

H2 CHEMISTRY

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CHEMICAL PERIODICITY

$$Z_{\text{eff}} = Z - \sigma$$

PHYSICAL PROPERTIES

Property	Explanation
Atomic radii decrease across a period	Z_{eff} <u>increases</u> across a period. The number of protons, and thus Z , <u>increases</u> , while σ <u>remains approximately constant</u> as the number of fully filled inner principle quantum shells remain the same
Atomic radii increase descending a group	Z_{eff} <u>decreases</u> descending a group. The number of protons, and thus Z , <u>increases</u> , while σ <u>increases</u> as the number of fully filled inner principle quantum shells increases
From Na to Al, the size of the cation is always smaller than the parent atom	The Z_{eff} <u>increases</u> from Na to Al as the cation has <u>one less shell of electrons</u> . Consequently, the <u>nucleus exerts a greater attractive force</u> on the valence electrons in the cation.
From P to Cl, the size of the anion is always larger than the parent atom	Both the anion and its parent atom have the <u>same number of protons</u> , making Z identical. The <u>anion</u> however, <u>has more electrons</u> than its parent atom, making the <u>nucleus attract the valence electron less strongly</u> in the anion
Size of isoelectronic ions decrease across a period	σ <u>remains constant</u> as they have the same number of inner electrons. Z <u>increases</u> , and thus the <u>nucleus attracts the valence electrons more strongly</u>
For more information about ionization energy, refer to the atomic structure cheatsheet	
1 st IE decreases descending a group	Z_{eff} <u>decreases</u> descending a group. Z <u>increases</u> descending a group while σ <u>increases</u> as well, but <u>more significantly</u>
2 nd IE > 1 st IE always	Electrons are removed from an ions with <u>increasing positive charges</u> , increasing the Z_{eff} and attracting electrons more strongly to the nucleus
Electronegativity increases across a period	Z_{eff} <u>increases</u> across a period. Z <u>increases</u> while σ <u>remains approximately constant</u> . The ability of an atom in a molecule to attract bonding electrons thus increases.
Electronegativity decreases descending a group	Z_{eff} <u>decreases</u> across a period. While Z <u>increases</u> , σ <u>increases more significantly</u> . Thus, the ability of an atom in a molecule to attract bonding electrons decreases.

Period 2	Li	Be		B	C*	N	O	F	Ne
Period 3	Na	Mg	Al		Si	P	S	Cl	Ar
Type	Metal			Metalloid		Nonmetal			
Structure	Metallic			Giant Molecular		Simple Molecular			
Bonding	Strong metallic bonds Depends on no. of valence e ⁻ Na < Mg < Al			Strong covalent bonds		Weak VDW forces Depends on the size of e ⁻ P ₄ < S ₈ >> Cl ₂ > Ar			
mp/bp	High			Very High		Low			
Electrical conductivity	Good conductors Depends on no. of valence e ⁻ – Na < Mg < Al			Poor conductors *Graphite is a slightly better conductor: mobile valence e ⁻		Insulators No mobile valence e ⁻			

CHEMICAL PROPERTIES

			Reaction with dry oxygen and heat	Reaction with dry chlorine and heat	Reaction with water	pH in water
Gp I	Strongly reducing	Na	$4\text{Na} + \text{O}_2 \rightarrow 2\text{Na}_2\text{O}$ Vigorous	$2\text{Na} + \text{Cl}_2 \rightarrow 2\text{NaCl}$ Very vigorous	$2\text{Na} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2$ Violent reaction with cold water	13
Gp II		Mg	$2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$ Very vigorous	$\text{Mg} + \text{Cl}_2 \rightarrow \text{MgCl}_2$ Vigorous	$\text{Mg} + \text{H}_2\text{O} \rightarrow \text{MgO} + \text{H}_2$ Vigorous reaction with steam	9
Gp III		Al	$4\text{Al} + 2\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3$ Vigorous initially	$2\text{Al} + 3\text{Cl}_2 \rightarrow 3\text{AlCl}_3$ Vigorous AlCl_3 may dimerize	$2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2$ Vigorous reaction with steam	7
Gp IV	Weakly reducing Weakly oxidising	Si	$\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2$ Slow	$\text{Si} + 2\text{Cl}_2 \rightarrow \text{SiCl}_4$ Slow	No reaction	7
Gp V		P	$\text{P}_4 + 3\text{O}_2 \rightarrow \text{P}_4\text{O}_6$ $\text{P}_4\text{O}_6 + 2\text{O}_2 \rightarrow \text{P}_4\text{O}_{10}$ Vigorous	$\text{P}_4 + 6\text{Cl}_2 \rightarrow 4\text{PCl}_3$ $\text{PCl}_3 + \text{Cl}_2 \rightarrow \text{PCl}_5$ Slow	No reaction	7
Gp VI		S	$\text{S} + \text{O}_2 \rightarrow \text{SO}_2$ $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$ Slow	$\text{S}_8 + 4\text{Cl}_2 \rightarrow 4\text{S}_2\text{Cl}_2$ $\text{S}_2\text{Cl}_2 + \text{Cl}_2 \rightarrow 2\text{SCl}_2$ Slow	No reaction	7
Gp VII	Strongly oxidising	Cl	$2\text{Cl}_2 + 7\text{O}_2 \rightarrow 2\text{Cl}_2\text{O}_7$ Slow		$\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{HCl}$ Acidic solution formed	2

OXIDES + PROPERTIES

Oxide	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₄ O ₆ P ₄ O ₁₀	SO ₂ SO ₃	Cl ₂ O (ClO ₂) Cl ₂ O ₇					
Oxidation number	+1	+2	+3	+4	+3, +5	+4, +6	+1, +4, +7					
No. of valence e ⁻	1	2	3	4	5	6	7					
Bonding	Ionic			Covalent								
Structure	Giant ionic lattices			Giant covalent	Simple molecular							
State at 20°C	Solid High bp due to large amount of energy required to break ionic bonds in the lattice (Na, Mg, Al) or giant covalent structure (Si)			Gas, <u>solid</u>		Gas, <u>liquid</u>	Gas, (liquid) liquid					
Molten electrical conductivity	Good Mobile ions present in molten state			Very poor No charged particles		No conductivity No mobile ions in liquid state						
Solubility in water	Soluble	Sparingly soluble	Insoluble Lattice energy highly exothermic		React with water to form strongly acidic solutions							
pH of solution	12 Strongly alkaline	9 Weakly alkaline	Please don't memorize these equations. Remember: oxidation states don't change on either side. Write the reactants product, and then balance all non-O and non-H elements and finally balance with water.		2 Strongly acidic							
	Na ₂ O(s) + H ₂ O(l) → 2NaOH(aq)	MgO(s) + H ₂ O(l) → Mg(OH) ₂ (aq)			P ₄ O ₆ (g) + 6H ₂ O(l) → 4H ₃ PO ₃ (aq)	SO ₂ (g) + H ₂ O(l) → H ₂ SO ₃ (aq)	Cl ₂ O(g) + H ₂ O(l) → 2HClO(aq)					
Oxide & hydroxide acid-base behaviour	Basic; Hydroxides are strongly alkaline			Amphoteric		Acidic						
	Na ₂ O(s) + 2HCl(aq) → 2NaCl(aq) + H ₂ O(l)	NaOH(aq) + HCl(aq) → NaCl(aq) + H ₂ O	MgO(s) + 2HCl(aq) → 2MgCl ₂ (aq) + H ₂ O(l)	Mg(OH) ₂ (aq) + 2HNO ₃ (aq) → Mg(NO ₃) ₂ (aq) + 2H ₂ O(l)	Al ₂ O ₃ (s) + 6HCl(aq) → 2AlCl ₃ (aq) + 3H ₂ O(l)	Al ₂ O ₃ (s) + 2NaOH(aq) + 3H ₂ O → 2Na ⁺ [Al(OH) ₄] ⁻ (aq)	SiO ₂ (s) + 2NaOH(aq) → Na ₂ SiO ₃ (aq) + H ₂ O(l)	P ₄ O ₆ (g) + 12NaOH(aq) → 4Na ₃ PO ₃ (aq) + 6H ₂ O(l)	P ₄ O ₁₀ (g) + 12NaOH(aq) → 4Na ₃ PO ₄ (aq) + 6H ₂ O(l)	SO ₂ (g) + 2NaOH(aq) → Na ₂ SO ₃ (aq) + H ₂ O(l)	SO ₃ (l) + 2NaOH(aq) → Na ₂ SO ₄ (aq) + H ₂ O(l)	Cl ₂ O(g) + 2NaOH(aq) → 2NaClO(aq) + H ₂ O(l)

CHLORIDES + PROPERTIES

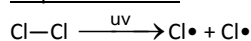
Oxide	NaCl	MgCl ₂	AlCl ₃	SiCl ₄	PCl ₃ PCl ₅	SCl ₂ S ₂ Cl ₂
Oxidation number	+1	+2	+3	+4	+3, +5	+1, +2
	Always positive: Chlorine is more electronegative				Oxidation number equal number of valence e ⁻	
Structure	Giant ionic lattice		Simple molecular Comparable e ⁻ negativities of Al and Cl	Simple molecular		
	Solid Na, Mg: Large amount of energy required to break ionic bonds			Liquid	Liquid, gas	Liquid, gas
Molten electrical conductivity	Good Mobile ions present in molten state		Very poor Conducts electricity in aqueous solution	Weak VDW forces		
	Dissolves		Dissolves to evolve HCl fumes			
Solubility in water	Good		Very poor	No conductivity		
	Mobile ions present in molten state		Conducts electricity in aqueous solution	No mobile ions in liquid state		
pH	7	6.5 Slightly acidic	3 Strongly acidic	2 Strongly acidic		
Equations	-	$\text{MgCl}_2(\text{s}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow [\text{Mg}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq})$	$\text{AlCl}_3(\text{s}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow [\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq}) + 3\text{Cl}^-(\text{aq})$	$\text{SiCl}_4(\text{l}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{SiO}_2(\text{s}) + 4\text{HCl}(\text{g})$	$\text{PCl}_3(\text{l}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{PO}_3(\text{aq}) + 3\text{HCl}(\text{g})$	$\text{PCl}_5(\text{l}) + 4\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{PO}_4(\text{aq}) + 5\text{HCl}(\text{g})$
						$2\text{S}_2\text{Cl}_2(\text{l}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 3\text{S}(\text{s}) + \text{SO}_2(\text{aq}) + 4\text{HCl}(\text{g})$

ORGANIC CHEMISTRY MECHANISM SUMMARY

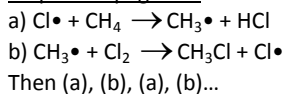
FREE RADICAL SUBSTITUTION (FRS)

Exemplified by the substitution of methane by chlorine

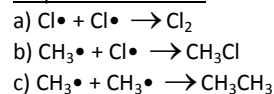
Step 1: Initiation



Step 2: Propagation

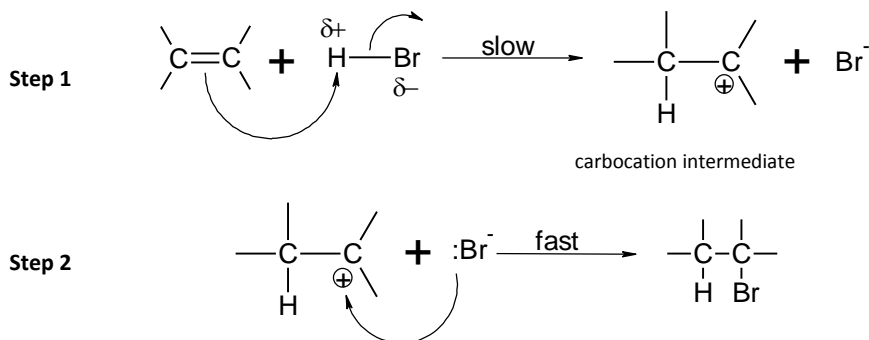


Step 3: Termination



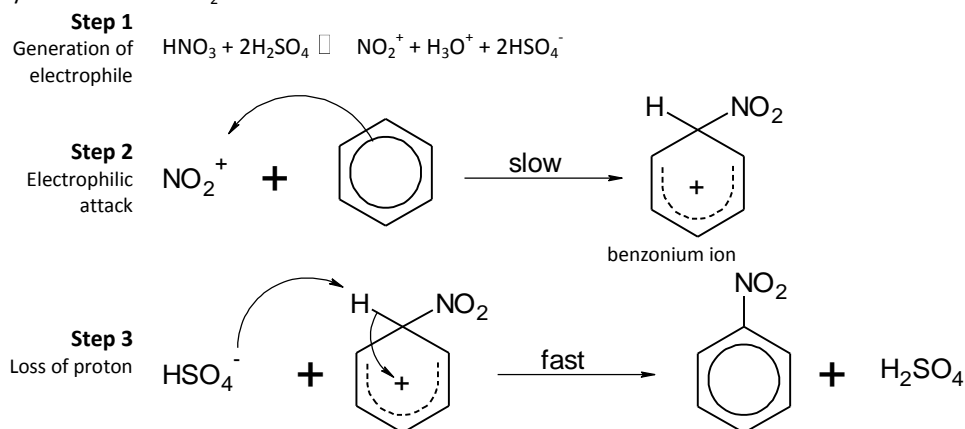
ELECTROPHILIC ADDITION

Exemplified by the addition of HBr to an alkene

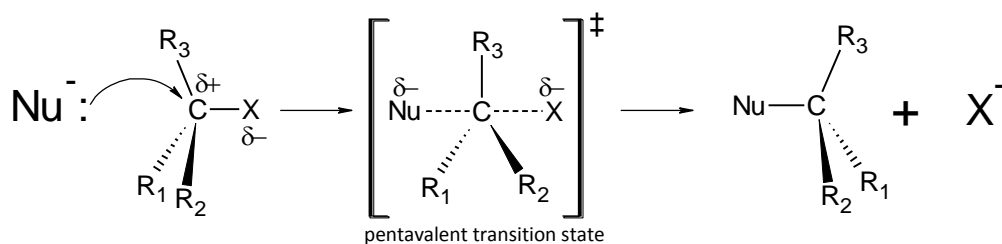


ELECTROPHILIC AROMATIC SUBSTITUTION

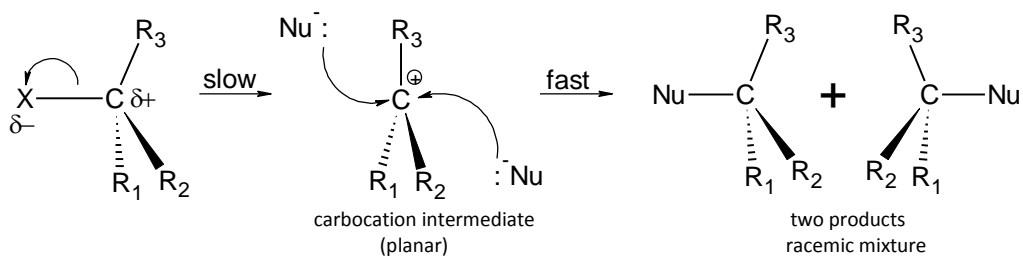
Exemplified by the addition of NO_2 to benzene



NUCLEOPHILIC SUBSTITUTION – $\text{S}_{\text{N}}2$ – ONE STEP

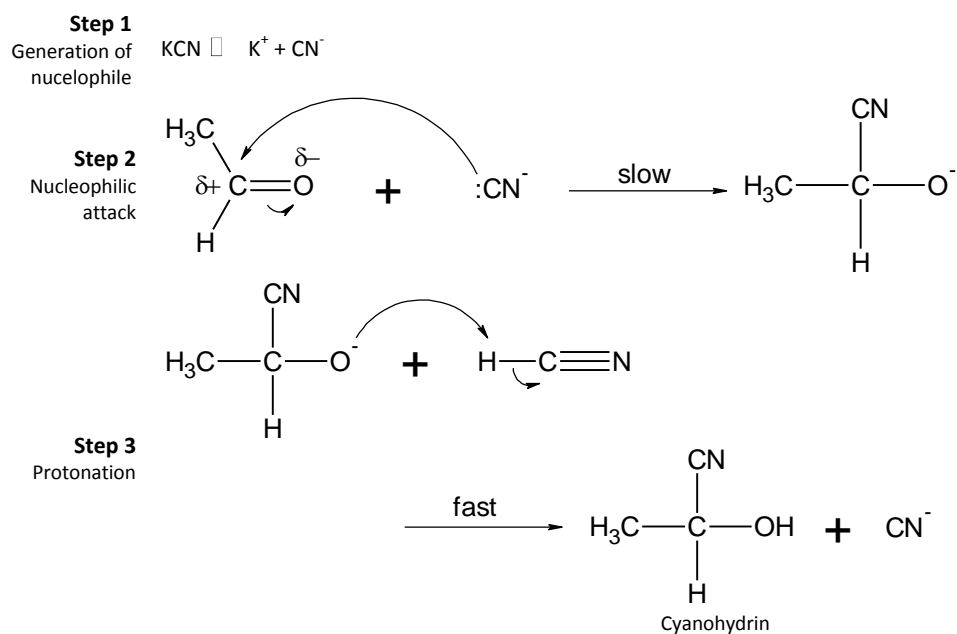


NUCLEOPHILIC SUBSTITUTION – S_N1 – TWO STEP



NUCLEOPHILIC ADDITION

Exemplified by the addition of CN⁻ to ethanal



BIOCHEMISTRY

AMINO ACIDS

Amino acids are zwitterionic – forms strong ionic bonds at isoelectric point (pI)

- Solubilities of amino acids are at a minimum at pI. Lattice energy is most exothermic at this point as the zwitterions experience the greatest ionic attraction
- Zwitterions have high melting points due to strong ionic bonds

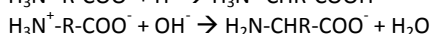
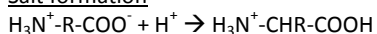
Classification of amino acids

Type	Nonpolar	Negatively charged	Positively charged	Uncharged
Example (R group)	Glycine (-H) Alanine (-CH ₃)	Aspartic acid (-CH ₂ COOH)	Lysine (-(CH ₂) ₄ NH ₂)	Serine (-CH ₂ OH) Cysteine (-CH ₂ SH)

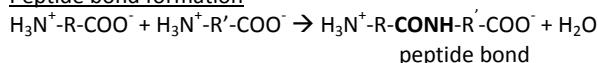
Reactions of amino acids

Two important reactions to remember

Salt formation

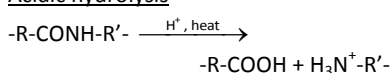


Peptide bond formation

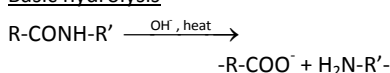


Hydrolysis of peptides

Acidic hydrolysis



Basic hydrolysis



Enzymatic hydrolysis

May be catalyzed by enzymes like trypsin, pepsin etc.

PROTEINS

The **primary structure** of a protein refers to the number and sequence of amino acids in a polypeptide chain.

- E.g.: ala-gly-leu-tyr-his-ala-leu-phe

The **secondary structure** of a protein refers to the local spatial conformation of the polypeptide backbone, in the form of either α -helices or β -pleated sheets.

α -helix

- Right-hand screw
- NH group in each peptide link is hydrogen-bonded to the CO group of the fourth following peptide link
- 3.6 AAs per turn

β -pleated sheet

- Stabilized by hydrogen-bonds between CO and NH groups in adjacent strands
- May be antiparallel or parallel
- Side chains on successive AA residues appear on opposite sides of the sheet

The **tertiary structure** of a protein refers to its three-dimensional structure of the polypeptide.

- Hydrogen bonding
 - Between polar side chains (-OH, -NH, =O, =NR groups)
- van der Waals forces
 - Electrostatic interactions among permanent or induced dipoles
 - Hydrophobic interactions – contributed by nonpolar side chains which cluster away from water to avoid destabilisation of side chains (a hydrophobic core is formed)
- Ionic interactions
 - Between two oppositely charged side chains (e.g. Asp and Lys) – usually groups that ionize in water
- Disulphide bridges
 - Between cysteine residues with the thiol (-SH) side chain
 - $\text{R}-\text{SH} + \text{HS}-\text{R}' + [\text{O}] \rightarrow \text{R}-\text{S}-\text{S}-\text{R}' + \text{H}_2\text{O}$

The **quaternary structure** of protein refers to the spatial arrangements and association of the polypeptide subunits of proteins.

- Haemoglobin as an example
 - Formed from four polypeptide chains

DENATURATION OF PROTEINS

Denaturation refers to the disruption in the secondary, tertiary and quaternary structure of proteins by the breaking of the non-covalent (but including disulphide bridges) interactions that hold these structures in their native conformation.

Effect of Temperature

- Heating causes an increase in the thermal vibration of the molecule
- Hydrogen bonding is disrupted
- Proteins denature and thus unfold

Effect of pH

- If pH is lowered far below pI, the protein will only contain positive charges
- Like charges repel each other and cause the denaturation of proteins
- Likewise for high pH

Effect of Heavy Metal Ions

- Heavy metal ions (Pb^{2+} , Cd^{2+} , etc) are positively charged
- Compete with positively charged groups for attraction with negatively charged groups
- Also bond with $-\text{SH}$ groups (especially Hg^{2+}) and disrupt disulphide bridges
- Resident metal ions in certain proteins may also be displaced

ENZYMES

Enzymes are biological catalysts – they increase the rate of reaction without themselves being changed at the end of the reaction. They catalyze reactions by providing an alternate route of reaction with lower activation energies.

Characteristics

Specificity: only certain substrates are acted upon by enzymes, and only a single type of reaction takes place

Large catalytic power: some enzymes can speed up reactions by a billion times

PHYSICAL & CHEMICAL PROPERTIES

ATOMIC STRUCTURE

Property	Explanation
The 4s orbital is filled before the 3d orbital	The 4s orbital is at a <u>lower energy level than the 3d orbital</u> , following Aufbau's principle, orbitals of lower energy are filled up first.
Electrons are first lost from the 4s orbital	When the 3d orbital is filled, it descends to a <u>lower energy level</u> than the 4s orbital, causing the 4s orbital to be <u>further away from the nucleus</u> , enabling electrons to be lost from the 4s orbital first
Cr has one electron in its 4s orbital	Chromium has one electron in its 4s orbital to <u>minimize electron-electron repulsion</u> within the 3d orbital
Cu has one electron in its 4s orbital	Copper has one electron in its 4s orbital to form a <u>symmetrical charge distribution</u> around the centre, forming a <u>full metal centre</u>
Subsequent IEs are higher	Subsequent atoms are being removed from a <u>nuclei with an increasing positive charge</u> , making them more difficult to remove
IE increases across a period	Across a period, there is <u>increasing nuclear charge</u> , but <u>approximately constant shielding effect</u> from inner shell electrons, leading to an <u>increase in effective nuclear charge</u> (electrons are harder to remove)
1 st IE of Al < Mg 1 st IE of Be < B 2 nd IE of Si < Al etc.	Al: $1s^2 2s^2 2p^6 3s^2 3p^1 \rightarrow Al^+: 1s^2 2s^2 2p^6 3s^2$ 3p electron is removed Mg: $1s^2 2s^2 2p^6 3s^2 \rightarrow Mg^+: 1s^2 2s^2 2p^6 3s^1$ 3s electron is removed Less energy is required to remove a 3p electron compared to a 3s electron since the <u>3p electron is higher in energy</u> , it has a <u>lower penetrating power</u> and is thus more easily removed
1 st IE of S < P 1 st IE of O < N 2 nd IE of Cl < S etc.	For S: removal of a paired 3p electron For P: removal of an unpaired 3p electron <u>Repulsion between the two paired 3p electrons</u> in S make it easier for one of the electrons to be lost, hence the IE of S is lower
2 nd IE of Na >> Mg	$Na^+: 1s^2 2s^2 2p^6 \rightarrow Na^{2+}: 1s^2 2s^2 2p^5$ 2p electron is removed $Mg^+: 1s^2 2s^2 2p^6 3s^1 \rightarrow Mg^{2+}: 1s^2 2s^2 2p^6$ 3s electron is removed The electron removed from Na^+ is in <u>the 2nd principle quantum shell</u> , which experiences <u>much less shielding effect</u> from inner-shell electrons, which <u>outweighs the lower nuclear charge</u> on Na as compared to the electron removed from Mg^+ is in the <u>3rd principle quantum shell</u>

Read Mr Wong's Chemical Bonding discussion at
<http://sg.geocities.com/tzeyang111777/chemistry/bonddis2.swf>

ALKANES

Property	Explanation
Non-polar	<u>Difference in electronegativities</u> of C and H atoms are <u>negligible</u> (id-id interactions)
bp/mp increases with molecular size	A larger electron cloud is <u>more easily polarized</u> and <u>id-id interactions become greater</u> , and since boiling involves the breaking of IMF, bp and mp increases with molecular size
bp/mp decreases with branching	A branched <u>isomer</u> has a smaller surface area and hence a <u>lower extent of IMF</u> between its molecules
Insoluble in polar solvents, soluble in non-polar solvents	
Density increases with molecular size; less dense than water	
Unreactive	Non-polar and saturated and do not contain any region of high e^- density

ALKENES

Property	Explanation
<i>Similar to alkanes</i>	
cis- isomers have higher bps than trans- isomers	The cis- isomer is <u>polar</u> and has pd-pd as well as id-id interactions, while the trans- isomer has only id-id interactions
cis- isomers have lower mps than trans- isomers	trans- isomers <u>pack better into a crystal lattice</u> and have higher mps than cis- isomers

HALOGEN DERIVATIVES

Property	Explanation
Less reactive than benzene (in ES)	<u>Highly electronegative</u> halogen <u>deactivates</u> the ring
Ar-X less reactive to S_N as compared to R-X	<u>Partial double bond character</u> in the arene C-X bond due to p-orbital overlap with the π -cloud The presence of the <u>e^- rich ring</u> hinder nucleophilic attack
Higher bp/mp than corresponding alkane	The alkane is non-polar and has only id-id interactions, where R-X has a <u>polar bond</u> and hence pd-pd interactions. Also, <u>the number of e^- is larger</u> , increasing id-id interactions.

HYDROXY COMPOUNDS

Acidity: The stability of the acid anion determines the acidity of a compound

Ethanol	<	Water	<	Phenol
alkoxide ion is <u>destabilized</u> by the <u>positive inductive effect</u> of the <u>e^- donating alkyl groups</u> Effects of substituents		Neither destabilizing or stabilizing effects are present		The phenoxide ion is <u>stabilized</u> by the <u>delocalization of the negative charge</u> into the <u>benzene ring</u>
Ethanol e^- releasing groups on the hydroxyl carbon <u>decreases acidity</u> as it <u>intensifies the negative charge</u> on the oxygen, <u>destabilizing the anion</u>				Phenol e^- releasing groups <u>decreases the acidity</u> of phenol as it <u>reduces the delocalization of the negative charge</u> on the oxygen into the ring, <u>destabilizing</u> the anion; the opposite is true for e^- withdrawing groups

CARBONYL COMPOUNDS

Property	Explanation
Higher bp than corr alkane, lower bp than corr alcohol	pd-pd interactions as compared the id-id interactions in alkanes lack of h-bonding when comparing with alcohols
Solubility in water decreases as number of C increases; soluble in organic solvents	Unable to form h-bonding with water. Higher carbonyl compounds have <u>larger hydrophobic groups</u> .

CARBOXYLIC ACIDS AND DERIVATIVES

Property	Explanation
Higher bp than corr alkanes and alcohols	RCOOH form <u>stronger intermolecular hydrogen bonds</u> than alcohols because the <u>-OH group is more polarized</u> due to the <u>presence of the e⁻ withdrawing -C=O group</u>
bp increases as molecular size increases	Increase in the number of e ⁻ <u>strengthens id-id interactions</u>
Lower RCOOH are soluble in water	<i>See solubility in carbonyl compounds</i>
More acidic than alcohols/phenols	The RCOO ⁻ anion is <u>resonance stabilized</u> due to the <u>delocalization of the negative charge over two highly electronegative O atoms</u>
Effects of substituents	<i>See effects of substituents in Alcohols</i> K _a increases with number of e ⁻ withdrawing groups K _a increases with distance of e ⁻ withdrawing groups from -COOH

	Acyl chlorides	Esters	Amides
Boiling point	<u>Unable to form h-bonding</u> , and experience <u>pd-pd interactions</u> and have <u>lower boiling points</u> than their parent carboxylic acids		Amides have a <u>-NH₂ group</u> and can form a <u>higher degree of h-bonding</u> , and usually have <u>higher boiling points</u> than their parent carboxylic acids
Solubility (non-polar solvents)	Soluble RCOCl hydrolyzes rapidly in water to form RCOOH	Insoluble	Fairly soluble in water due to <u>h-bonding</u>
Solubility (polar solvents)	Solubility decreases with size of hydrophobic group		Generally insoluble (lower amides are soluble)

Ease of SN

RCOCl	>	RCI	>	ArCl
<u>Highly polarized</u> alpha-carbon as it is bonded to <u>two highly electronegative atoms</u>		<u>Less polarized</u> alpha-carbon as it is only bonded to <u>one electronegative atom</u>		<u>Electron-rich</u> benzene ring <u>repels nucleophile</u>
<u>sp² hybridized</u> C experiences <u>less steric hindrance</u> (trig-planar)		<u>sp³ hybridized</u> C experiences <u>more steric hindrances</u> (tetra)		<u>Partial-double bond character</u> makes C-Cl bond harder to break

NITROGEN DERIVATIVES

Property	Explanation
Higher bp than corr alkanes, lower bp than corr alcohols	O-H h-bond is stronger than N-H h-bond as <u>O is more electronegative</u>
bp increases with molecular size	Increase in size of electron cloud <u>increases polarizability</u> resulting in greater IMF
Lower members are highly soluble in water (max 5C in amines)	<u>h-bonding with water</u> formed easily for both amines and amides; solubility decreases in higher members due to greater hydrophobic nature (also, phenylamine)
Amides are polar	The <u>highly electronegative N</u> is bonded to H, forming <u>h-bonding</u>
Tertiary amides have low bp	They <u>do not form h-bonding with each other</u> due to the <u>absence of a N-H bond</u> , however the form h-bonding with water and hydroxylic solvents
Amides are neutral	The <u>lone pair on N is delocalized</u> over the O-C-N moiety

Basicity of amines: The ability to donate the lone pair on N determines basicity

ArNH ₂	<	RR'R''NH	<	NH ₃	<	RNH ₂	<	RR'NH ₂
The lone pair on N is <u>delocalized into the benzene π-cloud</u> , making it <u>less available for dative bonding</u>		Tertiary amines have relatively low basicity due to <u>steric hindrance</u> from three bulky R groups				Electron releasing R groups increase basicity as they <u>increase the electron density of the lone pair on N</u> , making it <u>so very big more available</u> to accept a proton		
Effect of substituents on ArNH ₂ : K _b decreases with e ⁻ withdrawing substituents, and vice versa								

HALOGENS

Down group VII	Explanation
Volatility decreases	Boiling involves the overcoming of <u>id-id interactions</u> between the halogen molecules. The <u>size of the electron cloud increases</u> descending the group, and thus becomes <u>more polarizable</u> . Hence, boiling point increases.
Atomic and ionic radii increase	<u>Effective nuclear charge decreases</u> . Both <u>nuclear charge</u> and <u>shielding increase</u> , but the latter to a <u>more significant extent</u> .
Electronegativity decreases	
Oxidising power decreases	From standard electrode potential values
BDE decreases EXCEPT for F ₂	<u>Atomic size increases</u> due to decreasing effective nuclear charge. The orbitals are <u>less diffuse</u> , and the <u>orbital overlap</u> is consequently <u>less effective</u> . For F ₂ : There is great <u>electrostatic repulsion</u> between the <u>lone pairs on the F atoms</u> in F ₂ , leading to a <u>less effective orbital overlap</u> between the bonding orbitals.

REACTIONS

F ₂ oxidizes water	$2\text{F}_2(\text{g}) + 2\text{H}_2\text{O} \rightarrow 4\text{HF}(\text{aq}) + \text{O}_2(\text{g})$
Cl ₂ oxidizes water	$\text{Cl}_2(\text{g}) + 2\text{H}_2\text{O} \leftrightarrow 2\text{HOCl}(\text{aq}) + \text{HCl}(\text{g})$ $2\text{HOCl} \leftrightarrow 2\text{HCl}(\text{aq}) + \text{O}_2(\text{g})$
Halogens disproportionate in <u>cold</u> , aqueous alkalis to give <u>halide</u> and <u>halate (I) ions</u>	$\text{X}_2(\text{g}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{X}^-(\text{aq}) + \text{XO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$
Halogens disproportionate in <u>hot</u> , aqueous alkalis to give <u>halide</u> and <u>halate (V) ions</u>	$\text{X}_2(\text{g}) + 6\text{OH}^-(\text{aq}) \rightarrow 5\text{X}^-(\text{aq}) + \text{XO}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$
Halogens react with hydrogen to form hydrogen halides The vigour of reaction is dependent on the halogen's oxidising power	$\text{X}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow 2\text{HX}(\text{g})$
Halate (I) ions disproportionate upon heating to give <u>halide</u> and <u>halate (V) ions</u>	$3\text{XO}^-(\text{aq}) \rightarrow 2\text{X}^-(\text{aq}) + \text{XO}_3^-(\text{aq})$

HYDROGEN HALIDES

Down group VII	Explanation
Thermal stability decreases	Down Group VII, the valence orbitals become <u>more diffuse</u> , resulting in <u>less effective orbital overlap</u> , hence a <u>weaker H-X bond</u> is formed,
Acidity of increases	Acidity depends on HX bond strength. Since H-X <u>bond strength decreases</u> down the group, <u>acidity increases</u> down the group.

REACTIONS

HBr and HI are oxidised when heated with concentrated H ₂ SO ₄	$2\text{HBr}(\text{g}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{Br}_2(\text{g}) + \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
The reactions differ as I ⁻ is a strong reducing agent	$8\text{HI}(\text{g}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow 4\text{I}_2(\text{g}) + \text{H}_2\text{S}(\text{g}) + 4\text{H}_2\text{O}(\text{l})$

METAL HALIDES

	Colour	Excess NH ₃ (aq)	conc NH ₃ (aq)	Effect of sunlight	Why AgCl is soluble in NH ₃ (aq) but not AgBr/AgI: The K _{sp} values of AgBr/AgI are extremely low. Even when [Ag ⁺] is lowered when NH ₃ is added, the IP still exceeds K _{sp} such that AgBr/AgI remain insoluble.
AgCl	White	Soluble*	Soluble	Turns grey	
AgBr	Cream	Insoluble*	Soluble	Turns yellow	
AgI	Yellow	Insoluble*	Insoluble	No visible change	

REACTIONS

Heating MX in concentrated H ₂ SO ₄ produce their hydrogen halides. HBr and HI are further oxidised. See above.	$\text{NaX}(\text{s}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{NaHSO}_4(\text{s}) + \text{HX}(\text{g})$
HX can be prepared <i>in situ</i> by reacting MX with concentrated H ₃ PO ₄	$\text{NaX}(\text{s}) + \text{H}_3\text{PO}_4(\text{l}) \rightarrow \text{NaH}_2\text{PO}_4(\text{s}) + \text{HX}(\text{g})$
HX can be prepared <i>in situ</i> by reacting X ₂ with red phosphorus	$\text{P}_4(\text{s}) + 6\text{X}_2 \rightarrow 4\text{PX}_3$ $\text{PX}_3 + 3\text{H}_2\text{O}(\text{l}) \rightarrow 3\text{HX}(\text{g}) + \text{H}_3\text{PO}_3(\text{aq})$

DEFINITIONS

ORGANIC CHEMISTRY

Enantiomers

Stereoisomers which rotate plane-polarized light in opposite directions

Racemic mixture

A mixture of equal proportions of enantiomers where there is no net optical activity

Meso compound

An optically inactive compound with a plane of symmetry and more than one chiral center.

Electrophile

Electron-deficient species

Nucleophile

Electron-rich species

ENERGETICS

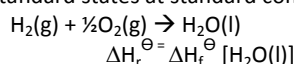
Hess' Law states that the enthalpy change of a reaction is determined by the initial and final state of the system and is independent of the pathway taken.

Standard enthalpy change of reaction - ΔH_r^\ominus

The heat change when molar quantities of reactants as specified by the chemical equation react to form products at standard conditions

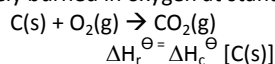
Standard enthalpy change of formation - ΔH_f^\ominus

The heat change when 1 mole of a pure compound in a specified state is formed from its constituent elements in their standard states at standard conditions.



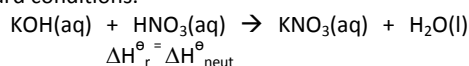
Standard enthalpy change of combustion - ΔH_c^\ominus

The heat evolved when 1 mole of a substance is completely burned in oxygen at standard conditions.



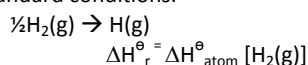
Standard enthalpy change of neutralization - $\Delta H_{\text{neut}}^\ominus$

The heat change when an amount of acid neutralizes a base to form 1 mole of water (in dilute aqueous solution) at standard conditions.



Standard enthalpy change of atomization - $\Delta H_{\text{atom}}^\ominus$

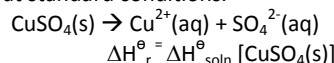
The heat change when 1 mole of atoms in the gas phase is formed from the element in the defined physical state under standard conditions.



Standard enthalpy change of solution - $\Delta H_{\text{soln}}^\ominus$

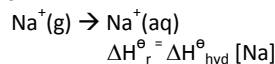
The heat change when 1 mole of solute is completely dissolved in enough solvent so that no further heat

change takes place on adding more solvent (infinite dilution) at standard conditions.



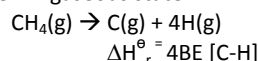
Standard enthalpy change of hydration - $\Delta H_{\text{hyd}}^\ominus$

The heat energy evolved when 1 mole of the gaseous ion is dissolved in a large amount of water at standard conditions



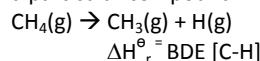
Bond energy - BE

The average energy absorbed when 1 mole of X-Y bonds are broken in gaseous state



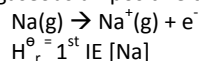
Bond dissociation energy - BDE

The energy required to break 1 mole of that particular X-Y bond in a particular compound in gaseous state.



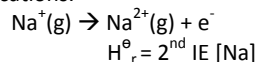
First ionization energy - 1st IE

The energy required to remove 1 mole of electrons from 1 mole of gaseous atoms in the ground state to form 1 mole of gaseous unipositive charged cations.



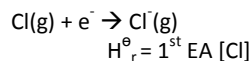
Second ionization energy - 2nd IE

The energy required to remove 1 mole of electrons from 1 mole of gaseous X^+ ions to form 1 mole of gaseous X^{2+} charged cations.



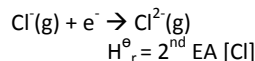
First electron affinity - 1st EA

The energy change when 1 mole of electrons are added to 1 mole of atoms in the gaseous state to form 1 mole of gaseous X^- ions



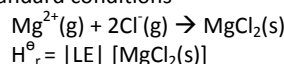
Second electron affinity - 2nd EA

The energy change when 1 mole of electrons are added to 1 mole of gaseous X^- ions to form 1 mole of gaseous X^{2-} ions



Lattice energy - |LE|

The heat change when 1 mole of pure solid ionic compound is formed from its constituent gaseous ions under standard conditions



KINETICS

Rate Equation

A mathematical equation that shows how the rate of reaction is dependent on the concentrations of the reactants. It relates the rate of reaction to the concentrations of the reactants raised to the appropriate power.

Rate constant – k

A proportionality constant in the rate equation of the reaction

Order of reaction w.r.t. a reactant

The power to which the concentration of that reagent is raised in the rate equation

Overall order of reaction

The sum of all powers to which concentrations of reactants are raised in the rate equation

Half-life – $t_{1/2}$

The time required for the concentration of a limiting reagent to decrease to half of its initial concentration

CHEMICAL EQUILIBRIA

Reversible reaction

Reactions that take place in both directions at comparable rates

Static equilibrium

A state in which there is no change in both macroscopic and microscopic properties in a system

Dynamic equilibrium

A reversible reaction in which the rate of the forward and backward reactions are equal and nonzero.

Degree of dissociation – α

The fraction of a reactant that has dissociated at a particular temperature

Apparent molecular mass – M_{app}

The weighted average of the relative molecular masses of all gases present in equilibrium

Le Chatelier's Principle states that if a system in equilibrium is subjected to a change which disturbs the equilibrium, the system responds in such a way as to counteract the effect of the change.

IONIC EQUILIBRIA

Brønsted-Lowry theory of acids and bases

A acid is a proton donor. A base is a proton acceptor. An acid-base reaction involves the transfer of a proton from an acid to a base.

Strong acid

An acid which undergoes complete dissociation in aqueous solution

Weak acid

An acid which undergoes partial dissociation in aqueous solution

Strong base

A base which undergoes complete ionization in aqueous solution

Weak base

A base which undergoes partial ionization in aqueous solution

Degree of ionization – α

The fraction of molecules which is ionized at equilibrium

Buffer solution

A solution which is able to resist a change in pH upon the addition of a small amount of acid or base

ELECTROCHEMISTRY

Standard electrode potential – E^\ominus

The potential of a half-cell relative to a standard hydrogen half-cell under standard conditions

Standard cell potential – E^\ominus_{cell}

The potential difference between two half-cells under standard conditions

TRANSITION METALS

Transition metal

A metal which forms one or more stable ions which have incompletely filled d-subshells

Complex

A complex contains a central metal ion linked to one or more surrounding ligands.

Ligand

An anion or a molecule which contains at least one atom bearing one lone pair of electrons which can be donated into the low-lying vacant orbital of the central metal atom/ion forming a dative bond.

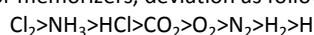
THINGS TO NOTE

GASES

Deviation from ideality occurs under

- **High pressure** – intermolecular distances become less negligible
- **Low temperature** – molecules move more slowly, IMF becomes less negligible
- When a gas has **strong intermolecular forces** e.g. h-bonding in NH_3
- When a gas molecule has a **large size** e.g. Cl_2

For memorizers, deviation as follows:

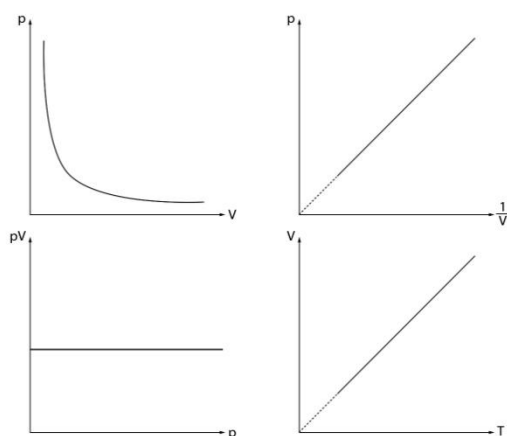


Please at least know		
$pV=nRT$		
p	V	R
Pa	m^3	8.31 J
atm	dm^3	0.082

Note the density of a gas is given by

$$\rho = m/V$$

Gas Graphs



The **partial pressure** of a gas is its **mole fraction** times its **total pressure**

The mole fraction is given by $n_{\text{gas}}/n_{\text{total}}$

STEREISOMERISM

Carbons that are definitely not chiral

sp^3 hybridized: triple bonded

sp^2 hybridized: double bonded or part of a benzene ring

n chiral centres give 2^n optical isomers

ORGANIC CHEMISTRY

$$n = C - \frac{1}{2}(H + X - N) + 1$$

Note the difference between **benzyl** and **phenyl**

- Phenyl is just a C_6H_5 group
- Benzyl has a CH_2 group attached to C_6H_5
- A cyclic ester may form from a hydroxy-acid

ARENES

Reactivity of attached groups and how they direct.

Activating	More reactive	
Amine	$-\text{NH}_2$	2,4 Directing
Hydroxy	$-\text{OH}$	
Alkyl	$(\text{CH}_2)_n\text{CH}_3$	
Aryl	C_6H_5	
reference!	H	
Halogen	$-\text{Cl}, -\text{Br}, -\text{I}$	3 directing
Aldehyde	$-\text{CHO}$	
Ester	$-\text{COO}-$	
Carboxylic acid	$-\text{COOH}$	
Ketone	$-\text{CO}-$	
Nitrile	$-\text{CN}$	
Nitrite	$-\text{NO}_2$	
Deactivating	Less reactive	

DISTINGUISHING TESTS

Remember to give the following

1. **Reagents and conditions**
2. **Observations**
3. **Equations**

MECHANISM DRAWING

1. **Name** the mechanism
e.g. "electrophilic addition"
2. Show the **polarization** of atoms
e.g. $\text{Br}^{\delta-}-\text{Br}^{\delta+}$
3. Draw **arrows** showing flow of electrons
4. **Label slow/fast steps**
Except in FRS and SN_2
5. **Number your steps**

CHEMICAL BONDING

Strong covalent bonds

- Have **multiple bonds**
- Have **short bond length** and **more effective orbital overlap** (small molecular size)
- Are **more polar** – have ionic character
- Strong ionic bonds
- Have **high lattice energy**
 - Large charges
 - Small radii