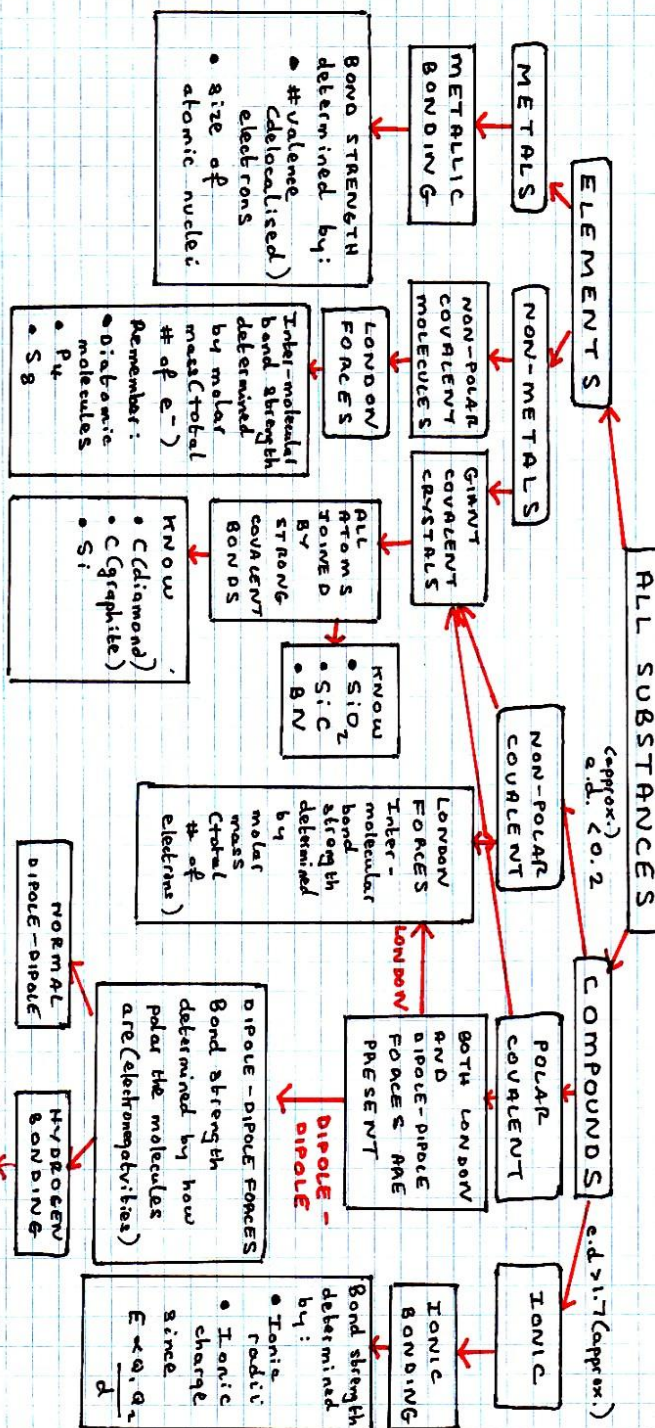- METALLIC BONDS
- HYDROGEN BONDS
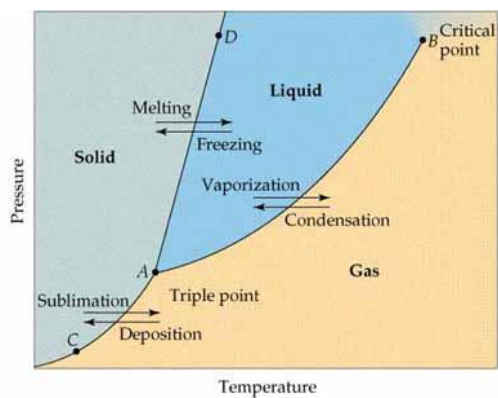- DIPOLE − DIPOLE (strength increases with increasing molecular polarity)
- LONDON FORCES (strength increases with molar mass)

← GENERALLY DECREASE IN STRENGTH (but lots of overlap!)

ALL SUBSTANCES

ELEMENTS

- **METALS** → **METALLIC BONDING**
  - Bond strength determined by:
    - # valence (delocalised) electrons
    - size of atomic nuclei

- **NON-METALS**
  - **NON-POLAR COVALENT MOLECULES** → **LONDON FORCES**
    - Inter-molecular bond strength determined by molar mass (total # of e^-)
    - Remember:
      - Diatomic molecules
      - P_4
      - S_8
  - **GIANT COVALENT CRYSTALS** → **ALL ATOMS JOINED BY STRONG COVALENT BONDS**
    - KNOW:
      - C (diamond)
      - C (graphite)
      - Si
    - KNOW
      - SiO_2
      - SiC
      - BN

COMPOUNDS (e.d. < 0.2, e.g. copper)

- **NON-POLAR COVALENT** → **LONDON FORCES**
  - Inter-molecular bond strength determined by molar mass (total # of electrons)

- **POLAR COVALENT** → **BOTH LONDON AND DIPOLE-DIPOLE FORCES ARE PRESENT**
  - (LONDON)
  - (DIPOLE − DIPOLE)
  - **NORMAL DIPOLE-DIPOLE**
    - DIPOLE-DIPOLE FORCES. Bond strength determined by how polar the molecules are (electronegativities)
  - **HYDROGEN BONDING**
    - Particularly strong dipole-dipole forces
    - Present in:
      - H_2O, HF, NH_3
      - Numerous organic compounds

- **IONIC** (e.d. > 1.7 approx.) → **IONIC BONDING**
  - Bond strength determined by:
    - Ionic radii
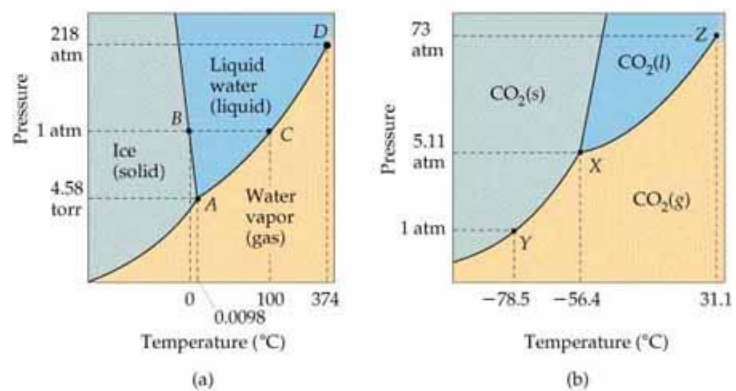   - Ionic charge
    - since $E \propto \dfrac{q_+ q_-}{d}$

Phase Diagrams

Typical phase diagram…….

The **critical point** is the temperature above which a vapour cannot be liquefied by pressure alone.

The phase diagram for H_2O is 'odd'……

Solubility Rules

SALTS	MOST ARE	EXCEPTIONS
NITRATES (NO_3^-) ACETATES (CH_3COO^-) CHLORATES (ClO_3^-)	SOLUBLE	None
SULPHATES (SO_4^{2-})	SOLUBLE	The sulphates of Ag^+, Ba^{2+}, Ca^{2+}, Hg^{2+}, Hg_2^{2+}, Pb^{2+} and Sr^{2+} are all insoluble.
BROMIDES (Br⁻) CHLORIDES (Cl⁻) IODIDES (I⁻)	SOLUBLE	The bromides, chlorides and iodides of Ag^+, Hg^{2+}, Hg_2^{2+} and Pb^{2+} are all insoluble
CHROMATES (CrO_4^{2-}) DICHROMATES ($Cr_2O_7^{2-}$)	SOLUBLE	The chromates of Ag^+, Ba^{2+} and Pb^{2+} are all insoluble.
HYDROXIDES (OH⁻) OXIDES (O^{2-})	INSOLUBLE	The alkali metal hydroxides and oxides are all soluble. The hydroxides and oxides of Ba^{2+}, Ca^{2+} and Sr^{2+} are moderately soluble.
CARBONATES PHOSPHATES	INSOLUBLE	The alkali metal carbonates and phosphates are, of course, all soluble.
SULPHIDES	INSOLUBLE	The alkali metal sulphides, along with BaS, CaS, MgS, $(NH_4)_2S$ and SrS are all soluble.
NOTES		
ALL ALKALI METAL SALTS, AND ALL AMMONIUM SALTS ARE <u>SOLUBLE</u>.		
THE SALTS OF MOST COMMON "HEAVY" METALS (silver, lead, mercury, for example) TEND TO BE <u>INSOLUBLE</u> (except, of course, their nitrates, acetates and chlorates).		

Diluting Solutions

When solvent (usually water) is added to dilute a solution, the <u>number of moles</u> of solute remains unchanged. Therefore:

(Initial molarity)(initial volume) = (final molarity)(final volume)

$$M_i \ \times \ V_i \ = \ M_f \ \times \ V_f$$

Acid-Base Definitions

Arrhenius Definitions of Acids and Bases: Acids are substances that, when dissolved in water, increase the concentration of H^+ ions. Likewise, bases are substances that, when dissolved in water, increase the concentration of OH^- ions.

Bronsted-Lowry Definitions of Acids and Bases: Acids are substances (molecules or ions) that can transfer a proton to another substance. Likewise, bases are substances that can accept a proton.

Lewis Acids and Bases: Lewis acids are defined as electron-pair acceptors; Lewis bases are defined as electron-pair donors.

Conjugate Acid-Base Pairs: An acid differs from its conjugate base (and vica versa) by H^+. (Every acid has a conjugate base formed by the removal of a proton from the acid, and every base has associated with it a conjugate acid formed by the addition of a proton to the base.)

Naming Acids

- The "ic" ending is used for the acid with the higher oxidation state; the "ous" ending is used for the acid with the lower oxidation state.
- The prefix "hypo" is used when the oxidation state is "really low"; the "per" prefix is used when the oxidation state is "really high".
- For example:

  $HClO$ (hypochlorous acid)   Cl has an oxidation state of +1.
  $HClO_2$ (chlorous acid)   Cl has an oxidation state of +3.
  $HClO_3$ (chloric acid)   Cl has an oxidation state of +5.
  $HClO_4$ (perchloric acid)   Cl has an oxidation state of +7.

Strong and Weak Acids and Bases

Strong acids are completely ionized in aqueous solution, weak acids are not.

The "Big Six" Strong Acids

$HClO_4$ (perchloric acid)
HNO_3 (nitric acid)
HCl, HBr, HI (hydrochloric, hydrobromic, and hydroiodic acids)
H_2SO_4 (sulphuric acid)

Two common examples of "moderate acids" that you should know are:

H_3PO_4 (phosphoric acid)
$(COOH)_2$ (oxalic acid)

Weak Monoprotic Acids

If we represent a general weak monoprotic cid as HA, we can write the equation for its ionization reaction in either of the following ways, depending on whether the hydrated proton is represented as $H_3O^+(aq)$ or $H^+(aq)$:

$$\text{either:} \quad HA_{(aq)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + A^-_{(aq)}$$

$$\text{or:} \quad HA \leftrightarrow H^+ + A^-$$
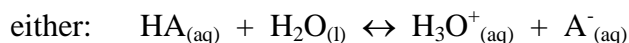
Because $[H_2O]$ is omitted from equilibrium constant expressions in aqueous solutions, the form of the equilibrium-constant expression is the same in either case:

$$K_a = \frac{[H_3O^+_{(aq)}][A^-_{(aq)}]}{[HA_{(aq)}]} \quad \text{or} \quad K_a = \frac{[H^+][A^-]}{[HA]}$$

K_a is called the acid dissociation const*ant* (or ***acid ionization constant***)**.**
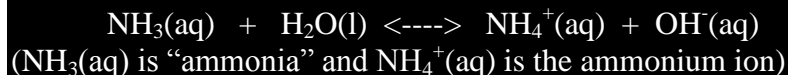
Weak Bases

If we generalize a weak base as B(aq), then the equilibrium for the weak base:

$$B(aq) + H_2O(l) <----> BH^+(aq) + OH^-(aq)$$
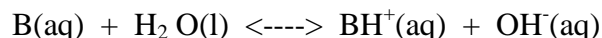
The equilibrium constant, symbolized by K_b, for such a reaction is called the **base ionization constant**, and the equilibrium law expression is:

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

The weak base you will most frequently encounter is an aqueous solution of ammonia, $NH_3(aq)$, and it ionizes as follows:

$$NH_3(aq) + H_2O(l) <----> NH_4^+(aq) + OH^-(aq)$$

($NH_3(aq)$ is "ammonia" and $NH_4^+(aq)$ is the ammonium ion)

Relative Strength of Acids and Bases

The stronger an acid, the weaker is its conjugate base; the stronger a base, the weaker is its conjugate acid.

The product of the acid-dissociation constant for an acid, K_a, and the base-dissociation constant, K_b, for its conjugate base is the ion-product constant for water, K_w.
Thus, $K_a \times K_b = K_w = 1.0 \times 10^{-14}$.

pK_a & pK_b

(In AP Chemistry, it is safe to assume that p(anything) = -log(anything)!)

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

Acid – Base Salts

THE SALTS FORMED FROM....			
STRONG ACIDS and STRONG BASES	will be.... NEUTRAL	WEAK ACIDS and STRONG BASES	will be.... BASIC
STRONG ACIDS and WEAK BASES	will be.... ACIDIC	WEAK ACIDS and WEAK BASES	could be slightly acidic or slightly basic - depending on the respective K_a and K_b values

Buffers

BUFFERS ARE SOLUTIONS THAT RESIST CHANGES IN pH ON ADDITION OF ACID OR BASE.

Buffer solutions consist of:

> EITHER ➔ a solution of a weak acid in the presence of one of its salts
> [e.g. ethanoic (acetic) acid and sodium ethanoate (acetate)]
> OR ➔ a solution of a weak base in the presence of one of its salts
> [e.g. ammonia solution, $NH_{3\,(aq)}$, and ammonium chloride]

Oxidation Numbers

1. The oxidation number of an element in the free, or un-combined, state is *zero.*

2. The oxidation number of a *monatomic ion* is equal to its charge.

3. In <u>all</u> compounds containing *Group IA alkali metals*, the oxidation number of the Group IA ion is +1.

4. In <u>all</u> compounds containing *Group IIA metals,* the oxidation number of the Group IIA ion is +2.

5. In <u>most</u> compounds containing *oxygen*, the oxidation number of oxygen is almost always -2.

6. In <u>most</u> compounds containing *hydrogen*, the oxidation number of hydrogen is almost always +1.

7. The algebraic sum of the oxidation numbers of all the atoms in the formula of a compound is zero.

8. The algebraic sum of the oxidation numbers of all the atoms in the formula of a polyatomic ion is equal to the charge on the ion.

Oxidation – Reduction Definitions

- A substance is said to be **oxidised** if it gains oxygen or loses hydrogen. Likewise, a substance is said to be **reduced** if it loses oxygen or gains hydrogen.

- The substance which brings about the oxidation is said to be the **oxidising agent**, and the substance which brings about the reduction is the **reducing agent**.

- **Oxidation** is a chemical change in which a substance loses electrons and **reduction** is a chemical change in which a substance gains electrons. Remember, OIL RIG !

- A substance is said to be **oxidised** during a chemical reaction if its oxidation number increases and a substance is said to be **reduced** if its oxidation number goes down.

Balancing Redox Equations in Acid and Basic Solutions

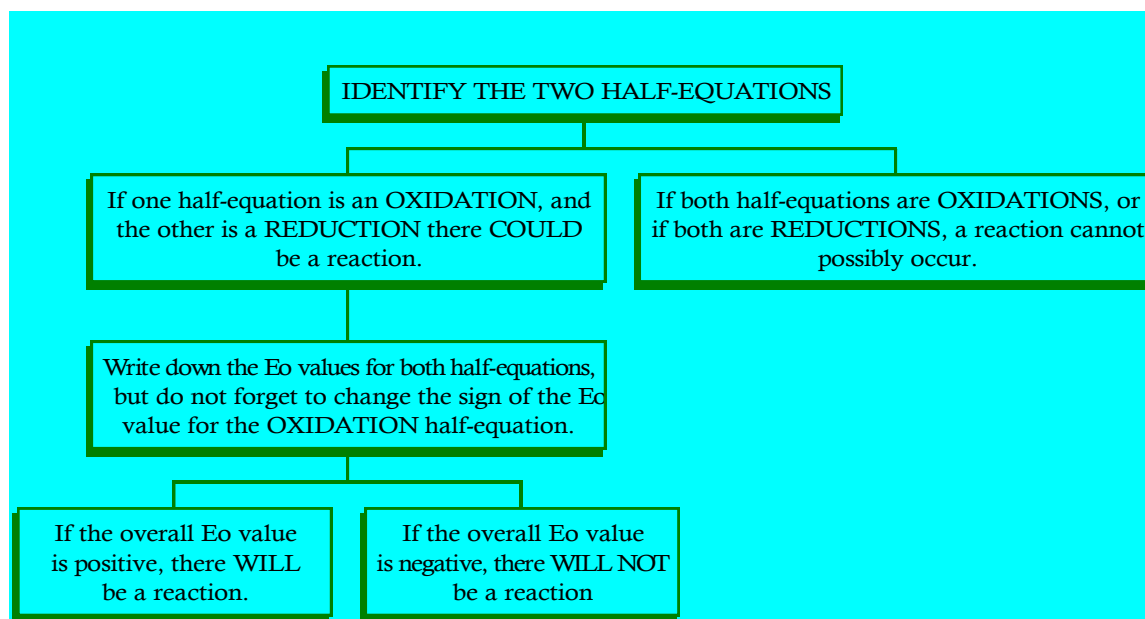| IN ACID SOLUTION	IN BASIC SOLUTION
Both H^+(aq) & H_2O present	Both OH^-(aq) & H_2O present
If you require an additional **H** atom, **add H^+** to the side where you require it.	If you require an additional **H** atom, **add H_2O** to the side where you require it, and **add OH^-** to the other side.
If you require an additional **O** atom, **add H_2O** to the side where you require it, and **add $2H^+$** to the other side.	If you require an additional **O** atom, **add $2OH^-$** to the side where you require it, and **add H_2O** to the other side.

Voltaic Cells

- Oxidation occurs at the anode and reduction occurs at the cathode.

- Electrons always flow through the wires, in the external circuit, from the anode to the cathode.

Standard Reduction Potentials

The chart is supplied; the other information needs to be memorized!

Fluorine has the greatest attraction for electrons

⇨ ⇨ ⇨

- *With fluorine, the forward reaction is far more likely to occur than the reverse reaction.*
- *Fluorine is the most easily reduced*
- *Fluorine is the best oxidizing agent*

Reaction		Product	$E°$
$F_2 (g) + 2e^-$	→	$2F^-$	2.87
$Co^{3+} + e^-$	→	Co^{2+}	1.82
$Au^{3+} + 3e^-$	→	$Au(s)$	1.50
$Cl_2 (g) + 2e^-$	→	$2Cl^-$	1.36
$O_2 (g) + 4H^+ + 4e^-$	→	$2H_2O(l)$	1.23
$Br_2 (l) + 2e^-$	→	$2Br^-$	1.07
$2Hg^{2+} + 2e^-$	→	Hg_2^{2+}	0.92
$Hg^{2+} + 2e^-$	→	$Hg(l)$	0.85
$Ag+ + e^-$	→	$Ag(s)$	0.80
$Hg_2^{2+} + 2e^-$	→	$2Hg(l)$	0.79
$Fe^{3+} + e^-$	→	Fe^{2+}	0.77
$I_2 (s) + 2e^-$	→	$2I^-$	0.53
$Cu^+ + e^-$	→	$Cu(s)$	0.52
$Cu^{2+} + 2e^-$	→	$Cu(s)$	0.34
$Cu^{2+} + e^-$	→	Cu^+	0.15
$Sn^{4+} + 2e^-$	→	Sn^{2+}	0.15
$S (s) + 2H^+ + 2e^-$	→	$H_2S(g)$	0.14
$2H^+ + 2e^-$	→	$H_2(g)$	0.00
$Pb^{2+} + 2e^-$	→	$Pb(s)$	-0.13
$Sn^{2+} + 2e^-$	→	$Sn(s)$	-0.14
$Ni^{2+} + 2e^-$	→	$Ni(s)$	-0.25
$Co^{2+} + 2e^-$	→	$Co(s)$	-0.28
$Tl^+ + e^-$	→	$Tl(s)$	-0.34
$Cd^{2+} + 2e^-$	→	$Cd(s)$	-0.40
$Cr^{3+} + e^-$	→	Cr^{2+}	-0.41
$Fe^{2+} + 2e^-$	→	$Fe(s)$	-0.44
$Cr^{3+} + 3e^-$	→	$Cr(s)$	-0.74
$Zn^{2+} + 2e^-$	→	$Zn(s)$	-0.76
$Mn^{2+} + 2e^-$	→	$Mn(s)$	-1.18
$Al^{3+} + 3e^-$	→	$Al(s)$	-1.66
$Be^{2+} + 2e^-$	→	$Be(s)$	-1.70
$Mg^{2+} + 2e^-$	→	$Mg(s)$	-2.37
$Na^+ + e^-$	→	$Na(s)$	-2.71
$Ca^{2+} + 2e^-$	→	$Ca(s)$	-2.87
$Sr^{2+} + 2e^-$	→	$Sr(s)$	-2.89
$Ba^{2+} + 2e^-$	→	$Ba(s)$	-2.90
$Rb^+ + e^-$	→	$Rb(s)$	-2.92
$K^+ + e^-$	→	$K(s)$	-2.92
$Cs^+ + e^-$	→	$Cs(s)$	-2.92
$Li^+ + e^-$	→	$Li(s)$	-3.05

- *With lithium, the reverse reaction is far more likely to occur than the forward reaction.*
- *Lithium is the most easily oxidized.*
- *Lithium is the best reducing agent.*

⇦ ⇦ ⇦

Lithium has the least attraction for electrons

Spontaneity of REDOX Reactions

IDENTIFY THE TWO HALF-EQUATIONS

If one half-equation is an OXIDATION, and the other is a REDUCTION there COULD be a reaction.

If both half-equations are OXIDATIONS, or if both are REDUCTIONS, a reaction cannot possibly occur.

Write down the Eo values for both half-equations, but do not forget to change the sign of the Eo value for the OXIDATION half-equation.

If the overall Eo value is positive, there WILL be a reaction.

If the overall Eo value is negative, there WILL NOT be a reaction

EMF and Free-Energy Change

For a reaction to be **spontaneous**, $\Delta G°$ must be negative and $E°_{CELL}$ must be positive.

When using the equation, $\Delta G° = $ -n. $\Im.E°$ (supplied), remember that:

$\Delta G° = $ standard free energy change (measured in **J/mol**) $\Leftarrow$ **N.B.!!**
n $=$ the number of moles of electrons **transferred** (for the equation as written)
$\Im =$ the faraday constant (96,500 C/mol)
$E° = $ **standard** cell potential (25°C and 101.3kPa)

The Nernst Equation (for Calculating Non-Standard Cell Potentials)

$$E_{cell} = E_{cell}^{o} - \frac{RT}{n\Im} \ln Q \quad = \quad E_{cell}^{o} - \frac{0.0592}{n} \log Q \quad \text{(at 25 °C)}$$

where........
$E_{CELL} = $ **non-standard** cell potential (in *volts*)
$E°_{CELL} = $ **standard** (all concentrations = 1 mol/L) cell potential (in *volts*)
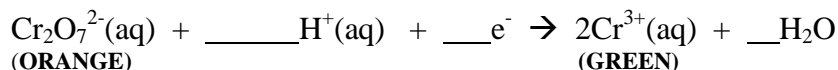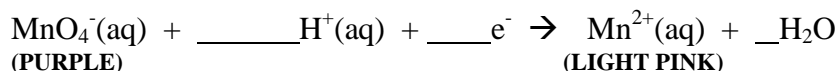n $=$ the number of moles of electrons **transferred**
Q $=$ the *reaction quotient* for the reaction
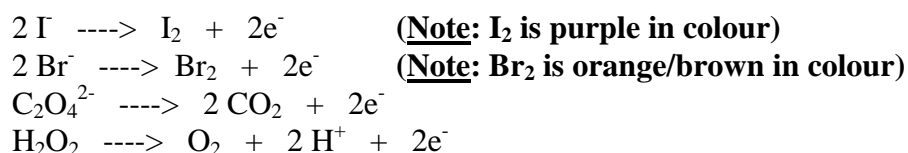$\Im =$ the faraday constant (96,500 C/mol)
R $=$ 8.314 J/mol.K
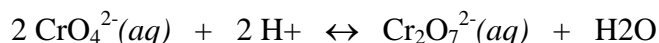
Common Oxidising Agents

Whenever you come across reactions involving either **permanganate** or **dichromate**, it is safe to assume that they will be redox reactions, and that the MnO_4^- or $Cr_2O_7^{2-}$ ions will be reduced. The **reduction half-equations** in **acidic** solution are as follows:

$MnO_4^-(aq)$ + _____$H^+(aq)$ + ____e^- → $Mn^{2+}(aq)$ + __H_2O
(PURPLE)   **(LIGHT PINK)**

$Cr_2O_7^{2-}(aq)$ + _____$H^+(aq)$ + ___e^- → $2Cr^{3+}(aq)$ + __H_2O
(ORANGE)   **(GREEN)**

Common Oxidation Half-Equations worth Knowing

$2 I^-$ ----> I_2 + $2e^-$ **(Note: I_2 is purple in colour)**
$2 Br^-$ ----> Br_2 + $2e^-$ **(Note: Br_2 is orange/brown in colour)**
$C_2O_4^{2-}$ ----> $2 CO_2$ + $2e^-$
H_2O_2 ----> O_2 + $2 H^+$ + $2e^-$

The Chromate (CrO_4^{2-}) – Dichromate ($Cr_2O_7^{2-}$) Equilibrium

$$2 CrO_4^{2-}(aq) + 2 H+ \leftrightarrow Cr_2O_7^{2-}(aq) + H2O$$

Which Substances Conduct Electricity?

SOLIDS	
Electrical Conductors	**Non-conductors (insulators)**
All metallic elements. All alloys. One non-metallic element - the *graphite* allotrope of carbon.	All non-metallic elements <u>except</u> graphite. All compounds.
LIQUIDS	
Electrical Conductors	**Non-conductors (insulators)**
All metallic elements All alloys Molten ionic compounds. These electrical conductors are also *electrolytes*.	Non-metallic elements All covalently-bonded compounds
AQUEOUS SOLUTIONS	
Electrical Conductors (Electrolytes)	**Non-electrolytes**
Aqueous solutions of **acids, bases** and **salts (ionic compounds).** These electrical conductors are also *electrolytes*.	Aqueous solutions of covalent compounds do not conduct electricity and are, therefore, *non-electrolytes*

Predicting the sign of ΔS for physical and chemical changes

- For a given substance, the solid state will have a lower entropy than the liquid which, in turn, will have a lower entropy than the gas.

- When the temperature is increased without a change of state occurring, the entropy increases.

- When a solid dissolves in water, the entropy of the system will increase.

- When simpler molecules are combined into more complex molecules the molecular complexity increases and the entropy decreases.

Gibbs Free Energy

A CHANGE CAN ONLY BE SPONTANEOUS IF IT IS ACCOMPANIED BY A DECREASE IN GIBBS FREE ENERGY.

If, at constant temperature, ΔG is negative, the process is spontaneous.
If, at constant temperature, ΔG is positive, the process is not spontaneous (or spontaneous in the reverse direction.
If, at constant temperature, ΔG = 0, the system is at equilibrium.

Since ΔG° = ΔH° - TΔS° (given),

ΔH	ΔS	ΔG	spontaneous at which temperatures
-	+	-	ALL
+	-	+	NONE
+	+	+ or -	HIGH
-	-	+ or -	LOW

Non-Standard Gibbs Free Energy Changes

Using the equation, $\Delta G = \Delta G^o + RT\ln Q$ (or $\Delta G = \Delta G^o + 2.303RT\log Q$) (both given),

- ΔG and ΔG^o values are always given/calculated in kJ/mol.

- The Universal Gas Constant, R, must be used as 8.314 J/mol-K.

- You will need to divide RTlnQ (since it is in joules) by 1000 before adding it to ΔG^o (which is in kJ)

- T must be in **Kelvin**.

ΔG and K

Since $\Delta G^o = -RT\ln K$ (or $\Delta G^o = -2.303RT\log K$) (given), it follows that:

ΔG^o negative	$K > 1$	spontaneous reaction (in forward direction)
$\Delta G^o =$ zero	$K = 1$	Spontaneous in neither direction
ΔG^o positive	$K < 1$	reverse reaction is spontaneous

You should be able to re-arrange the equation to find K:

$$K = e^{\frac{-\Delta G^o}{RT}}$$

and, remember that:

- ΔG^o values are always given / calculated in kJ/mol.

- The Universal Gas Constant, R, must be used as 8.314 J/mol.K.

- Remember that RT is in joules; whereas ΔG^o is in kJ!

- Gas pressures must be in atm; solution concentrations must be in mol/L (molarity); the concentrations of pure solids and pure liquids are to be taken as equal to 1.

- T must be in Kelvin.

- For reactions involving gases, K_p is to be used; for reactions involving aqueous solutions, solids and liquids, K_c is to be used.

Organic Chemistry

Organic Chemistry is essentially all memorization. Refer to Unit K in your notes!

Naming Complexes

When naming a complex ion, first give the name(s) of the ligand(s), in alphabetical order, followed by the name of the metal.

Note the following:

- If a ligand is an anion whose name ends in -ite or -ate, the final e is changed to o. (E.g. change sulphate to sulphato and change nitrite to nitrito).
- If the ligand is an anion whose name ends in -ide, the ending is changed from -ide to -o. (E.g. change chloride to chloro and cyanide to cyano).
- If the ligand is a neutral molecule, its common name is used. The important exceptions to this, however, are that water is called aqua, ammonia is called ammine, and CO is called carbonyl.
- When there is more than one of a particular ligand, the number of ligands is designated by the appropriate Greek prefix: di-, tri-, tetra-, penta-, hexa-, hepta-, etc.
- If the complex ion is an anion, the suffix -ate is added to the metal name. The Latin name is often used for the metal in this case. For example, ferro rather than iron and cupro rather than copper.
- Following the name of the metal, the oxidation number of the metal is given using Roman numerals.