AS Chemistry

Completed version

Michelle Chen
chensimichelle@gmail.com

Content

Atomic Structure 5
Electronic Configuration 6
    Energy Level and Orbital 6
    Ionization Energy 8
Moles and Equations 10
    Relative mass, Mole and Avogadro constant 10
Chemical Bond 13
    Electronegativity 13
    Chemical Bond 14
    Coordinate bond 14
    Molecular Orbital 15
    Orbital Hybridization 16
        Hybridization of carbon 16
        Hybridization of Nitrogen 18
    VSEPER (Valence Shell Electron Pair Repulsion) 19
Structures 20
    Intermolecular force (IMF) 21
        Dipole: 21
    Intermolecular force 22
    Physical property of water 22
    Ideal Gas 23
Enthalpy Change 24
    Definitions of Enthalpy Change 24
    Hess Law 25
        Formation & Reaction 25
        Combustion & Formation 25
        Bond Energy & Reaction 26
    Reaction Pathway Diagram 27
Reaction Kinetics 28
    Boltzmann Distribution 28
    Catalysis 29
Equilibrium 30
    Equilibrium and Le Chatelier's Principles 30
    Equilibrium Constant 30
    Industrial process involves reversible reaction 32
        Acid and base 33
Nitrogen and Sulphur compounds 34
    Nitrogen and its compounds 34
    Environmental issues 34
Period 3 35
    Periodicity of Physical Properties 35
        Radius 35

First ionization energy ... 36
Melting point ... 37
Conductivity ... 38
Periodicity of Chemical Properties ... 39
Reaction with oxygen ... 39
Reaction with chlorine ... 40
Group II & VII ... 41
Group II ... 41
Reaction with water ... 41
Thermal Decomposition of Group II Carbonates and Nitrates ... 41
Group VII ... 42
Reaction with Hydrogen ... 42
Displacement Reaction between Halogen ... 42
Reaction with concentrated sulfuric acid ... 43
Testing for Halide Ions ... 43
Reactions Involve Chlorine ... 44
Basic Organic Chemistry ... 45
Homologous series ... 45
Nomenclature ... 46
Terms for nomenclature ... 46
Steps for nomenclature ... 46
Isomers ... 47
Formulae ... 49
Physical Property of Organic Compound ... 49
Alkane ... 51
Substitution ... 51
Combustion ... 51
Cracking ... 51
Mechanism -free radical substitution ... 52
Alkene ... 53
Electrophilic Addition ... 53
Additional polymerisation ... 53
Mechanism-Electrophilic Addition ... 54
Oxidation ... 55
Halogenoalkane ... 56
Nucleophilic Substitution ... 56
Elimination ... 56
Mechanism-nucleophilic substitution ... 57
Hydrolysis of halogenoalkane ... 58
Nitrile ... 58
Alcohol ... 59
Substitution and Reduction ... 59
Dehydration ... 59
Esterification ... 60

Oxidation 61
Carboxylic Acid 62
Carbonyl Compound 63
Nucleophilic Addition 63
Oxidation of Aldehyde...63
Mechanism-Nucleophilic addition 64
Chemical Test of Organic Compound 65
Infra-red spectrum 67
Key terms of Organic Chemistry...68
Mass Spectrometry 72
Principle...72
Mass Spectrum of Isotopes ^{13}C 73
Mass Spectrum of Isotopes Br and Cl...74

Atomic Structure

All the substance in the universe is composed by atoms. Atoms are mostly empty space surrounding a very small, dense nucleus that contains protons and neutrons; electrons are found in shells in the empty space around the nucleus

	Proton	Neutron	Electron
Relative mass	1	1	Ignored
Relative charge	+1	0	-1
Found at	nucleus	nucleus	outside of nucleus

The mass of an atom concentrates on nucleus and depends on the total number of proton and neutron. Nucleus is positively charged due to the presence of protons. Atoms have no net charge because the number of protons is always the same with electrons.

For a given atom, we may write its symbol in the following way:

$$^{y}_{x}\mathrm{A}$$

A is the symbol of the element which always goes with proton number
y represents its mass number
x represents its proton number
mass number = nucleon = proton number + neutron number

Isotope are the atoms with the same proton number (of the same element) but different neutron number.

$$^{1}_{1}\mathrm{H} \qquad ^{2}_{1}\mathrm{D}$$

Hydrogen and deuterium are a pair of isotopes. Deuterium has one more neutron in its nuclear, thus is heavier than hydrogen.

Isotopes have the same chemical properties, because they have the same nuclear charge and the same electron configuration. But they may have different physical properties, such as density and mass.

Electronic Configuration

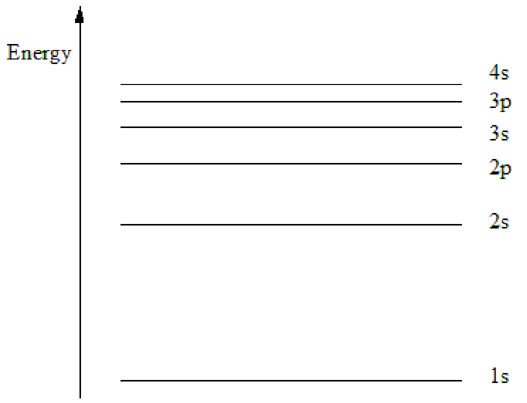
Energy Level and Orbital

Due to the nuclear charge, electrons are held in the empty space of the atom. The distribution of the electrons follows a regular pattern.

Principle quantum number (n)	Decide the energy of the electrons; it shows the distance between electrons and nucleus. Larger the number, further away the orbital and higher energy are found in the electron in it. It has the same meaning with shell.
Subshell	One shell may have different subshells. Electrons in different subshell have different energy.
Orbital	Orbital is the space that electrons can be found. Each subshell may have different orbitals and each orbital can held two electrons at most.

Principal quantum number	2[nd] quantum number	3[rd] quantum number	4[th] quantum number
Shell	Subshell	orbital	Spin direction
1	s	1s	↑↓
2	s	2s	↑↓
	p	$2p_x$, $2p_y$, $2p_z$	
3	s	3s	↑↓
	p	$3p_x$, $3p_y$, $3p_z$	
	d	$3d_{xy}$, $3d_{xz}$, $3d_{yz}$, d_{x2-y2}, $3d_{z2}$	

Draw a diagram to show energy levels of an atom



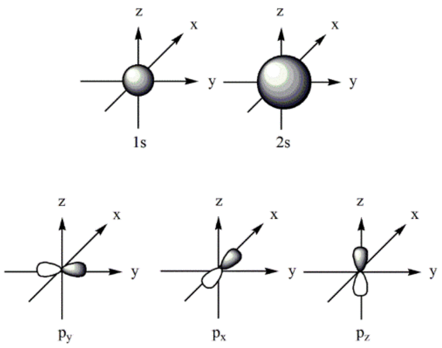
Electrons in the orbitals of the same subshell has the same energy. Thus, subshell is sometimes called energy level.

Give the order of sub-shells according to their energy from the lowest to highest.

1s 2s 2p 3s 3p 4s 3d 4p

The energy we talk about here is the potential energy of electrons in each orbital. The potential energy of electron is negatively correlated with nuclear attraction. Thus, electrons in inner orbitals experience stronger nuclear attraction and have lower energies.

Shape of Subshell



Laws that dominate the occupation of electrons

1. Electrons enter the lowest available energy level in their ground state.
2. When in orbitals of equal energy, electrons will try to remain unpaired.
3. Two electrons can go in each orbital, providing they are of opposite spin

These three laws help us to give the electronic configuration of any given atoms

		1s	2s	2p			3s	3p	
$_{13}$Si	$1s^2 2s^2 2p^6 3s^2 3p^2$	↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	↿	↿

s subshell has only one orbital, thus, can accommodate two electrons at most.
p subshell has three orbitals and can accommodate six electrons at most.

			4s	3d				
$_{25}$Mn	$1s^2 2s^2 2p^6 3s^2 3p^2$**$4s^2$ $3d^5$**	[Ar] $1s^2 2s^2 2p^6 3s^2 3p^6$	$4s^2$ ↿⇂	↿	↿	$3d^5$ ↿	↿	↿
$_{25}Mn^{2+}$	$1s^2 2s^2 2p^6 3s^2 3p^2$**$3d^5$**	[Ar] $1s^2 2s^2 2p^6 3s^2 3p^6$	$4s^0$	↿	↿	$3d^5$ ↿	↿	↿

Note that 4s orbital has lower energy compared with 3d orbitals. Thus, electrons enter 3d orbital only when 4s orbital is occupied. 4s orbital is further away from nucleus compared with 3d, thus, electrons from 4s orbital are removed first when atoms form cations.

Electronic Configuration of Atoms

$_{24}$Cr	$1s^2 2s^2 2p^6 3s^2 3p^6$ **$4s^1$ $3d^5$**
$_{29}$Cu	$1s^2 2s^2 2p^6 3s^2 3p^6$ **$4s^1$ $3d^{10}$**

Electronic Configuration of Ions

Cr^{2+}	$1s^2 2s^2 2p^6 3s^2 3p^6$ **$3d^4$**
Cu^{2+}	$1s^2 2s^2 2p^6 3s^2 3p^6$ **$3d^9$**
Cu^+	$1s^2 2s^2 2p^6 3s^2 3p^6$ **$3d^{10}$**

The energy difference between 4s orbitals and 3d is small. The 4s electrons is sometimes promoted to 3d orbitals to make 3d subshell become half-filled or full-filled. Because 3d subshell is more stable in this way. Thus, Thus, copper and chromium has only one electron in 4s orbitals.

Ionization Energy

Give the *definition* of first Ionization Energy and use an *equation* to show the First Ionization Energy of Na.

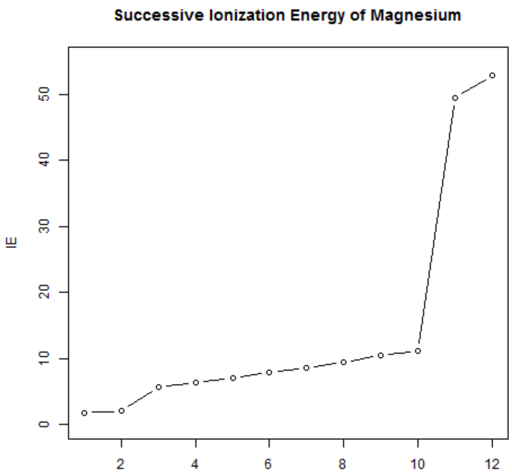
The energy required to remove one mole electrons from one mole gaseous sodium atoms to form one mole gaseous sodium ions with one positive charge.

$Na(g) \rightarrow Na^{+}(g) + e^{-}$

Give the *definition* second Ionization Energy and use an *equation* to show the second Ionization Energy of Na.

The energy required to remove one mole electrons from one mole gaseous sodium ions with one positive charge to form one mole gaseous sodium ions with two positive charges.

$Na^{+}(g) \rightarrow Na^{2+}(g) + e^{-}$



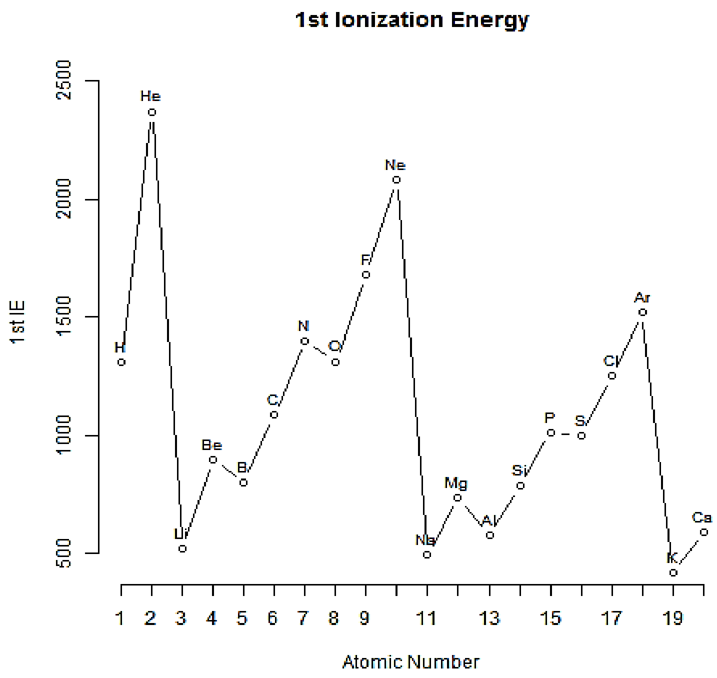
Ionization energy is correlated with the nuclear attraction. Stronger attraction between electrons and nuclear results in higher ionization energy.

In successive ionization energy, electrons are removed from outer shells prior to inner shells. Electrons in the same shell require similar energy to remove them. Electrons in inner shell require much more energy to remove compared with those in outer shells.

Factors affect IE

Shielding Effect	It is the decrease of nuclear attraction experienced by outer electrons due to the presence of inner electrons.
Nuclear Charge	Higher nuclear charge, larger nuclear attraction
Distance from Nucleus	Further away from nucleus, weaker nuclear attraction.

Give the Diagram of First Ionization Energy of first 20 Elements



Explain the *general increase* across the period

Nuclear charge increases across the period while their shielding effects remain almost constant. The distance of outermost electron from nuclear decreases. Therefore, attraction between nuclei and outermost electrons increases and it takes more energy to remove electrons away.

Explain why *noble gas elements* have the highest ionization energy in each period

Their nuclear charge is highest in each period, thus has the greatest attraction.

Explain the *sharp decrease* between the last element of the period and the first element in next period.

Shielding effect and distance from nuclear increase dramatically when it comes to the next period, outweigh the increase of nuclear charge. Thus, attraction decreases and it takes much less energy to remove electrons.

Explain why the first ionization energy of Magnesium is higher than Aluminum.

Outermost electron of magnesium is at 3s while that of aluminum is at 3p. 3p electron is more shielded than 3s electron, so it takes less energy to remove them.

Explain why the first ionization energy of Nitrogen is higher than Oxygen

The 3p orbitals of nitrogen are singly filled while that of oxygen has paired electrons in it. Paired electrons tend to repel each other, so it takes less energy to remove them.

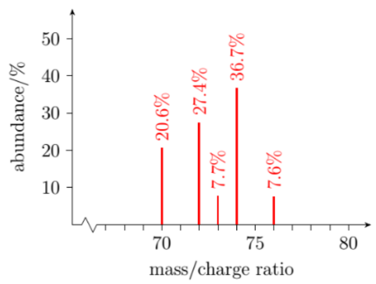
Explain the general decrease down the group.

Shielding effect and distance from nuclear increase dramatically down the group outweigh the increase of nuclear charge. Thus, it takes much less energy to remove electrons.

Moles and Equations

Relative mass, Mole and Avogadro constant

1. **Give definitions of following terms**
   a) **Relative Atomic Mass**
   Average mass of naturally occurring atoms of an element on a scale where an atom of carbon-12 has a mass of exactly 12 units.
   b) **Relative Isotopic Mass**
   Mass of particular isotope of an element on a scale where an atom of carbon-12 has a mass of exactly 12 units.



Isotope are the atoms with the same proton number but different neutron number.

This is a mass spectrum of all the isotopes of an element shows. X-axis shows mass per charge of each isotope while y-axis shows the relative abundance of the species.

$$relative\ atomic\ mass = \sum isotopic\ mass \times relative\ abundance$$

$$A_r = \frac{70 \times 20.6 + 72 \times 27.4 + 73 \times 7.7 + 74 \times 36.7 + 76 \times 7.6}{100} = 72.7$$

Each carbon-12 atom has exactly 12 nucleons. Thus, one unit mass is very close to the mass of a nucleon. Thus, the relative isotopic mass of any atom can be predicted from their nucleon.

2. **Give definitions of following terms**
   a) **Relative Molecular Mass**
   The relative mass of one molecule of the compound on a scale where the carbon-12 isotope has a mass of exactly 12 units.
   b) **Relative Empirical Mass**
   The relative mass of all the atoms shown in the empirical formula where the carbon-12 isotope has a mass of exactly 12 units.

Compounds such as sodium chloride cannot show all of their atoms in the formula, because it is giant ionic structure. Thus, NaCl just tell us the ratio of atoms in the compound. 78.5 is the relative formula mass instead of molecular mass.

3. **Give definitions of following terms**

   a) **Mole**

   Amount of that substance that has the same number of specific particles (atoms, molecules or ions) as there are atoms in exactly 12g of the carbon-12 isotope

   b) **Avogadro Constant**

   The number of atoms in exactly 12g of the carbon-12 isotope, which is 6.0×10^{23}

   c) **Molar mass**

   The mass of one mole substance

In any substance $n = \frac{mass}{molar\ mass}$ unit of molar mass is $\mathrm{g\ mol^{-1}}$

In solution $n = volume \times concentration$ unit of concentration is $\mathrm{mol\ dm^{-3}}$

In gas $n = \frac{volume}{molar\ volume}$ unit of molar volume is $\mathrm{dm^3\ mol^{-1}}$

Molar volume of any gas at 1 atm and 298 K is $24\ dm^3\ mol^{-1}$

Calculation involves titration

To calculate number of water in hydrated ethanedioic acid, $H_2C_2O_4 \cdot xH_2O$.

A 6.30g sample of hydrated ethanedioic acid, $H_2C_2O_4 \cdot xH_2O$, was dissolved in water and the solution made up to 250 cm^3. A 25.0 cm^3 sample of this solution was acidified and titrated with 0.100 mol dm^{-3} potassium manganate (VII) solution. 20.0 cm^3 of this potassium manganate (VII) solution was required to react fully with the ethanedioate ions, present in the sample.

$$2\mathrm{MnO_4^-} + 6\mathrm{H^+} + 5\mathrm{H_2C_2O_4^{2-}} \rightarrow 2\mathrm{Mn^{2+}} + 10\mathrm{CO_2} + 8\mathrm{H_2O}$$

Mole of $\mathrm{KMnO_4}$ in $20\ \mathrm{cm^3}$ solution $n = 20.0 \times 10^{-3}\ \mathrm{dm^3} \times 0.1\ \mathrm{mol\ dm^{-3}} = 2 \times 10^{-3}\ \mathrm{mol}$

Mole of $\mathrm{H_2C_2O_4}$ in $25\ \mathrm{cm^3}$ solution $n = \frac{5}{2} \times 2 \times 10^{-3} = 5 \times 10^{-3}\mathrm{mol}$

Mole of $\mathrm{H_2C_2O_4}$ in $250\ \mathrm{cm^3}$ solution $n = 5 \times 10^{-3} \times 10 = 5 \times 10^{-2}\ \mathrm{mol}$

Molar mass of $\mathrm{H_2C_2O_4 \cdot xH_2O}$ $M = \frac{6.3}{5 \times 10^{-2}} = 126\ \mathrm{g\ mol^{-1}}$

$$x = \frac{126 - (2 \times 1 + 12 \times 2 + 16 \times 4)}{18} = 2$$

Calculation involves percentage yield

$$percentage\ yield = \frac{real\ yield}{ideal\ yield}$$

2.30g of ethanol were mixed with an excess of aqueous acidified potassium dichromate (VI). The reaction mixture was then boiled under reflux for one hour.

$$\mathrm{CH_3CH_2OH + 2[O] \rightarrow CH_3CO_2H + H_2O}$$

The desired organic product was then collected by distillation. The yield of product was 60.0%. What mass of product was collected?

Mole of ethanol $n = \frac{2.3}{12\times2+16\times1+1\times6} = 5\times10^{-2}\ \mathrm{mol}$

Ideal mass of ethanoic acid $m = 5\times10^{-2}\ \times(12\times2+16\times2+1\times4) = 3\ \mathrm{g}$

Mass of ethanoic acid collected $m = 3\times60\% = 1.8\ \mathrm{g}$

Calculation involves gas

To find molecular formula of a hydrocarbon

10 cm^3 of a gaseous hydrocarbon, C_xH_y, was reacted with 100 cm^3 of oxygen gas, an excess. The final volume of the gaseous mixture was 95 cm^3. This gaseous mixture was treated with concentrated, aqueous sodium hydroxide to absorb the carbon dioxide present. This reduced the gas volume to 75 cm^3. All gas volumes were measured at 298K and 100 kPa

$$\mathrm{C_xH_y} + \left(\mathrm{x} + \frac{\mathrm{y}}{4}\right)\mathrm{O_2} \rightarrow \mathrm{xCO_2} + \frac{\mathrm{y}}{2}\mathrm{H_2O}$$

Volume of $\mathrm{CO_2}$ produced: $95 - 75 = 20\ cm^3$

Volume of $\mathrm{O_2}$ reacted: $100 - 75 = 25\ cm^3$

$\frac{\mathrm{n(C_xH_y)}}{\mathrm{n(CO_2)}} = \frac{1}{x} = \frac{\frac{10\times10^{-3}}{24}}{\frac{20\times10^{-3}}{24}} = \frac{10}{20}$ $x = 2$

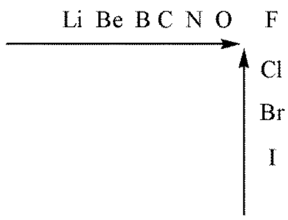
$\frac{\mathrm{n(C_xH_y)}}{\mathrm{n(O_2)}} = \frac{1}{x+\frac{y}{4}} = \frac{\frac{10\times10^{-3}}{24}}{\frac{25\times10^{-3}}{24}} = \frac{10}{2}$ $y = 2$

Molecular formular of the hydrocarbon is $\mathrm{C_2H_2}$

Chemical Bond

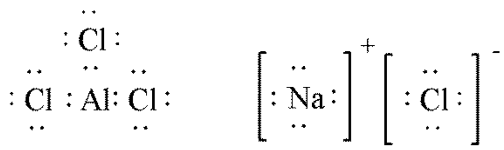
Electronegativity

Give the *definition of electronegativity* and use a diagram to show how electronegativity of elements change in the periodic table.



Electronegativity: the ability of a bonding atom to attract bonding electrons.
Fluorine is the atom with highest electronegativity, further away from fluorine in periodic table, lower electronegativity the atom has.
Higher nuclear attraction results in higher electronegativity. Thus, electronegativity changes in the same pattern as ionization energy. Atoms with higher ionization energy also have higher electronegativity while atoms with lower ionization energy also have lower electronegativity.
In electronegativity, we do not take noble gas elements into consideration because they normally do not for covalent bonds with others.

Give *dot-and-cross diagram* of the following compounds. State the type of bond in each compound and use the idea of electronegativity to *explain why they are different*.



$AlCl_3$ NaCl

For *aluminum chloride*, the difference of electronegativity of two bonding atoms are not big enough to give rise to electron transfer, they still share electrons. So, it is *covalent bond* that hold aluminum atom and chlorine atom together.
For *sodium chloride*, the difference of electronegativity of two bonding atoms is big enough, so electron transfer from sodium, the atom with low electronegativity, to chlorine, the atom with high electronegativity. Thus, it is *ionic bond* held two elements together.

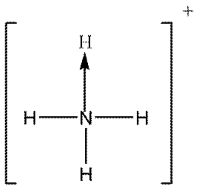
Chemical Bond

Type of Bond	Atoms involved	Particles involved	Definition
Ionic bond	Atoms with high EG gains electrons Atoms with low EG lose electrons	Cation and anion	Electrostatic force between cation and anion
Covalent bond	Atoms with high EG share electrons by orbital overlap	Atoms	Electrostatic force between bonding nuclei and bonding electrons.
Metallic bond	Atoms with low EG delocalized their outer electrons	Cation and delocalized	Electrostatic force between cation lattice and free electrons.

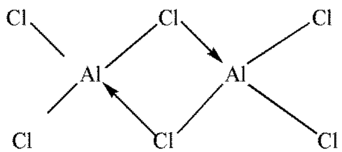
EG= electronegativity

Coordinate bond

Give the structure of the following compound:



NH_4^+



Al_2Cl_6

In coordinate bonds, bonding electrons are contributed by only one of the bonding atoms.

Molecular Orbital

Covalent bonds form when atomic orbital overlap to form molecular orbital. Each molecular orbital accommodates two electrons (bonding pair) moving around two nuclei. Normally, only atomic orbital with signal electron will be involved in the formation of molecular orbital.

Draw diagrams to show the σ bonds (head-to-head) formed in hydrogen, chlorine and hydrochloride.

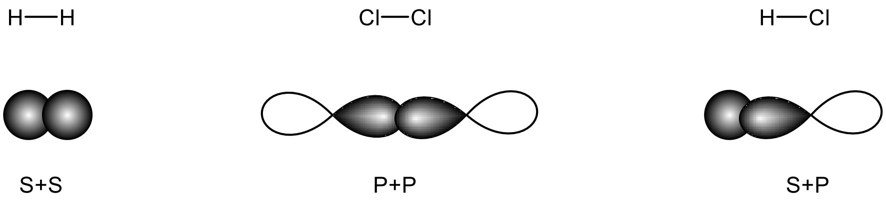
H 1s^1

Cl 1s^{2}2s^{2}3p^5

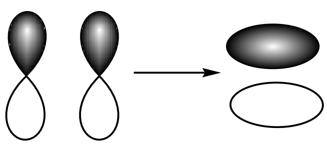
In H_2, two 1s orbital overlap to form a σ bond.

In HCl, one 1s orbital overlap with a 3p orbital to form a σ bond.

In Cl_2, two 3p orbitals overlap to form a σ bond.



Draw diagrams to show the π Bond (side-to-side)



σ bond has higher percentage of overlap, thus, σ bond is formed in prior to π bond.

Single bond involves only σ bond. **Double bond** involves a σ bond and a π bond while **triple bond** involves a σ bond and two π bonds.

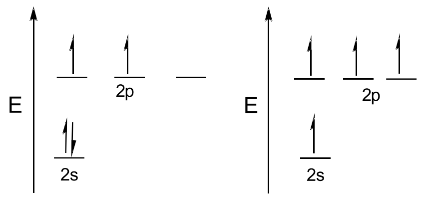
Explain why hydrogen has larger bond energy compared with chlorine.

Larger atomic size results smaller orbital overlap. Thus, the longer bond length and smaller bond energy.

Orbital Hybridization

Hybridization of carbon

Hybridization is a theory to explain the formation of covalent bonds. We are going to talk about the hybridization of carbon first.

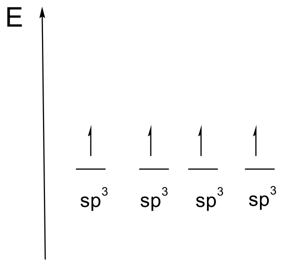
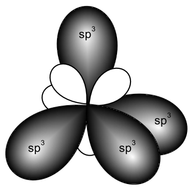
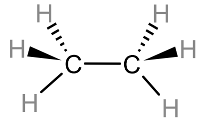
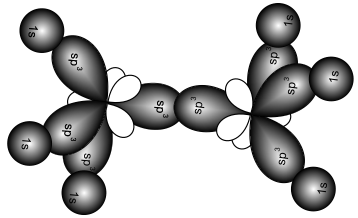
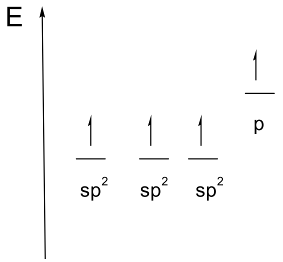
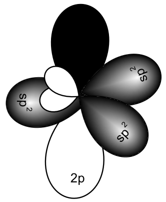
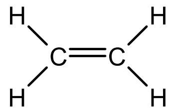
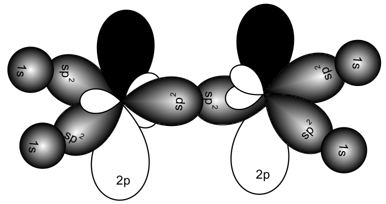
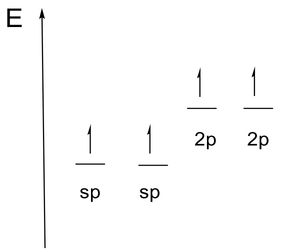
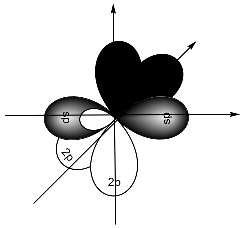
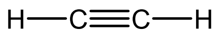
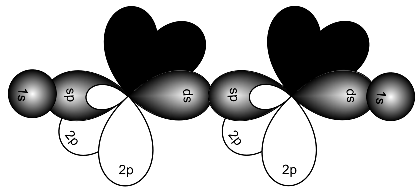


Before hybridization, carbon atom promotes one of its 2s electrons to 2p orbitals, creating four half-filled orbitals.

In sp^3 hybridization, one 2s orbital hybridize with three 2p orbitals to form four sp^3 hybridized orbitals. The four orbitals are degenerate (at the same energy level). The shape of sp^3 orbital is different from either s orbital or p orbital. And the angle between the orbitals is 109.5°. Each sp^3 orbital can form a σ bond. Thus, a sp^3 hybridized carbon form four σ bonds.

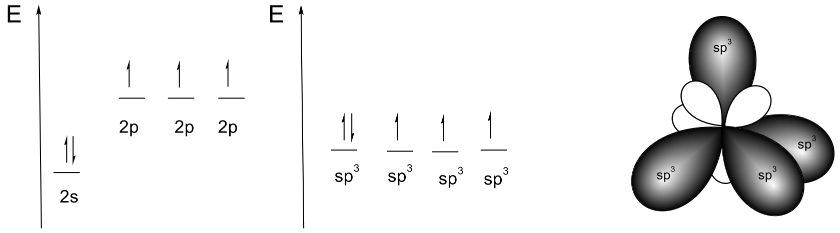
In sp^2 hybridization, one 2s orbital hybridize with two 2p orbitals to form three sp^2 hybridized orbitals. The three orbitals are degenerate (at the same energy level). The shape of sp^2 orbital is the same with sp^3. The angle between the sp^2 orbitals is 120°, thus, three orbitals are in the same plane. The unhybridized p orbital is perpendicular to the plane. Each sp^2 orbital can form a σ bond. Thus, a sp^2 hybridized carbon form three σ bonds while the unhybridized p orbital is involved in the formation of π bond.

In sp hybridization, one 2s orbital hybridize with one 2p orbitals to form two sp hybridized orbitals. The angle between the sp orbitals is 180°. Two unhybridized p orbital is perpendicular to the each other as well as hybridized orbitals. Each sp orbital can form a σ bond. Thus, a sp hybridized carbon form two σ bonds while the unhybridized p orbital is involved in the formation of π bond. Two π bonds are formed, one is above and below σ bond while other is in the front and at the back of the σ bond.

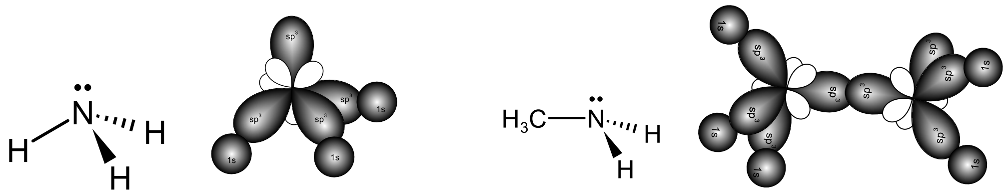
Hybridization	Energy diagram	Orbital arrangement	Geometry	Bonds formed	Example	
sp^3			Tetrahedral 109.5 °	Four σ bond No π bond		
sp^2			Trigonal planar 120 °	Three σ bonds One π bond		
sp			Linear 180 °	Two σ bond Two π bonds		

Hybridization of Nitrogen

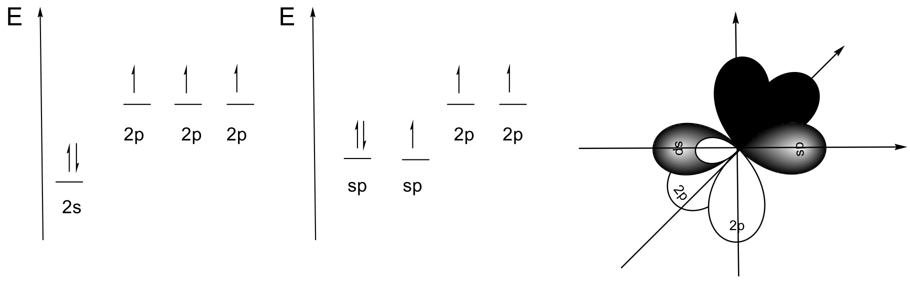
sp³ hybridization



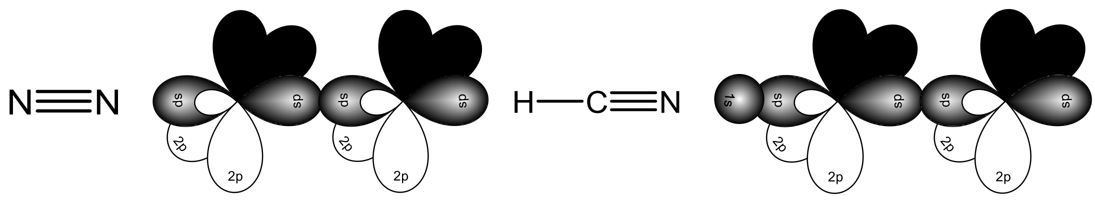
One of sp³ orbital is filled with two electrons and will not form covalent bonds with the other atoms. Because lone pair exerts larger repulsion, the bond angle between the other three orbitals is 107°.



sp hybridization



One of the sp orbital is filled with lone pair, thus sp nitrogen form only one σ bond and two π bond.

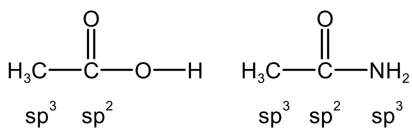


To find the way of hybridization of a certain atom, we need first find out the number of π bond.

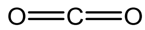
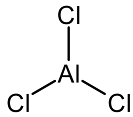
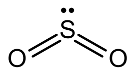
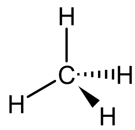
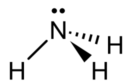
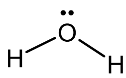
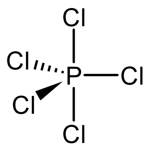
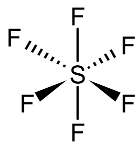
If no π bond is found on the atom, it is sp³ hybridized

If one π bond is found, it is sp² hybridized

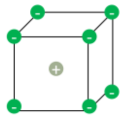
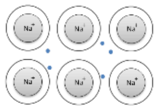
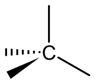
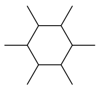
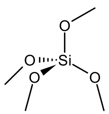
If two π bond is found, it is sp hybridized



VSEPER (Valence Shell Electron Pair Repulsion)

No. of electron pairs	No. of bond pairs	No. of lone pairs	Shape	Bond Angle	Example
2	2	0	Linear	180°	Carbon dioxide 
3	3	0	Trigonal Planar	120°	Aluminum chloride 
3	2	1	Non-linear	117°	Sulfur dioxide 
4	4	0	Tetrahedral	109.5°	Methane 
	3	1	Pyramidal	107°	Ammonia 
	2	2	V Shape	104.5°	Water 
5	5	0	Trigonal Bipyramidal	120° 90°	Phosphorous pentachloride 
6	6	0	Octahedral	90°	Sulfur hexafluoride 

Structures

Structure	Diagram	Particles	Force	Factors affects the strength	Melting point	Conductivity
Giant ionic lattice	Sodium chloride 	Ions	Ionic bond	Charge density	High Strong ionic bond breaks.	No conductivity in solid. It only conducts electricity when it is in aqueous solution or in molten state. Because ions can move in these conditions.
Giant metallic lattice	Sodium 	Cation & delocalized electrons	Metallic bond	Charge density & number of delocalized electrons	High Strong metallic bond breaks.	Good conductor. More delocalized electrons, better conductor.
Giant molecules	Diamond 	Atoms	Covalent bond	Bond length	High Strong covalent bond breaks.	Insulator
	Graphite 					Good conductor. It has delocalized electrons in its big π bond.
	Silicon oxide 					Insulator
Simple molecules	hydrogen H—H	Molecules	IMF	Number of electrons	Low Weak IMF breaks.	Not conductor. Unless it reacts with water.

Intermolecular force (IMF)

Dipole:

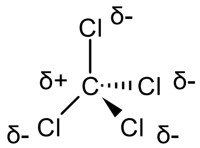
What is dipole and use the idea of electronegativity to how dipoles come into being.
Dipole occurs when the positive center and negative center of a molecule do not coincide with each other. The difference of electronegativity of two bonding atoms can give rise to bond polarity. If bond polarity cannot cancel each other in a polyatomic molecule, then the molecule has dipole as well.

Give examples of *non-polar* diatomic and polyatomic molecules and *polar* diatomic and polyatomic molecules:

Non-polar molecues

Cl—Cl

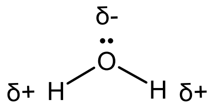
no polar bond in the molecule



polar bonds canceled with each other

Polar molecues

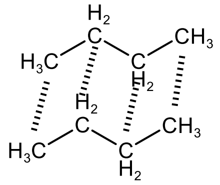
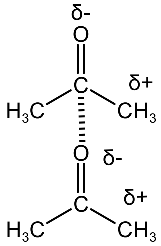
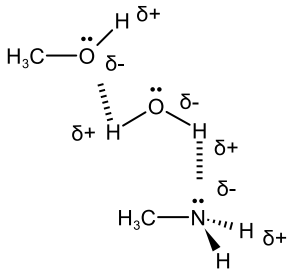
$\delta+$ $\delta-$
H—Cl



polar bonds present, and polar bonds cannot canceled with each other

Describe how instantaneous dipole and induced dipole force come into being.
Instantaneous dipole arises from the uneven distribution of electrons at instant. If another molecule is close enough, its electrons distribution will become uneven due to the induction. The force between instantaneous dipole and induced dipole is also called id-id.

Intermolecular force

Type	examples	Molecules involved	Factors effects its strength
Instantaneous dipole & Induced Dipole		All the molecule	Molecules with more electrons has stronger id-id force between each other. For organic molecule, straight chain has stronger id-id force than branched chains
Forces between Permanent Dipole		Polar molecules	Polarity of molecules
Hydrogen bond		Molecules with hydrogen bond to nitrogen, oxygen and fluorine can form hydrogen bond with the lone pair on oxygen, nitrogen and fluorine.	Number of hydrogens can form hydrogen bond

Physical property of water

Special physical property of water resulted by hydrogen bond:

- Water has higher melting point compared with other hydrides of its group
- Good surface tension
- Solid state has lower density than liquid

Ideal Gas

Give the *equation* of Ideal gas

$$PV = nRT$$

Give the *units* of the following factors

P	Pascal	Pa
V	Cubic meter	m^3
T	Kelvin	K
n	Mole	mol

State the *pre-assumption* of ideal gas

1. The size of the gas molecule can be ignored compared with the volume they occupied.
2. There is no intermolecular force between molecules.
3. All the collisions between gas molecules are elastic.
4. The movement of gas molecules is rapid and random.
5. Temperature of gas is relevant to the average kinetic energy of the molecules.

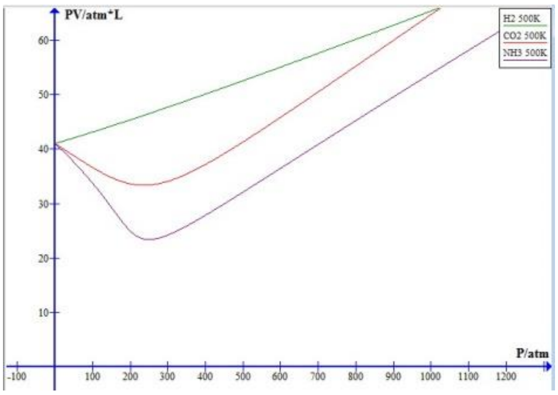
State the condition that encourage ideal gas behavior

temperature	High
Pressure	Low

Gas molecules move violently at high temperature; thus, it is harder for them to form intermolecular force and behave more like ideal gas.

Gas molecules are further away from each other when pressure gets lower, so intermolecular force are less significant when pressure decrease.

Give the diagram of deviation from ideal gas behavior of H_2, N_2, NH_3.



When pressure increases, PV decreases at first. Because higher pressure brings molecules closer together. IMF formed between molecules, further decreasing the distance between molecules.

Ammonia behaves least ideally, because they are able to form hydrogen bond which is much stronger than other types of intermolecular force.

When pressure becomes too high, the distance between molecules is too small to further compress the gas. This is due to the repulsion between the particles.

Enthalpy Change

Definitions of Enthalpy Change

Standard Enthalpy Change of	Symbol	Sign	Definition: *Enthalpy change involved when*	example
Reaction	ΔH_r^θ	+/-	The substance reacts in the mole shown in the equation	$C_2H_6O(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$
Formation	ΔH_f^θ	+/-	One mole compound formed from its elements	$C(s) + 2H_2(g) \rightarrow CH_4(g)$
Combustion	ΔH_c^θ	-	One mole compound burned in **excess** oxygen	$C_2H_6O(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$
Neutralization	ΔH_n^θ	-	One mole of water formed from neutralization	$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$
Solution	ΔH_{sol}^θ	+/-	One mole substance dissolved in large amount of water	$NaCl(s) + aq \rightarrow NaCl(aq)$
Atomization	$\Delta H_{\mathrm{atm}}^\theta$	+	One mole of gaseous atoms formed from its elements	$C(graphite) \rightarrow C(g)$
Bond Energy	E	+	One mole of bond broken into gaseous atoms	$H\text{-}H(g) \rightarrow 2H(g)$

"in their standard states and under standard conditions" *must be emphasized at the end of each definitions.*

Formation of oxides is sometimes the same with the combustion of elements.

$\Delta H_c^\theta[\mathrm{C}]$ $\mathrm{C(s) + O_2(g) \rightarrow CO_2(g)}$ $\Delta H_f^\theta[\mathrm{CO_2}]$ $\mathrm{C(s) + O_2(g) \rightarrow CO_2(g)}$

But this is not always the case

$\Delta H_c^\theta[S]$ $S(s) + O_2(g) \rightarrow SO_2(g)$ $\Delta H_f^\theta[SO_3]$ $S(s) + \frac{3}{2}O_2(g) \rightarrow SO_3(g)$

Atomization of diatomic elements is sometimes twice the bond energy

$\Delta H_{atm}^\theta[Cl]$ $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$ $E(\mathrm{Cl-Cl})$ $\mathrm{Cl-Cl(g) \rightarrow 2Cl(g)}$

But this is not aways the case

$\Delta H_{atom}^\theta[Br]$ $\frac{1}{2}Br_2(l) \rightarrow Br(g)$ $E(\mathrm{Br-Br})$ $\mathrm{Br-Br(g) \rightarrow 2Br(g)}$

$$\Delta H_{atom}^\theta[Br] > \frac{1}{2}E(Br - Br)$$

This is because the standard state of bromine is liquid, thus atomization involves both vaporization and bond dissociation.

Hess Law

State what is Hess Law

The enthalpy change of a reaction is independent on the route it takes as long as the initial condition and final condition is the same

Formation & Reaction

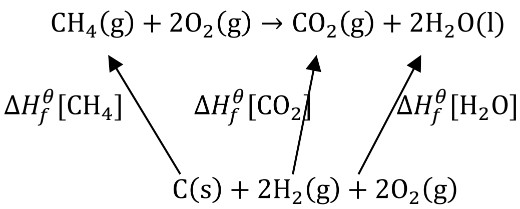
Calculate the enthalpy change of combustion of methane, using the value provided below.

$\Delta H_f^\theta[\mathrm{CO_2}]$ $\quad \mathrm{C(s) + O_2(g) \rightarrow CO_2(g)}$ $\quad -394\ \mathrm{kJ\ mol^{-1}}$

$\Delta H_f^\theta[\mathrm{H_2O}]$ $\quad \mathrm{H_2(g) + \frac{1}{2}\ O_2(g) \rightarrow H_2O(l)}$ $\quad -286\ \mathrm{kJ\ mol^{-1}}$

$\Delta H_f^\theta[\mathrm{CH_4}]$ $\quad C\mathrm{(s) + 2H_2(g) \rightarrow CH_4(g)}$ $\quad -74\ \mathrm{kJ\ mol^{-1}}$

To construct the cycle using the value provided, we need to add all the elements involved in the formation of these compounds as the third part.



$$\Delta H_c^\theta[\mathrm{CH_4}] = \Delta H_f^\theta[\mathrm{CO_2}] + 2\Delta H_f^\theta[\mathrm{H_2O}] - \Delta H_f^\theta[\mathrm{CH_4}]$$
$$= -394 + 2 \times (-286) - (-74) = -892\ \mathrm{kJ\ mol^{-1}}$$

Combustion & Formation

Calculate the enthalpy change of combustion of propanone, using the value provided below.

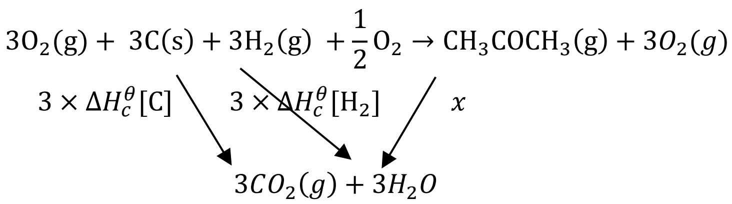
$\Delta H_c^\theta[\mathrm{C}]$ $\quad \mathrm{C(s) + O_2(g) \rightarrow CO_2(g)}$ $\quad -394\ \mathrm{kJ\ mol^{-1}}$

$\Delta H_c^\theta[\mathrm{H_2}]$ $\quad \mathrm{H_2(g) + \frac{1}{2}\ O_2(g) \rightarrow H_2O(l)}$ $\quad -286\ \mathrm{kJ\ mol^{-1}}$

$\Delta H_f^\theta[\mathrm{CH_3COCH_3}]$ $\quad \mathrm{2C(s) + 3H_2(g)\ + \frac{1}{2}O_2 \rightarrow CH_3COCH_3(g)}$ $\quad -254\ \mathrm{kJ\ mol^{-1}}$

$\Delta H_c^\theta[\mathrm{CH_3COCH_3}]$ $\quad \mathrm{CH_3COCH_3 + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)}$ $\quad x$

To construct the cycle using the value provided, we need to add oxygen at the either side of the equation of formation. Then we add all the oxides produced in the combustion of these compounds as the third part.

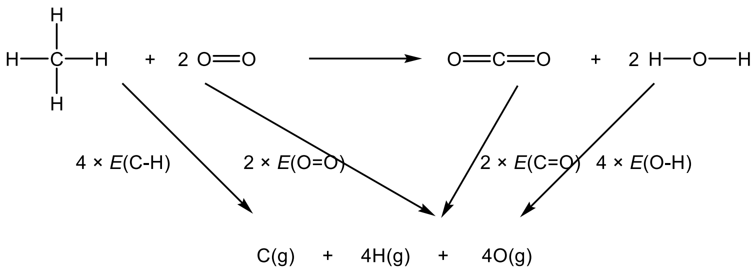


$$x = 3 \times \Delta H_c^\theta[\mathrm{C}] + 3 \times \Delta H_c^\theta[\mathrm{H_2}] - \ \Delta H_f^\theta[\mathrm{CH_3COCH_3}]$$
$$= 2 \times (-394) + 3 \times (-286) - (-254) = 1786\ \mathrm{kJ\ mol^{-1}}$$

Bond Energy & Reaction

Use the value below to calculate the enthalpy change of combustion of methane

$E(\mathrm{C-H})$	$\mathrm{C-H \rightarrow C(g) + H(g)}$	$410\ \mathrm{kJ\ mol^{-1}}$
$E(\mathrm{O=O})$	$\mathrm{O=O \rightarrow 2O(g)}$	$496\ \mathrm{kJ\ mol^{-1}}$
$E(\mathrm{C=O})$	$\mathrm{C=O \rightarrow C(g) + O(g)}$	$740\ \mathrm{kJ\ mol^{-1}}$
$E(\mathrm{O-H})$	$\mathrm{O-H \rightarrow O(g) + H(g)}$	$460\ \mathrm{kJ\ mol^{-1}}$



$$\Delta H_c^{\theta} = 4 \times E(\mathrm{C-H}) + 2 \times E(\mathrm{O=O}) - 2 \times E(\mathrm{C=O}) - 4 \times E(\mathrm{O-H})$$
$$= 4 \times 410 + 2 \times 496 - 2 \times (740) - 4 \times (460) = -892\ \mathrm{kJ\ mol^{-1}}$$

In an experiment to calculate the enthalpy change of combustion of a fuel, 1.5g (0.0326 mol) of the fuel was used to heat 200g of water. The temperature of the water rose from 25°C to 55°C. The specific heat capacity of water is 4.18 $\mathrm{Jg^{-1}\,K^{-1}}$.

Using the information above, what is the experimental value for the enthalpy change of combustion, ΔH_c, of the fuel?

$$\Delta Q = cm\Delta T = 4.18 \times 200 \times 30 = 25.08\ \mathrm{kJ}$$

$$\Delta H_c = \frac{25.08}{0.0326} = 791.4\ \mathrm{kJ\ mol^{-1}}$$

Reaction Pathway Diagram

Give the definition of following terms:

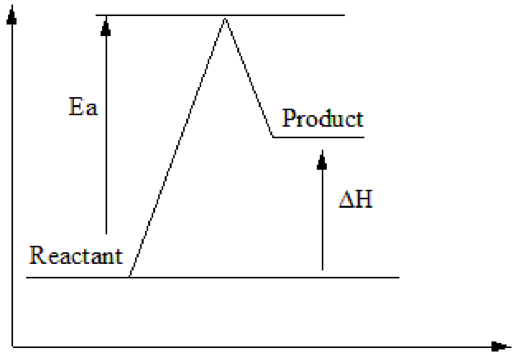
Activation energy:

Minimum energy that is needed for a particle to have successful collision.

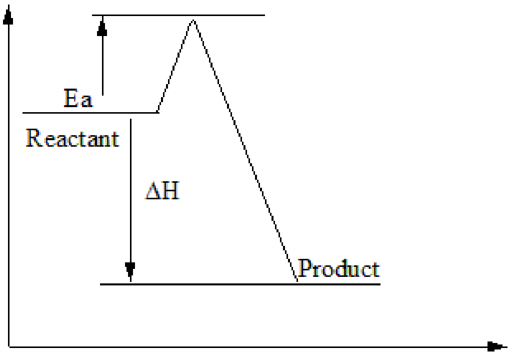
Catalyst:

Substances that speed up reaction rate by providing an alternative pathway with lower activation energy and stay chemically unchanged at the end of reaction.

Draw the energy diagram of an *endothermic* reaction. Notify the enthalpy change and activation energy in the diagram.



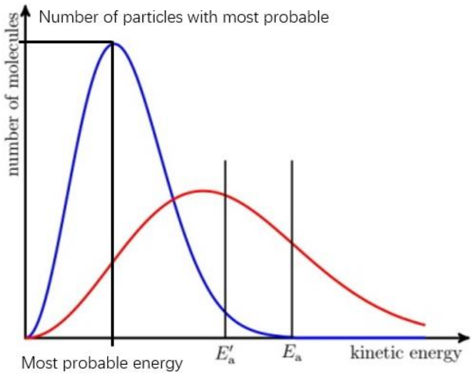
Draw the energy diagram of an *exothermic* reaction. Notify the enthalpy change and activation energy in the diagram.



Reaction Kinetics

Boltzmann Distribution

Draw Boltzmann distribution at both higher and lower temperature. Label each curve. Notify *activation energy* with and without catalyst.



The blue curve shows the Boltzmann distribution at lower temperature while the red curve shows the distribution at higher temperature.
The most probable energy is higher when temperature rises while the number of particles with the most probable energy is lower.

Explain why temperature increase would result in an increasing reaction rate in terms of both *Boltzmann distribution and collision theory.*
When temperature increased, there will be more particles with energy higher than activation energy. Thus, the proportion of successful collision would be increased.
Particle moves faster at higher temperature; thus, higher collision frequency is expected.

Explain why adding catalyst is able to speed up a reaction in terms of *Boltzmann distribution.*
Catalysts speed up reaction by providing a pathway with lower activation energy. Thus, in the presence of catalyst, there will be more particles with energy higher than activation energy and the proportion of successful collision would be increased.

Catalysis

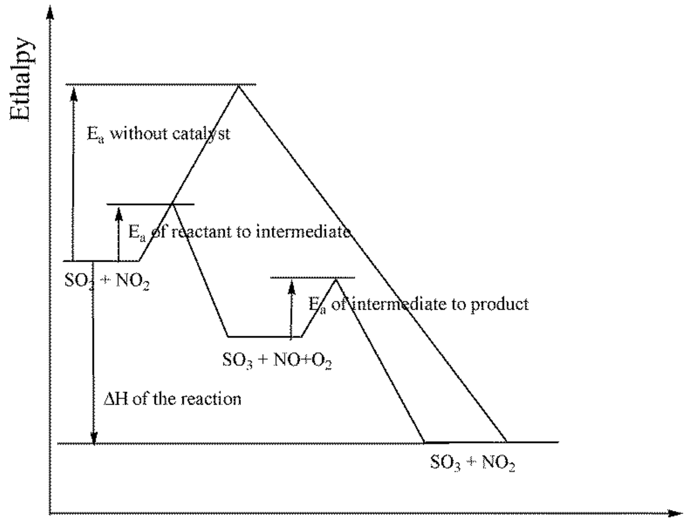
Homogeneous catalysis

Catalysis in which catalyst and reacting mixture are in the same phase.

e.g. $SO_2 + NO_2 \rightarrow SO_3 + NO$

$2NO + O_2 \rightarrow 2NO_2$

$SO_3 + H_2O \rightarrow H_2SO_4$



Heterogeneous catalysis

Catalysis in which catalyst and reacting mixture are not in the same phase.

e.g. Iron is used as catalyst in the reaction $N_2 + 3H_2 \rightarrow 2NH_3$

Mechanism of catalysis involved adsorption, reaction and desorption.

Equilibrium

Equilibrium and Le Chatelier's Principles

Give the definitions of the following concepts

1. Equilibrium:

A state in which the rate of forward and reverse reactions being equal and the concentration of reactants and products remaining constant

2. Le Chatelier's principle:

If a change is made to a system at dynamic equilibrium, the position of equilibrium moves to minimise this change

State how the following changes will have effect on the position of equilibrium.

Factor	Change	Effects on equilibrium	Factor	Change	Effects on equilibrium
Temperature	Increase	Favor endothermic reaction	Pressure	Increase	Favor the side with less gas molecules.
	Decrease	Favor exothermic reaction		Decrease	Favor the side with more gas molecules.
Concentration of reactant	Increase	Move to RHS	Concentration of product	Increase	Move to LHS
	Decrease	Move to LHS		Decrease	Move to RHS

Equilibrium Constant

$$\mathrm{mA + nB \leftrightharpoons pC + qD}$$

Give the equilibrium expression and its unit of the above equation:

$$K_c = \frac{[\mathrm{C}]^p[\mathrm{D}]^q}{[\mathrm{A}]^m[\mathrm{B}]^n}$$

Only temperature would change the value of K_c

2.00 mol of dinitrogen tetroxide was sealed in a container at 350K. After equilibrium had been established the total pressure was 140 kPa and the mixture of gases contained 1.84 mol of dinitrogen tetroxide.?

	$2NO_2(g)$	$\leftrightharpoons N_2O_4(g)$
Initial	0	2.00
Reacted	0.16×2	2-1.84=0.16
Equilibrium	0+0.16×2	1.84

$$K_c = \frac{[\mathrm{N_2O_4}]}{[\mathrm{NO_2}]^2} = \frac{1.84\ \mathrm{mol\ dm^{-3}}}{(0.32\ \mathrm{mol\ dm^{-3}})^2} = 18.0\ \mathrm{mol^{-1}dm^3}$$

What is partial pressure?

In gas mixture, the pressure contributed by each component is called partial pressure.

For the mixture contain 0.32 mol NO_2 and 1.84 mol N_2O_4 with total pressure of 140 kPa

$$P_{total}V = n_{total}RT$$

$$p(\mathrm{NO_2}) = n_{\mathrm{NO_2}}RT = \frac{n_{\mathrm{NO_2}}}{n_{total}} \times n_{total}RT = \frac{n_{\mathrm{NO_2}}}{n_{total}}P_{total} = \frac{0.32}{0.32 + 1.84} \times 140 = 20.74\ \mathrm{kPa}$$

$$p(\mathrm{N_2O_4})V = n_{\mathrm{N_2O_4}}RT = \frac{n_{\mathrm{N_2O_4}}}{n_{total}} \times n_{total}RT = \frac{n_{\mathrm{N_2O_4}}}{n_{total}}P_{total} = \frac{1.84}{0.32 + 1.84} \times 140 = 119.26\ \mathrm{kPa}$$

$$P_{total} = p(\mathrm{NO_2}) + p(\mathrm{N_2O_4})$$

So partial pressure of a certain substance is its mole fraction times the total pressure.

Give the equilibrium expression (K_p) of the following reaction and calculate its value using the data above

$$2\mathrm{NO_2(g)} \leftrightharpoons \mathrm{N_2O_4(g)}$$

$$K_p = \frac{p(\mathrm{N_2O_4})}{p^2(\mathrm{NO_2})}$$

$$K_p = \frac{119.26\ kPa}{(20.74\ ka)^2} = 0.277\ \mathrm{kPa^{-1}}$$

Industrial process involves reversible reaction

Process	Equation and Use of its products	Condition	Its effect on	
			yield	**rate**
Haber Process	**Equation:** $N_2(g) + 3H_2(g) \leftrightharpoons 2NH_3(g)$ **Use:** Fertilizer Explosive	**Pressure** 200 atm	Increase Fewer molecules on RHS	Increase Increase collision frequency
		Temperature 450℃	Decrease Forward reaction is exothermic	Increase Increase successful collision
		Catalyst Iron	No effect	Increase Lower Ea
Contact Process	**Equation:** $2SO_2(g) + O_2(g) \leftrightharpoons 2SO_3(g)$ **Use:** Fertilizer Explosive	**Pressure** 1-2 atm		
		Temperature 450℃	Decrease Forward reaction is exothermic	Increase Increase successful collision
		Catalyst V_2O_5	No effect	Increase Lower Ea

Acid and base

Give the definitions and examples of the following terms:

Acid:

Proton donor

Base:

Proton acceptor

Strong acid/base:

Acid or base that completely dissociate in water

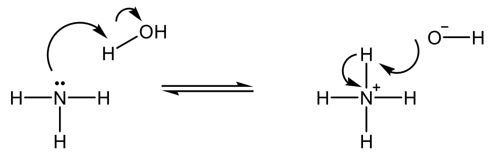
Weak acid/base:

Acid or base that partially dissociate in water

Give an ionic equation to show how ammonia behave as a base and use diagrams to show the structure of each substance in the equation.

$H_2O(l) + NH_3(aq) \leftrightharpoons OH^-(aq) + NH_4^+(aq)$

Acid Base Conjugate Base Conjugate Acid

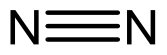
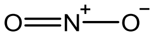
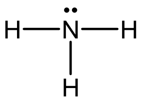


Water is the proton donor; thus, it is acid. It gives proton and become hydroxide, which is the conjugate bas of water.

Ammonia accepts a proton; thus, it is base. It accepts proton and become ammonium, which is the conjugate acid of ammonia.

Nitrogen and Sulphur compounds

Nitrogen and its compounds

Nitrogen		It is very unreactive because the triple bond is strong and non-polar
Nitrogen dioxide		It is formed either in lightening or car exhaust. $$\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g)$$
Ammonia		Ammonia is weak base because it can act as proton acceptor. $H_2O(l) + NH_3(aq) \leftrightharpoons OH^-(aq) + NH_4^+(aq)$ Ammonia can be displaced from its salt when strong base is added. $NH_4Cl(aq) + NaOH(aq) \rightarrow NaCl(aq) + NH_3(aq) + H_2O(l)$

Environmental issues

Compounds	Environmental problems	Original sources
Sulphur dioxide	**Acid Rain:** reaction takes place in atmosphere $SO_2 + O_2 \rightarrow SO_3$ $SO_3 + H_2O \rightarrow H_2SO_4$ Acid rain is sulfuric acid.	Combustion of fossil fuel
Nitrogen oxide	**Acid Rain:** reaction takes place in atmosphere NO_2 acts as catalyst in the oxidation of SO_2. $SO_2 + NO_2 \rightarrow SO_3 + NO$ $2NO + O_2 \rightarrow 2NO_2$ **Photochemical smog:** Oxides of nitrogen (NO and NO_2) can react with unburned hydrocarbons to form peroxyacetyl nitrate, PAN, which is a component of photochemical smog.	Car Exhaust

Nitrogen oxides can be removed from car exhaust by catalytic converter

$$4CO(g) + 2NO_2(g) \rightleftharpoons 4CO_2(g) + N_2(g)$$

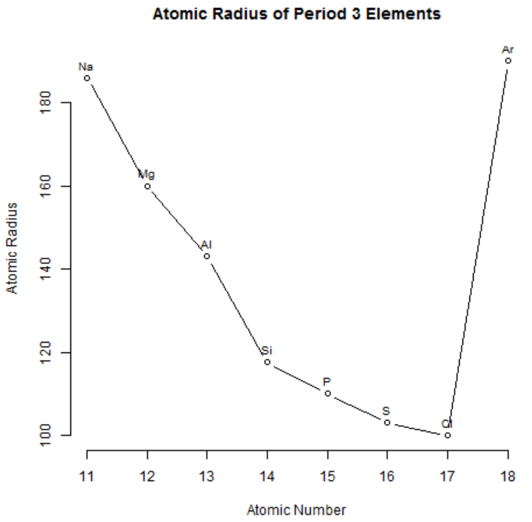
The reaction is catalyzed by platinum.

Period 3

Periodicity of Physical Properties

Radius

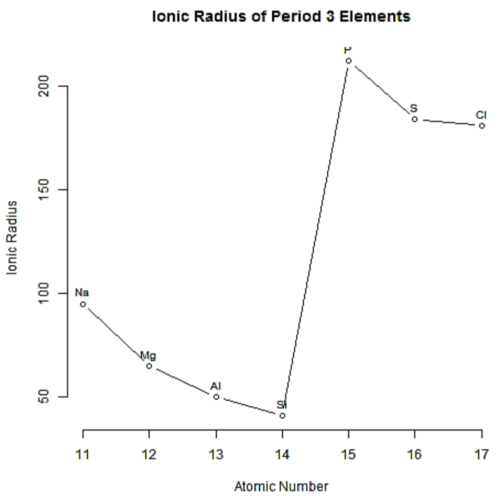
1. Plot *atomic radii* against atomic number for the elements in Period 3 and explain the trend.



For the elements across period 3, they have similar shielding effect, but their nuclear charge increased. Thus, the attraction between nuclear and electrons become greater across the period, result in decreased atomic radius.

The atomic radius of argon is anomaly high because they are held by id-id.

2. Plot *ionic radii* against atomic number for the elements in period 3.



Explain

a. The change of ionic radii compared with its atomic radii.

From Na to Si, ionic radii are smaller than atomic radii, since ions have one shell less than atoms. Thus, the attraction between nuclear and electrons is greater in ions result in smaller radius.

From P to Cl, ionic radii are bigger than atomic radii, since ions have more electrons. Because of the repulsion between electrons, the attraction between nuclear and electrons is weaker in ions result in bigger radius.

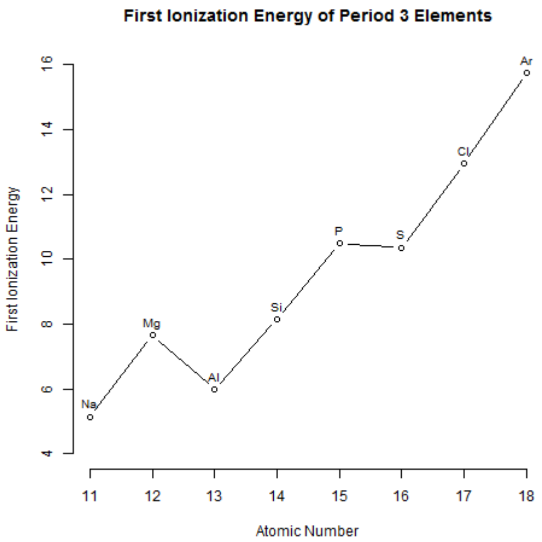
b. The trend of ionic radii (from Na to Si & from P to Cl)

From Na to Si, their ions have the same electron number, but nuclear charge increased as proton number increased. Thus the attraction between nuclear and electrons is increasing result in decreasing radius.

From P to Cl, their ions have the same electron number, but nuclear charge increased. Thus the attraction between nuclear and electrons is increasing result in decreasing radius.

First ionization energy

Plotting the *first ionization energy* against atomic number for the elements in period 3.



Explain

a. The general increase of 1st IE.

b. Nuclear charge increases across the period while their shielding effects remain almost constant. The distance of outermost electron from nuclear decreases, thus takes more energy to remove electrons away.

b. The fluctuation

Mg to Al

Outermost electron of magnesium is at 3s while that of aluminum is at 3p. 3p electron is more shielded than 3s electron, so it take less energy to remove them.

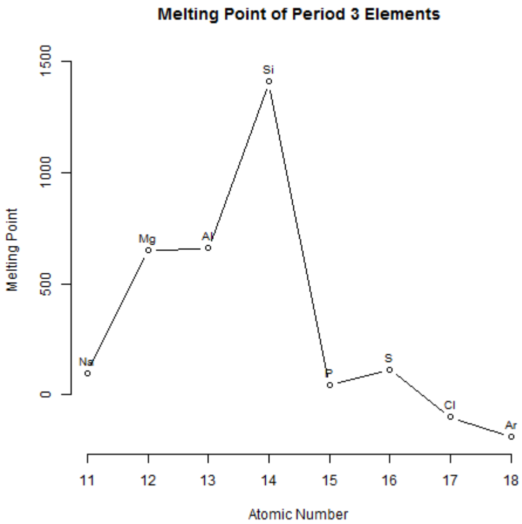
P to S

The 3p orbitals of phosphorous are singly filled while that of Sulphur has paired electrons in it. Paired electrons tend to repel each other, so it takes less energy to remove them.

- Physical properties such as atomic size, ionic size, electronegativity and ionization energy all depend on nuclear attraction.
- Larger attraction, smaller atomic size, higher electronegativity and higher ionization energy.
- Nuclear attraction is decided by nuclear charge and shielding effect.

Melting point

1. **Plot *melting point* against atomic number for the elements in period 3. Draw the structure of each element.**



Explain

a. The increase of m.p from Na to Al

They are metallic structure and metallic bond needs to be broken during melting. From Na to Al, metallic bond strength increased as charge density of cations increased, thus more energy is needed to melt.

Not all the outer electrons in aluminum is delocalized because the charge density of Al^{3+} is very big. Thus, the increase of melting point from Mg to Al is not obvious.

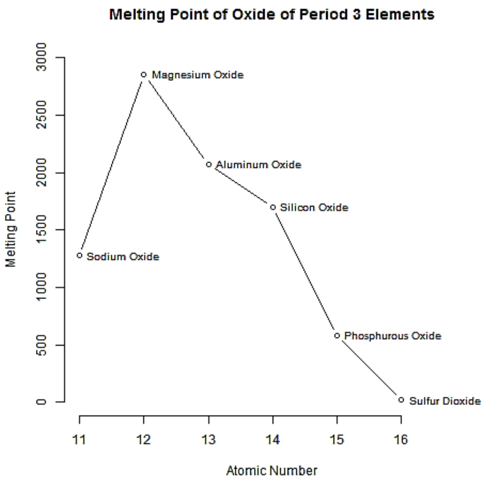
b. The high m.p of Si.

It is giant molecules and covalent bond need to be broken during melting. Covalent bond is very strong, thus large amount of energy is needed to melt it.

c. The variation of m.p form P to Ar

They are simple molecules and van der waal force need to be broken during melting. Van der waal force increased as number of electrons increased, element S greatest amount of electrons because there are 8 sulfur atoms in each molecule while Argon has fewest amount of electrons because it is monoatomic.

2. **Plot *melting point* against atomic number for the oxides of elements in period 3. Draw the structure of each oxide.**



Explain

a. The increase of m.p from Na_2O to MgO.

Both of them are ionic structure and ionic bonds need to be broken before melting. Ionic bond of MgO is stronger than Na_2O due to its higher charge density.

Al_2O_3 is ionic compound with covalent character, thus have lower melting point than MgO.

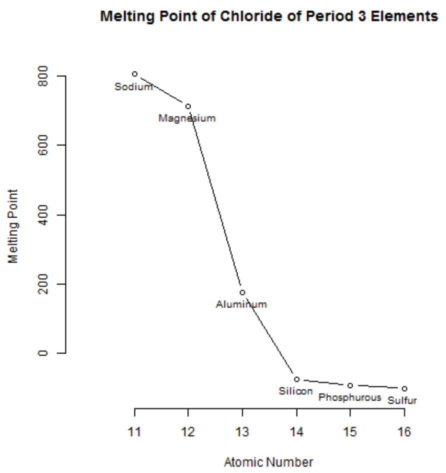
b. The high m.p of SiO_2.

It is giant molecules and covalent bond need to be broken during melting. Covalent bond is very strong, thus large amount of energy is needed to melt it.

c. The different of m.p of P_4O_{10} and SO_2

They are simple molecules held by weak van der waal's force. Van der waal force increased as number of electrons increased. So P_4O_{10} has higher melting point than SO_2.

3. **Plot the *melting point* against atomic number for the *chlorides* of elements in period 3. State the structure of each chloride.**



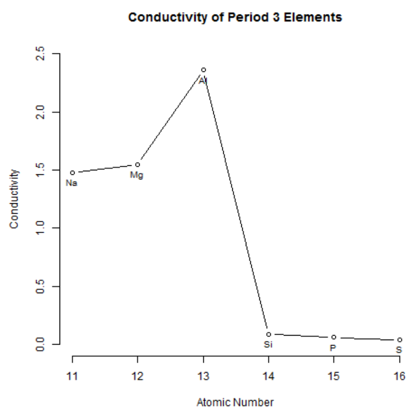
Sodium chloride and magnesium chloride is ionic structure. Ionic bond need to be broken before it melts.

Aluminum chloride, silicon chloride and sulfur chloride are simple molecules and van der waal's force need to be broken before it melts.

Al_2Cl_6 has much more electrons than other chloride, thus its van der waal's force is significantly stronger.

Conductivity

Plotting the *conductivity* against atomic number for the elements in period 3.



Explain

1. **The increase of conductivity from Na to Al**

They are metallic structure and be able to conduct electricity due to the delocalized electrons in it. The number of delocalized electrons increased from Na to Al, thus conductivity increase in the same way.

2. **The special character of Si.**

It is semi-conductor.

3. **The non-conductors: P, S, Cl.**

No mobile charged particles in them.

Periodicity of Chemical Properties

Reaction with oxygen

Elements	Reaction with O_2	Observation	Reaction of the oxide with water	pH of the resulting solution
Na	$4Na + O_2 \rightarrow 2Na_2O$	Yellow Flame	Basic oxide: $Na_2O + H_2O \rightarrow 2NaOH$	14
Mg	$2Mg + O_2 \rightarrow 2MgO$	White Flame	Basic oxide: $MgO + H_2O \rightarrow Mg(OH)_2$ The reaction is very slight, since $Mg(OH)_2$ is almost insoluble	10
Al	$4Al + 3O_2 \rightarrow 2Al_2O_3$	White Flame	Amphoteric oxide: Reaction with HCl: $Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$ Reaction with NaOH: $Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$	Insoluble in water
Si	$Si + O_2 \rightarrow SiO_2$	Slow Reaction	Acidic oxide: Reaction with NaOH $SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$	Insoluble in water
P	$4P + 5O_2 \rightarrow 2P_2O_5$	Yellow Flame	Acidic oxide: $P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$	3
S	$S + O_2 \rightarrow SO_2$	Blue Flame	Acidic oxide: $SO_2 + H_2O \rightarrow H_2SO_3$	3

For combustion reaction, strong heat is needed to help substance to overcome the high activation energy.

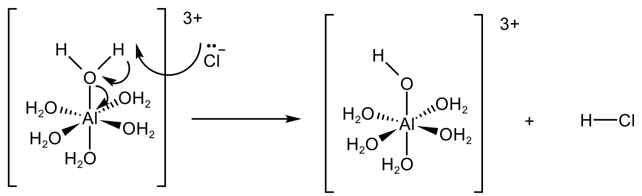
In aqueous solution, there is no covalent bond in aluminum chloride and they exist as free ions. Note that although aluminum oxide can react with both acid and base, it is actually very inert. It only reacts with strong acid and strong base.

Ionic oxide is basic oxide while simple molecule is acidic oxide.

Reaction with chlorine

Elements	Reaction with Cl_2	Observation	Reaction of the chloride with water	pH of the solution
Na	$2Na(s)+Cl_2(g) \rightarrow 2NaCl(s)$	Yellow Flame and gives white solid	$NaCl(s)+ aq \rightarrow Na^+(aq)+Cl^-(aq)$	7
Mg	$2Mg(s) + Cl_2(g) \rightarrow 2MgCl_2(s)$	White Flame and gives white solid	$MgCl_2(s)+ aq \rightarrow Mg^{2+}(aq)+ 2Cl^-(aq)$	6.5
Al	$2Al(s) + 3Cl_2(g) \rightarrow Al_2Cl_6(s)$	Aluminum glows when pass heated dry chlorine over it and gives white solid	Two reactions take place when aluminum chloride dissolve in water Dissolve: $Al_2Cl_6(s)+ aq \rightarrow 2Al^{3+}(aq) + 6Cl^-(aq)$ Hydrolysis: $[Al(H_2O)_6]^{3+}(aq) \rightarrow [Al(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$ Endothermic reaction and gives an acidic solution $Al_2Cl_6(s) + 12H_2O(l) \rightarrow [Al(H_2O)_5(OH)]Cl_2(aq)+ 2HCl(aq)$	3
Si	$Si(s) + 2Cl_2(g) \rightarrow SiCl_4(l)$	Slow reaction and gives colorless liquid	$SiCl_4 (l)+ 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(aq)$ White precipitate and fume forms	2
P	$2P(s) + 5Cl_2(g) \rightarrow 2PCl_5(s)$	White flame and gives pale yellow solid	$PCl_5(s)+ 2H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$	1

Ionic chlorides dissolve in water while molecular chlorides hydrolyze in water.



Aluminum chlorides hydrolyze in water because the charge density of Al^{3+} is too high; thus, it takes an electron of a hydrogen and release a proton, resulting in acidic solution.

Group II & VII

Group II

Reaction with water

Element	Color of Flame test	Reaction with water	Observation	pH	Solubility	
					OH^-	SO_4^{2-}
Be				INCREASE	INCREASE	DECREASE
Mg	White	$H_2O(l)$: $Mg(s) + 2H_2O(l) \rightarrow Mg(OH)_2(s) + H_2(g)$	Very slow reaction			
		$H_2O(g)$: $Mg(s) + 2H_2O(g) \rightarrow MgO(s) + H_2(g)$	Magnesium glows when passing heated water steam over it			
Ca	Red	$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$	Vigorous reaction with effervescence			
Sr	Red	$Sr + 2H_2O \rightarrow Sr(OH)_2 + H_2$				
Ba	Green	$Ba + 2H_2O \rightarrow Ba(OH)_2 + H_2$				

Try to explain the trend of their reaction with water down the group.
Atomic radius increases down the group, thus outer electrons are becoming further away from the nuclei. Elements down the group get higher tendency to lose electrons, so reaction with water become more vigorous down the group.
State the use of calcium carbonate and calcium hydroxide in agriculture.
Neutralize acidic soil.

Thermal Decomposition of Group II Carbonates and Nitrates

Elements	Thermal Decomposition of Carbonates	Thermal Decomposition of Nitrates	Thermal Decomposition of Hydroxides	Decom-position Temperature
Mg	$MCO_3 \rightarrow MO + CO_2$	$2M(NO_3)_2 \rightarrow 2MO + 4NO_2 + O_2$ Brown gas is evolved.	$M(OH)_2 \rightarrow MO + H_2O$	INCREASE
Ca				
Ba				

Group VII

Reaction with Hydrogen

Element	State at r.t.p	Color	Reaction with Hydrogen	Observation	Bond Strength of H-X	Thermal Stability of HX
F_2	Gas	Pale yellow	$F_2(g)+H_2(g) \rightarrow 2HF(l)$	Explode in dark	DECREASE	DECREASE
Cl_2	Gas	Pale green	$Cl_2(g)+H_2(g) \rightarrow 2HCl(g)$	Explode in direct sunlight		
Br_2	Liquid	Brown	$Br_2(g)+H_2(g) \rightarrow 2HBr(g)$ The reaction is easily reversed when E_a is provided.	React when heated		
I_2	Solid	Grey	$I_2(g)+H_2(g) \rightleftharpoons 2HI(g)$ Decomposition of HI is quite easy.	React reversibly with the presence of catalyst		

Iodine is grey-black when solid, purple when gas, deep blue when combined with starch， orange when dissolved in aqueous KI.

Try to explain the boiling point down the group.

For elements, they are simple molecules and held by weak van der waal's force, which increase as the number of electrons increase. Thus, melting point increases down the group.

For hydrides, melting points increase down the group because van der waal's force increases down the group. While HF is an exception because they are held by hydrogen bond which is stronger than id-id and pd-pd.

Displacement Reaction between Halogen

Give observation of the following reaction if reaction takes place.

Halogen added	NaCl(aq)	NaBr(aq)	NaI(aq)
$Cl_2(g)$	No Reaction	solution turn brown	solution turn orange initially, form black ppt after a while
$Br_2(l)$	No Reaction	No Reaction	solution turn orange initially, form black ppt after a while
$I_2(s)$	No Reaction	No Reaction	No Reaction

Give equations of reactions take place.

Reaction 1 $\mathrm{Cl_2(aq) + 2NaBr(aq) \rightarrow 2NaCl(aq) + Br_2(aq)}$

Reaction 2 $\mathrm{Cl_2(aq) + 2NaI(aq) \rightarrow 2NaCl(aq) + I_2(s)}$

Reaction 3 $\mathrm{Br_2(aq) + 2NaI(aq) \rightarrow 2NaBr(aq) + I_2(s)}$

$$Cl_2(aq) + 2NaBr(aq) \rightarrow 2NaCl(aq) + Br_2(aq)$$

If a displacement reaction takes place, the element at LHS must be more reactive than the element at RHS. In reaction 1, chlorine is more reactive than bromine, so it can displace bromine from its compound.

Reaction with concentrated sulfuric acid

Halide Ion	Reaction of Halide with conc. sulfuric acid	Observation	Explanation
Chloride	$NaCl + H_2SO_4 \rightarrow HCl + NaHSO_4$	Fume	Larger the anion, higher the tendency to lose electron. Thus, the reducing power increases down the group.
Bromide	$NaBr + H_2SO_4 \rightarrow HBr + NaHSO_4$	Fume	
	$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$	Brown gas evolved	
Iodide	$NaI + H_2SO_4 \rightarrow HI + NaHSO_4$	Fume	
	$2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$	Purple gas evolved	
	$6HI + H_2SO_4 \rightarrow 3I_2 + S + 4H_2O$	Purple gas evolved, yellow solid formed	
	$8HI + H_2SO_4 \rightarrow 4I_2 + H_2S + 4H_2O$	Purple, smelly gas evolved	

In the following reaction sulfuric acid is oxidant while bromine is the oxidized product.

$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$

If a redox reaction takes place, the oxidant has stronger oxidizing power than its than its oxidized product. The reaction tells us that sulfuric acid has stronger oxidizing power than bromine.

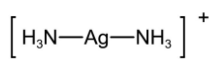
Strongest Oxidant	$\mathbf{F_2}$	$\rightarrow$	HF	
oxidizing power decrease	Cl_2	$\rightarrow$	HCl	*reducing power increase*
down the group	Br_2	$\leftrightharpoons$	HBr	*down the group*
	I_2	$\leftrightharpoons$	**HI**	**Strongest Reductant**

Testing for Halide Ions

Halide Ion	Color of silver halide	Addition of Dilute Ammonia water	Addition of Concentrated Ammonia water
Chloride	White precipitate	Dissolve	Dissolve
Bromide	Cream precipitate	Not Dissolve	Dissolve
Iodide	Yellow precipitate	Not Dissolve	Not Dissolve

Give equation to show the reaction between silver halide and ammonia.

$$AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]Cl(aq)$$



A complex is formed in this reaction

Reactions Involve Chlorine

Disproportionation

A reaction in which same species that is oxidized and reduced in a same reaction.

Chlorine with cold alkali

Cl_2 + 2NaOH → NaCl + NaOCl + H_2O

Sodium Chlorate(I)

Chlorine with hot alkali

3Cl_2 + 6NaOH →5 NaCl + $NaClO_3$ + 3H_2O

Sodium Chlorate(V)

Use of Chlorine

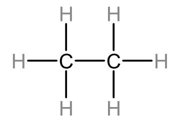
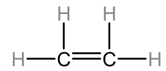
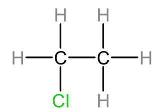
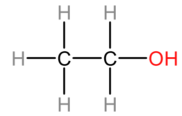
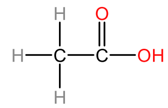
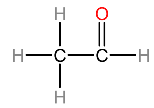
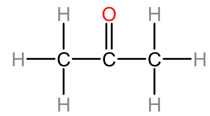
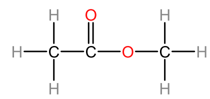
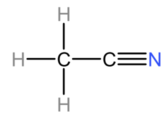
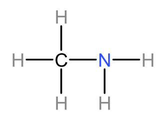
Disinfection kill bacteria

Bleach Cl_2 +H_2O → HCl + **HOCl**

HOCl is the active component.

Basic Organic Chemistry

Homologous series

Groups	General Formula	Functional Group	Characteristic of its name	Example	Reactions involved
Alkane	C_nH_{2n+2}		-ane		1. Free radical substitution 2. Cracking
Alkene	C_nH_{2n}	C=C	-ene		1. Electrophilic addition 2. Oxidation
Halogeno-alkane	$C_nH_{2n+1}X$	-X	chloro- bromo-		1. Nucleophilic substitution 2. Elimination
Alcohol	$C_nH_{2n+2}O$	-OH	-ol		1. Nucleophilic substitution 2. Elimination 3. Esterification 4. Oxidation
Carboxylic Acid	$C_nH_{2n}O_2$	-COOH	-oic acid		1. Acidic reaction 2. Esterification 3. Reduction
Aldehyde	$C_nH_{2n}O$	-CHO	-al		1. Nucleophilic addition 2. Condensation 3. Oxidation
Ketone	$C_nH_{2n}O$	-CO-	-one		1. Nucleophilic addition 2. Condensation
Ester	$C_nH_{2n}O_2$	-COO-	-yl -oate		1. Hydrolysis
Nitrile	$C_nH_{2n-2}N$	-CN	-ane nitril		1. Hydrolysis 2. Reduction
Amine	$C_nH_{2n+3}N$	$-NH_2$	-lamine		1. Nucleophilic substitution

Nomenclature

Terms for nomenclature

Number of Carbon atoms	One	Two	Three	Four	Five	Six
Prefix	Meth-	Eth-	Prop-	But-	Pent-	Hex-

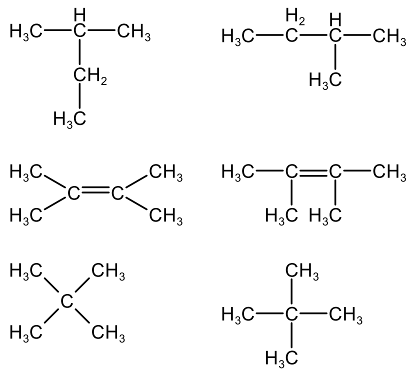
Homologous Series	Alkane	Alkene	Alcohol	Carboxylic acid	Aldehyde	Ketone	Ester
Suffix	-ane	-ene	-ol	-oic acid	-al	-one	-yl -oate

Functional group	F	Cl	Br	I	-OH	-CN	
name	Fluoro-	Chloro-	Bromo	Iodo-	Hydroxyl-	Nitrile-	

Steps for nomenclature

Step 1 find the longest chain

Compounds should be rearranged to make sure the main chain (parent chain) has largest carbon number.

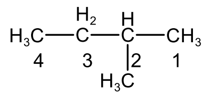


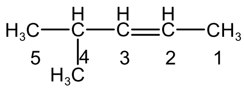
These are two different ways to show the same molecule.

The representation at the right will be preferred, since it put all the possible carbons in parent chain.

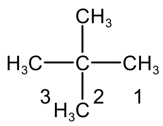
Step 2 order the carbon on the main chain

The end closer to branches or functional group should be named as the first carbon.

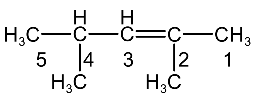




Step 3 end the name with suffix



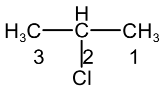
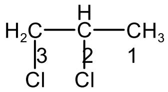
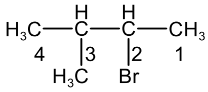
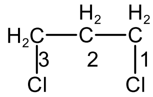
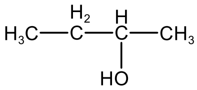
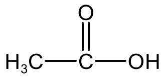
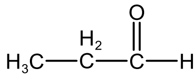
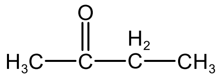
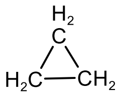
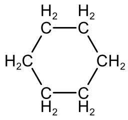
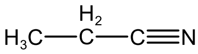
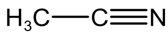
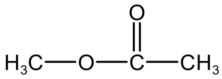
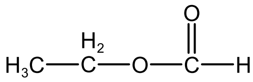
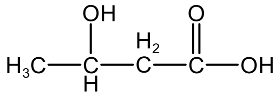
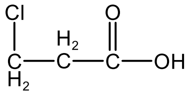
Dimethylpropane



2,4-dimethylpent-2-ene

Arabic number is used to show the position of functional group. Comma separates Arabic numbers. Hyphen separates letters and numbers.

Give names of the following organic compounds

			
2-chloropropane	1,2-dichloropropane	2-bromo-3-methylbutane	1,3-dichloropropane
			
Butan-2-ol	Ethanoic acid	prapanal	Butone
			
Cyclopropane	Cyclohexane	Propanenitrile	Ethanenitrile
			
Methyl ethanoate	Ethyl methanoate	3-hydroxybutanoic acid	3-chloropropanoic acid

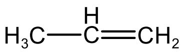
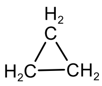
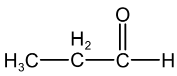
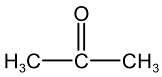
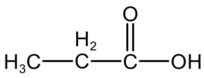
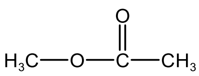
When there are more than one functional group and one of them is carboxylic acid. We name the whole compound as an acid.

Isomers

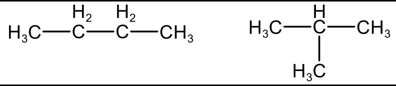
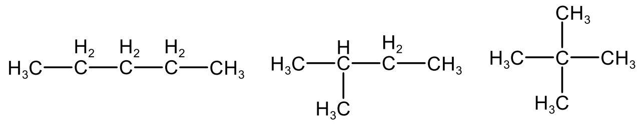
Structural isomer are compounds with the same molecular formula but different structure.
There are three kinds of structural isomer:

Functional group isomer: Isomers have different functional group.
Chain isomer: isomers with different carbon arrangement.
Position isomer: isomers with the same carbon arrangement but have their functional group at different position.

Functional Group Isomer

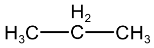
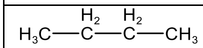
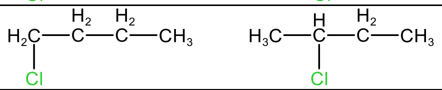
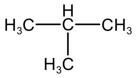
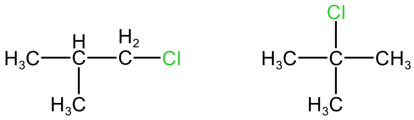
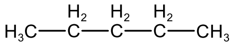
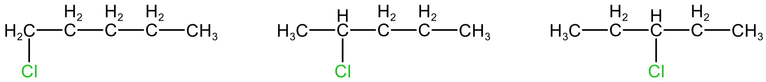
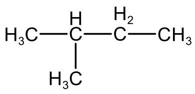
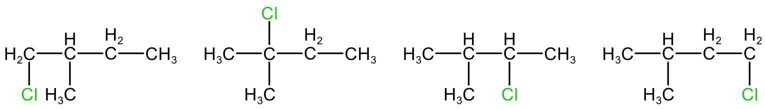
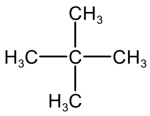
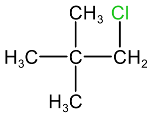
Formula	Isomer1	Isomer2
C_nH_{2n}		
C_3H_6	Propane	Cyclopropane
$C_nH_{2n}O$		
C_3H_6O	Propanal	Propanone
$C_nH_{2n}O_2$		
$C_3H_6O_2$	Propanoic acid	Methyl propanoate

Chain isomers

Carbon number	Chain isomers
4	
5	

Chain isomer exists only when there are more than three carbon atoms in the compound.

Position isomer

Chain	Position isomers
	
	
	
	
	
	

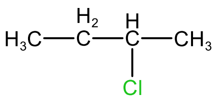
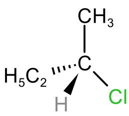
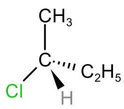
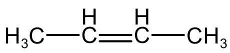
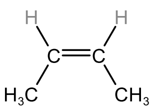
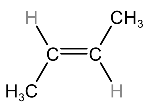
If two methyl groups bond with the same carbon, they are symmetrical to each other. Thus, the chlorine atom bond with either methyl group would produce the same isomer.

Stereoisomer are compounds with the same structure but different arrangement in space.

There are two kinds of stereoisomer:

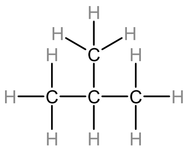
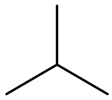
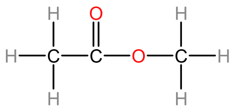
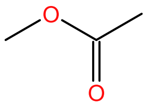
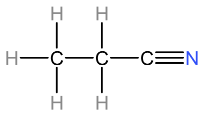
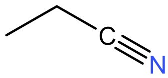
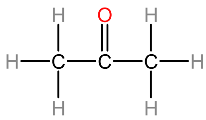
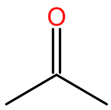
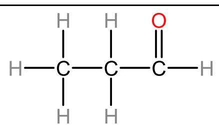
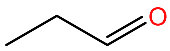
Optical isomer: compounds form non-superimposable mirror image, due to chiral center. Chiral centre is the carbon bonds with four different groups.

Geometrical isomer: cis-trans isomer due to the block of free notation by π bond.

Structure	Isomer 1	Isomer 2
		
	 cis but-2-ene	 trans but-2-ene

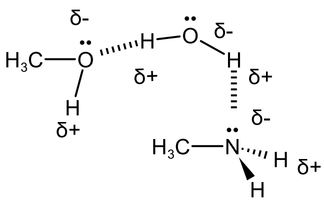
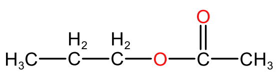
If both carbon with π bond connects with two different groups, there are geometrical isomers.

Formulae

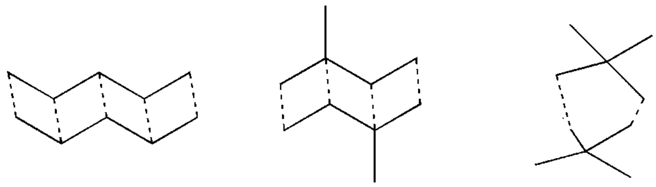
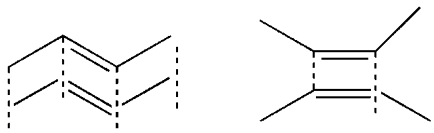
Type of Formula	Structure Formula	Displayed Formula	Skeletal Formula
Methyl propane	$(CH_3)_3CH$		
Methyl ethanoate	$CH_3CO_2CH_3$		
Propane nitrile	CH_3CH_2CN		
Propanone	CH_3COCH_3		
Propanal	CH_3CH_2CHO		

Physical Property of Organic Compound

Solubility

Organic Compounds	Polar Solvent H_2O	Non-Polar Solvent $CHCl_3$	Explanation
Hydrocarbon	insoluble	soluble	Easer for hydrocarbon to form id-id with non-polar solvent.
Alcohol & Carboxylic Acid	soluble	insoluble	Easier for them to form hydrogen bond with water. 
Ester	insoluble	soluble	No hydrogen atom bonded to oxygen atom in ester, so hard for them to form hydrogen bond with water. 

Boiling Point

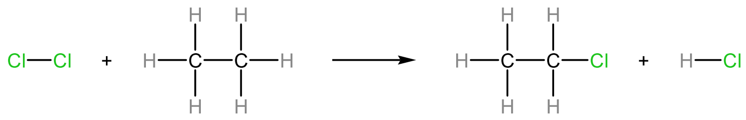
Across Homologous Series		Hydrocarbon	Carbonyl Compound	Alcohol & Carboxylic Acid
	State at room temperature	Gas when carbon number is less than 4.	Volatile liquid	Liquid even when carbon number is 1.
	Explanation	Weak id-id between hydrocarbon molecules requires little energy to break. Permanent dipole force between carbonyl compounds requires more energy to break compared with id-id. Hydrogen bond between alcohol and carboxylic acid, require a lot energy to break.		
Within Homologou		CH_4	C_2H_6	C_3H_8
	Trend	Boiling point increases as number of carbon increases		
	Explanation	Id-id force between hydrocarbon increased as the number of electrons increase.		
Chain Isomer		$CH_3CH_2CH_2CH_2CH_3$	$(CH_3)_2CHCH_2CH_3$	$(CH_3)_4C$
	Trend	Boiling point decreases as number of branch increases		
	Explanation	 More branch of the molecules, harder for them to be packed together weakening V.D.W		
Stereo Isomer		Cis but-2-ene	Trans but-2-ene	
	Trend	INCREASE		
	Explanation	 Easier for trans-structure to be packed together		

Alkane

Substitution

Mechanism	Reagent	Product (family)	Condition
Free Radical Substitution	Cl_2	Halogenoalkane	Ultra Violet Light

Use the reaction of CH_4 and Cl_2 as example. Give both symbol equation (show the structure of each chemical) and word equation.



chloromethane

Combustion

Use the complete combustion of C_xH_y as example. Balance the equation

$$C_xH_y + \left(x + \frac{y}{4}\right) O_2 \rightarrow xCO_2 + \frac{y}{2} H_2O$$

Give the equation when large hydrocarbon ($C_{20}H_{42}$) is burnt.

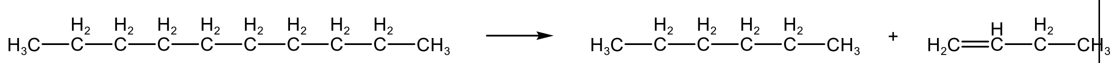
$$C_{20}H_{42} + 20\frac{1}{2}O_2 \rightarrow 10CO_2 + 21\ H_2O + 10C$$

For long chain hydrocarbon, its incomplete combustion may produce graphite as well.

Cracking

Product (family)	Condition1	Condition2
Alkane + Alkene	High Temperature Catalyst	High Temperature High Pressure

Use the cracking of $C_{10}H_{22}$ as example. One of the products is C_6H_{14}. Give both symbol equation (show the structure of each chemical) and word equation.



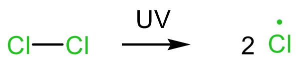
decane hexane butene

The products of cracking are at radon. Any C-C bond can be broken in the process. It is even possible to just get a hydrogen and dectene.

Mechanism -free radical substitution

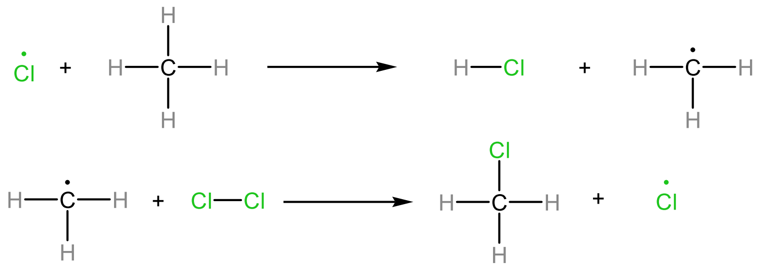
Describe the Mechanism of Substitution. Use CH_4 and Cl_2 as example

1. **Initiation**



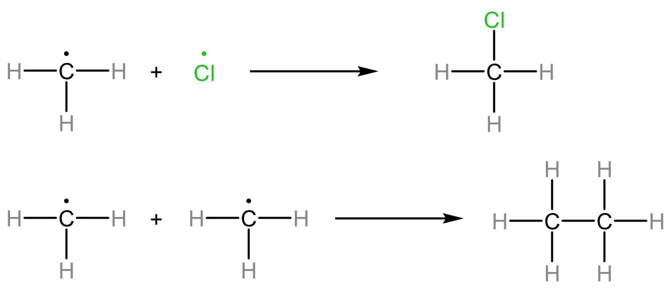
This is **homolytic fission**, because bond electrons are equally shared by bonding atoms when covalent bond breaks.
The chlorine atom is called **free radical**, because it has an unpaired electron.
In initiation, a molecule breaks into two free radicals.

2. **Propagation (give at least 2 different equations)**



In propagation, a molecule reacts with a free radical and forms a new molecule and a new free radical.

3. **Termination (give at least 2 different equations)**



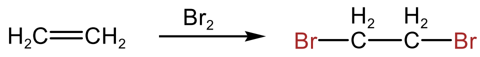
In termination, two free radical joint to form a new molecule.

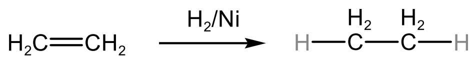
Alkene

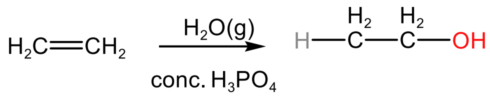
Electrophilic Addition

	Reagent	Product (Family)	Condition		Use
			Temperature	Catalyst	
1	Bromine water	Halogenoalkane	Room temperature	NA.	Test for C=C
2	Hydrogen Bromide	Halogenoalkane	Room temperature	NA.	
3	Steam	Alcohol	Heat	Phosphorous Acid	Manufacture of Alcohol
4	Hydrogen	Alkane	Heat	Nickel	

Use ethene as example. Give both symbol equation (show the structure of each chemical) and the name of products.

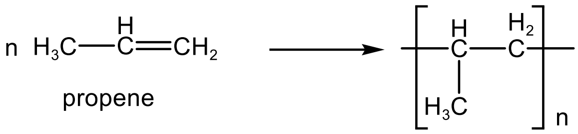

1,2-dibromoethane




ethanol

Additional polymerisation

Show the polymerization of propene. Give symbol equation (show the structure of each chemical) and the name of product.



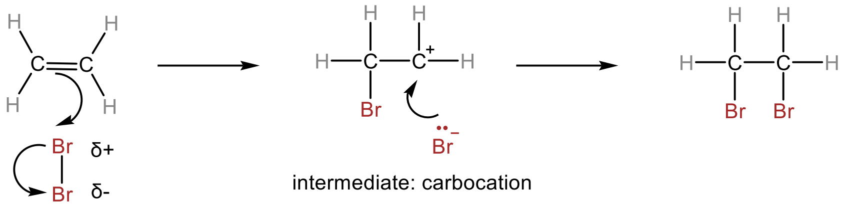
polypropene

Use of Polymer	Environmental Problem
Plastic	1. Non-biodegradable; waste landfill sites 2. Produce toxic gas on combustion

Mechanism-Electrophilic Addition

Use C_2H_4 and HBr as example to show the mechanism of this electrophilic addition.

Use curve arrows to describe the movement of electrons

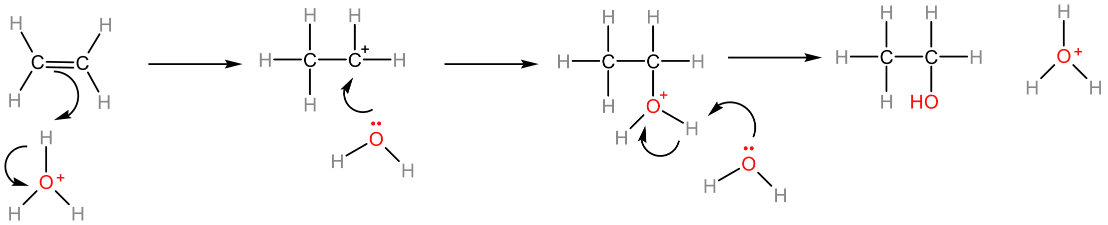


Bromine molecule acts electrophile, because it accepts a pair of electrons from the π bond.

Bromine molecule is non-polar. The dipole is induced by the presence of double bond.

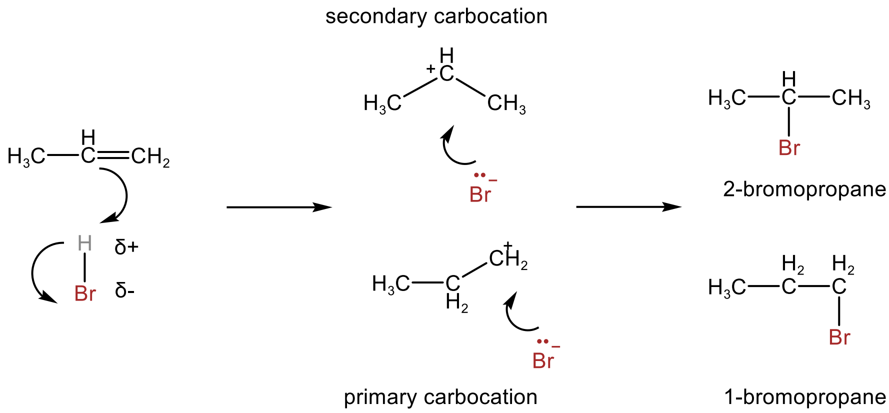
Use C_2H_4 and steam as example to show the mechanism of this electrophilic addition.

Use curve arrows to describe the movement of electrons



Use C_3H_6 and HBr as example to show the mechanism of this electrophilic addition and their two products. Explain which one is the major product.

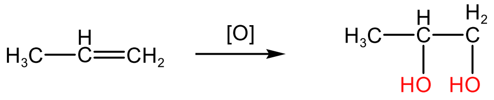
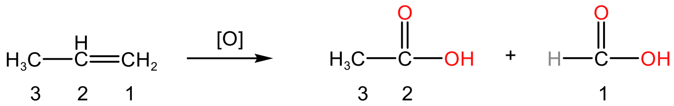
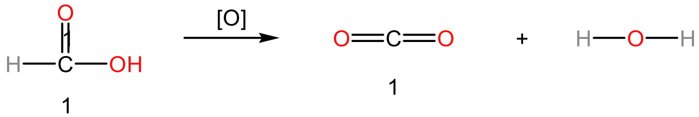
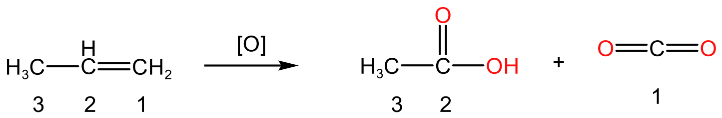
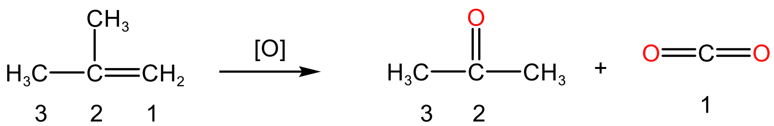
Use curve arrows to describe the movement of electrons



2-bromopropane is the major products because it is formed via secondary carbocation while 1-bromopropane is from primary carbocation. Secondary carbocation is more stable than primary carbocation because alkyl groups is electron releasing and able to reduce the charge density on carbocation.

H tend to be added to the carbon with more H according to Markovnikov's rule

Oxidation

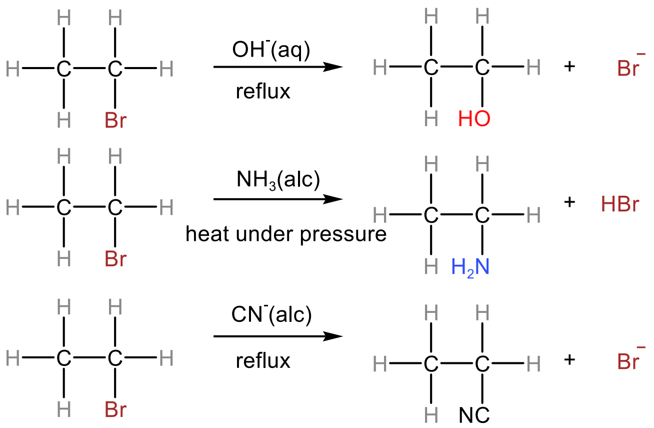
<table>
<tr><td colspan="2">Oxidant</td><td>Condition</td></tr>
<tr><td>Name</td><td>Acidified Potassium Manganate (VII)</td><td>cold dilute： π bond is broken and a diol is produced
</td></tr>
<tr><td>Formula</td><td>$KMnO_4/H^+$</td><td rowspan="3">Hot concentrated: both the σ bond and the π bond are broken. So, the molecule breaks into two.

If the carbon atom (with π bond) bonds with hydrogen, it would be oxidized into carboxylic acid.

If methanolic acid is formed, it will be further oxidized into carbon dioxide.

Thus, the overall reaction concerning oxidation of propene can be written in this way.

For the carbon bonds with no hydrogen, it will be oxidized into a ketone.</td></tr>
<tr><td>Oxidation number</td><td>+7 → +2</td></tr>
<tr><td>Color change</td><td>Purple to colorless</td></tr>
</table>

Halogenoalkane

Nucleophilic Substitution

Reagent		Product (family)	Condition	
			Reflux	Solvent
1	Hydroxide	alcohol	YES	Water
	OH^-	-OH		
2	Ammonia	amine	YES	Ethanol
	NH_3 Heat under pressure	- NH_2		
3	Cyanide	nitril	YES	Ethanol
	CN^-	-CN		

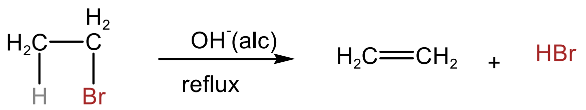
Use bromoethane as example. Give both symbol equation (show the structure of each chemical).



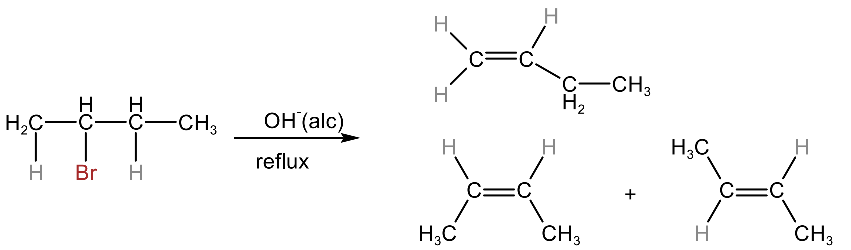
Elimination

Reagent	Product	Reflux	Solvent
alkali	alkene	YES	ethanol

Use Bromoethane as example. Give both symbol equation (show the structure of each chemical).



For 2-bromobutane, the bromine atom can eliminate with the hydrogen on both sides.



cis but-2-ene

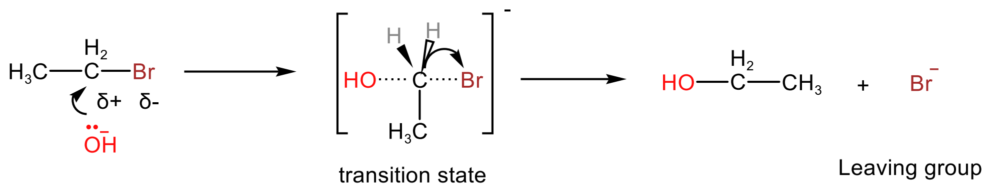
trans but-2-ene

This elimination reaction gives three different isomers. Because but-2-ene has geometrical isomers

Mechanism-nucleophilic substitution

Use C_2H_5Br and OH^- as example to show the mechanism of this reaction.

S_N2

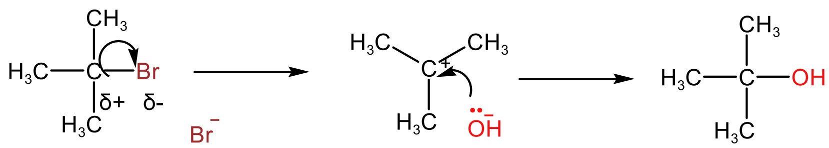


Hydroxide attack the carbon from the opposite site of C-Br bond. C-O bond is forming while C-Br bond is breaking, so both bonds are represented by dash line. Bromide is squeezed out by hydroxide; it is called leaving group.

Primary halogenoalkane proceeds in S_N2 pathway.

Use $(CH_3)_3CBr$ and OH^- as example to show the mechanism of this reaction.

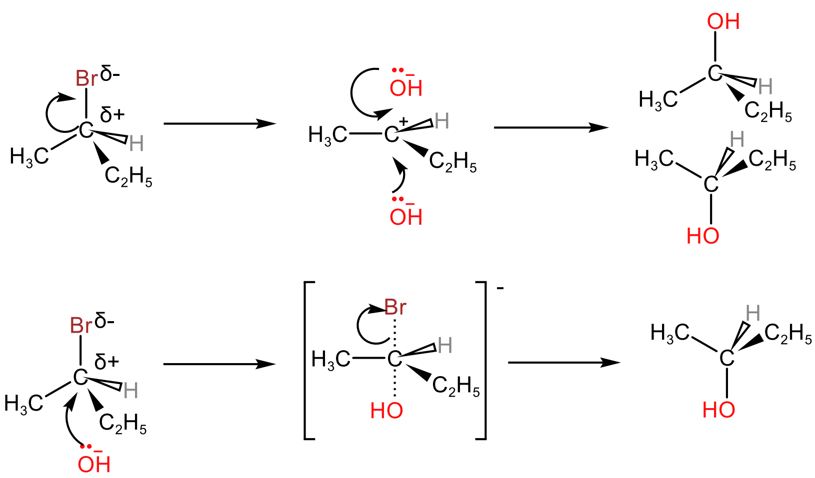
S_N1



Tertiary halogenoalkane proceeds in S_N1 pathway.

C-Br bond breaks to form a carbocation which is then attacked by nucleophile.

Why optical isomers may be produced when nucleophilic substitution proceed by S_N1 mechanism.



In S_n1 mechanism, nucleophile may attack carbocation in both directions, giving rise to a chiral center. Because the chances been attacked in both directions are equal, two isomers in equal amount.

In S_{n2} mechanism, nucleophile can attack the molecule only in one direction.

Secondary halogenoalkane tends to proceed through both S_N1 and S_N2 pathway.

Hydrolysis of halogenoalkane

Warm halogenoalkane in aqueous silver nitrate solution, precipitate will appear. The following reactions take place.

Hydrolysis of halogenoalkane: $C_2H_5X + H_2O \rightarrow C_2H_5OH + HX$

X can be Cl, Br or I.

Precipitation of silver halide: $HX(aq) + AgNO_3(aq) \rightarrow AgX(s) + HNO_3(aq)$

The time it takes for the appearance of precipitate depends on the rate of hydrolysis while the rate of hydrolysis depends on the bond energy of C-X.

The time it takes for precipitate appear:

$$C_2H_5Cl > C_2H_5Br > C_2H_5I$$

Iodine has largest atomic size thus C-I bond is weakest while chlorine has the smallest atomic size thus C-Cl bond is strongest among the three.

Application of ammonia water can be used to distinguish the halogen atoms.

Halogen	Color of Precipitate	Dilute ammonia water	Conc. ammonia water
Chlorine	White	Dissolve	Dissolve
Bromine	Cream	Not dissolve	Dissolve
Iodine	Yellow	Not dissolve	Not dissolve

Nitrile

Hydrolysis		
Reagent	Product (family)	Equation
Acidic Hydrolysis	Functional Group Carboxylic acid	$H_3C{-}C{\equiv}N + 2H_2O \xrightarrow[\text{heat}]{H^+} H_3C{-}C(=O){-}OH + NH_4^+$
Basic Hydrolysis	Functional Group Salt	$H_3C{-}C{\equiv}N + H_2O + OH\text{-} \xrightarrow[\text{heat}]{OH^-} H_3C{-}C(=O){-}O^- + NH_3$

Reduction		
Reagent	Product (family)	Equation
Formula $LiAlH_4$	Functional Group $-NH_2$	$H_3C{-}C{\equiv}N + 4[H] \xrightarrow{LiAlH_4} H_3C{-}CH_2{-}NH_2$

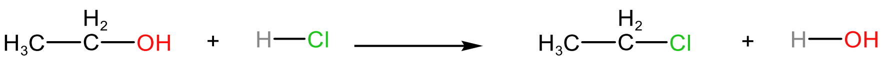
Alcohol

Substitution and Reduction

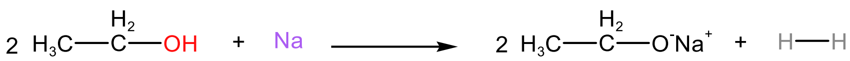
Type of Reaction	Reagent Name & Formula	Condition Reflux	Product	Observation
Substitution	HCl	YES	Chloroethane	
	PCl_5	NO		FUME
	PCl_3	YES		
	$SOCl_2$	NO		FUME
Reduction	Na	No	Sodium ethoxide	Bubble

Example

1. Give an equation (show the structure of reagents and products) of the reaction between HCl and C_2H_5OH



2. Give an equation (show the structure of reagents and products) the reaction between Na and C_2H_5OH



3. Give an equation to show the substitution reaction of ethanol and PCl_5, $SOCl_2$ and PCl_3 respectively.

$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + HCl + POCl_3$

$C_2H_5OH + SOCl_2 \rightarrow C_2H_5Cl + SO_2 + HCl$

$3C_2H_5OH + PCl_3 \rightarrow C_2H_5Cl + H_3PO_3$

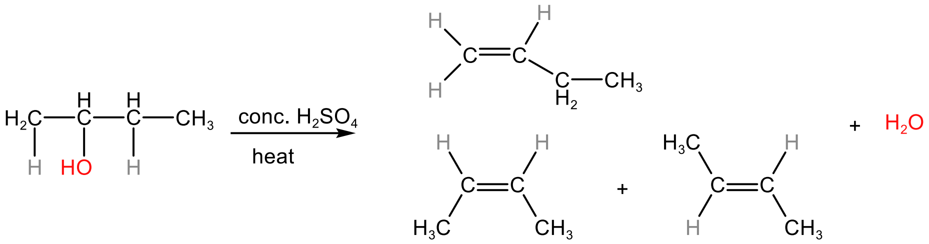
The –OH group on carboxylic acid can also be replaced with Cl in the presence of PCl_5.

Dehydration

Condition1	Condition2	Product
Heat with Conc. H_2SO_4	Strong heat with Al_2O_3	Alkene

Example

Products of the dehydration of butan-2-ol.



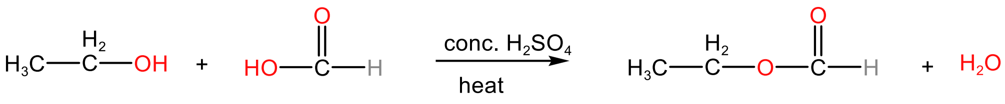
The alcohol can eliminate with the hydrogen on both sides.

Esterification

Reagent	Condition		Product
	Reflux	Catalyst	
Carboxylic acid	YES	concentrated sulfuric acid	Ester

Example

1. Give both symbol equation (show the structure of reagents and products) and word equation of the formation of ethyl methanoate

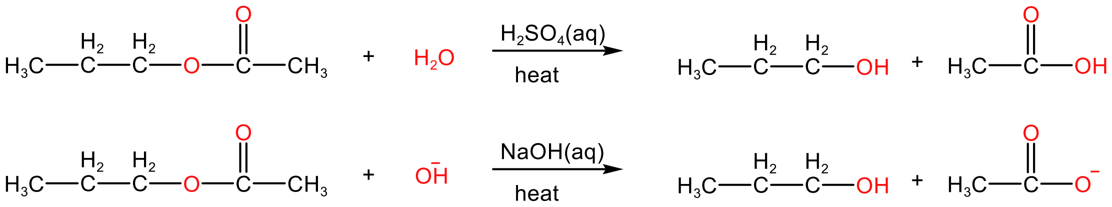


Ethanol + methanoic acid ethyl methanoate

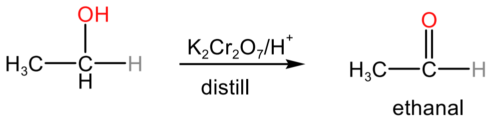
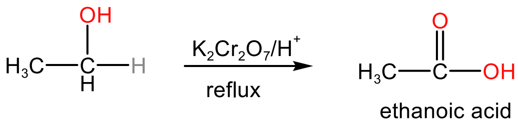
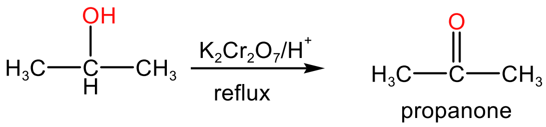
Type of Reaction	Condition		Product
	Reflux	Catalyst	
Ester Hydrolysis	Yes	Mineral acid	Alcohol & Carboxylic Acid
	Yes	Alkali	Alcohol & Salt

Example

Give both symbol equation (show the structure of reagents and products) of the hydrolysis of propyl ethanoate under different conditions



Oxidation

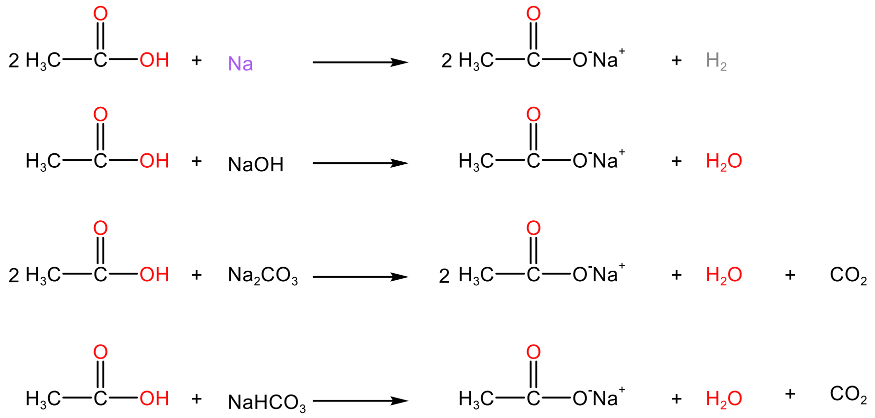
<table>
<tr><td colspan="2">Oxidant</td><td>Reagent</td><td>Product</td></tr>
<tr><td>Name</td><td>Acidified potassium dichromate (VI)</td><td rowspan="2">Primary alcohol</td><td>Aldehyde is formed if distillation is used to prevent further oxidation
</td></tr>
<tr><td rowspan="2">Formula</td><td rowspan="2">$K_2Cr_2O_7/H^+$</td><td>Carboxylic Acid is formed under reflux
</td></tr>
<tr><td colspan="2">Give the equation of the oxidation of ethanol.
$CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$
$CH_3CH_2OH + 2[O] \rightarrow CH_3COOH + H_2O$</td></tr>
<tr><td rowspan="2">Valency change</td><td rowspan="2">+6 → +3</td><td>Secondary alcohol</td><td>Ketone is formed
</td></tr>
<tr><td colspan="2">Give the equation of the oxidation of propan-2-ol.
$CH_3CH(OH)CH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$</td></tr>
<tr><td>Color change</td><td>Orange→ Green</td><td>Tertiary alcohol</td><td>No Reaction</td></tr>
</table>

Carboxylic Acid

React as an organic acid

Reagent Name & Formula	Condition Reflux	Product		Observation
1. Sodium Na	NO	Salt	Hydrogen	Bubble
2. Sodium Hydroxide NaOH	NO		Water	
3. Sodium Carbonate Na_2CO_3	NO		Carbon Dioxide	Bubble
4. Sodium Hydrogencarbonate $NaHCO_3$	NO		Carbon Dioxide	Bubble

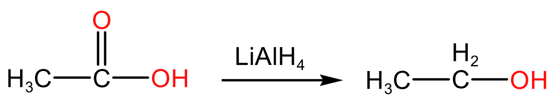
Use ethanoic acid as example. Give both symbol equation(show the structure of each chemical).



Reduction

Reagent Name & Formula	Product	Reflux	Solvent
$LiAlH_4$ Lithium tetrahydridoboaluminate	Alcohol	NO	dry ether

Use ethanoic acid as example to how it can be converted to alcohol.



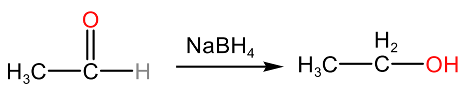
$CH_3COOH + 4[H] \rightarrow CH_3CH_2OH + H_2O$

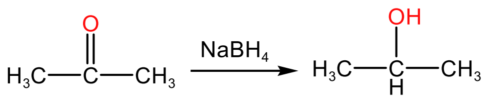
Carbonyl Compound

Nucleophilic Addition

	Reagent	Product (Family)	Condition	
			Reflux	Solvent or Catalyst
1	$NaBH_4$ Sodium hydridoborate	Alcohol	Yes	Water
2	HCN Hydrogen Cyanide	Hydroxyl Nitrile	Yes	Water KCN as catalyst

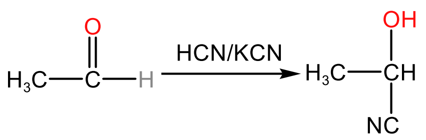
Use ethanal as example. Give both symbol equation (show the structure of each chemical) and the name of products.

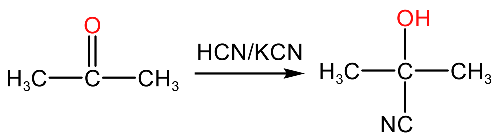




$CH_3CHO + 2[H] \rightarrow CH_3CH_2OH$ $CH_3COCH_3 + 2[H] \rightarrow CH_3CH(OH)CH_3$

Besides $NaBH_4$, $LiAlH_4$ and H_2/Ni can also be used in the reduction reaction.

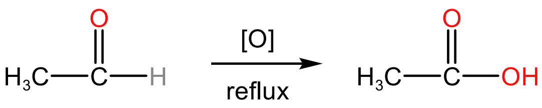




Oxidation of Aldehyde

	Reagent	Product (Family)	Observation	Reflux
1	Acidified potassium manganite (VII)	Carboxylic Acid	Purple to colorless $MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$	YES
2	Acidified potassium dichromate (VI)		Orange to green $Cr_2O_7^{2-} + 14H^+ + 5e \rightarrow 2Cr^{3+} + 7H_2O$	YES
3	Tollen's Reagent $AgNO_3$ in $NH_3(aq)$		Silvery mirror $Ag^+ + e \rightarrow Ag$	YES
4	Fehling's Reagent $Cu(OH)_2$		Red precipitate $2Cu(OH)_2 + e \rightarrow Cu_2O + 2H_2O + [O]$	YES

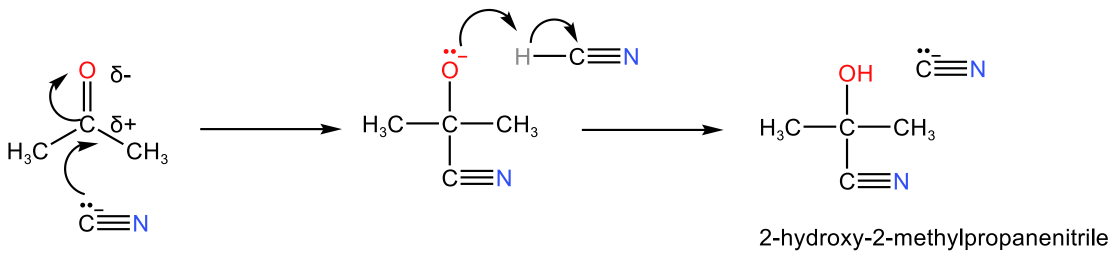
Aldehyde is oxidized into carboxylic acid



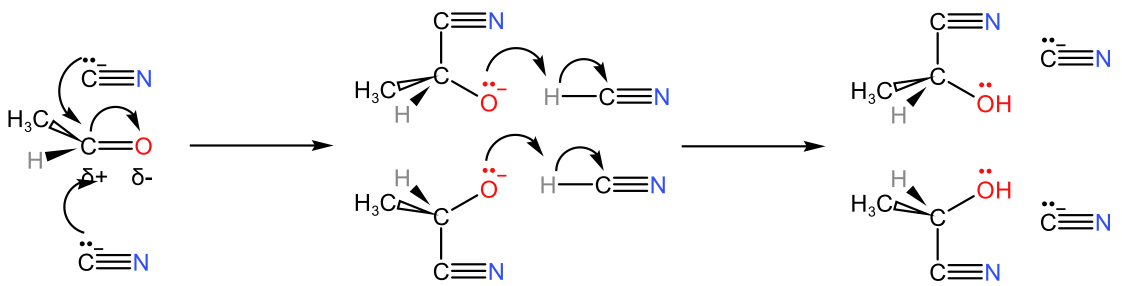
$CH_3CHO + 2[H] \rightarrow CH_3CH_2OH$

Mechanism-Nucleophilic addition

Use propanone and hydrogen cyanide as example to show the nucleophilic addition

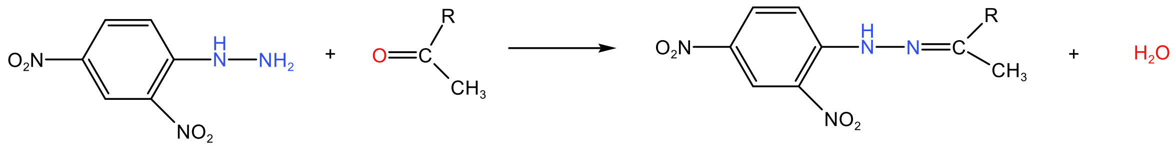


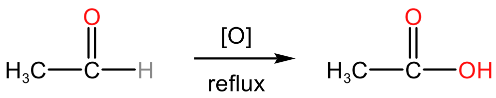
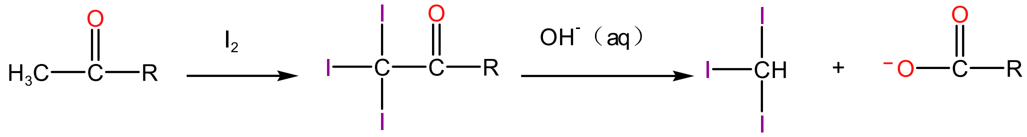
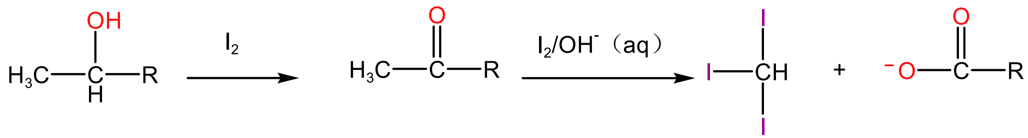
Use a diagram to show why the reaction between ethanal and hydrogen cyanide would produce two optical isomers of equal amount.



Ethanal is a planar. Cyanide can attack the carbon from both sides of the plane. Thus, a mixture of optical isomers will be formed.

Chemical Test of Organic Compound

Functional group	Reagent	Chemical Reaction		Observation
Alkene C=C	Bromine water	$H_2C{=}CH_2 \xrightarrow{Br_2} Br{-}CH_2{-}CH_2{-}Br$		Bromine water decolorize
Alcohol -OH	Na	$2\ H_3C{-}CH_2{-}OH + Na \longrightarrow 2\ H_3C{-}CH_2{-}O^-Na^+ + H{-}H$		Bubble
Acid -COOH	Na Na_2CO_3	$2\ H_3C{-}C({=}O){-}OH + Na \longrightarrow 2\ H_3C{-}C({=}O){-}O^-Na^+ + H_2$ $2\ H_3C{-}C({=}O){-}OH + Na_2CO_3 \longrightarrow 2\ H_3C{-}C({=}O){-}O^-Na^+ + H_2O + CO_2$		Bubble
Carbonyl group	2,4-DNPH	 2,4-dinitrophenylhydrazine orange precipitate Both ketone and aldehyde can give positive results with 2,4-DNPH		Orange precipitate
Aldehyde CHO	Tollens's Reagent	Oxidation $H_3C{-}C({=}O){-}H \xrightarrow[\text{reflux}]{[O]} H_3C{-}C({=}O){-}OH$	Reduction $Ag^+ + e \rightarrow Ag$	Silvery mirror

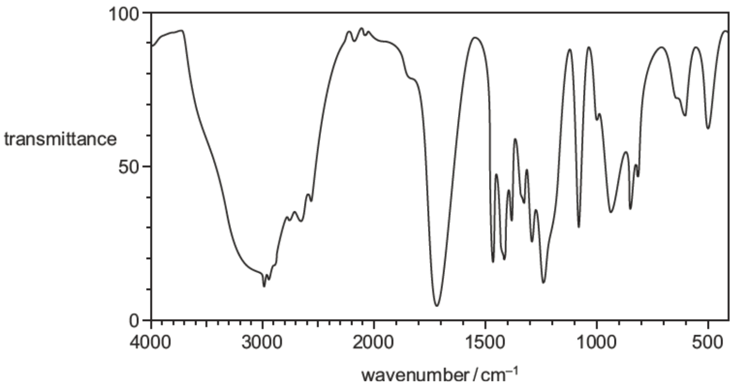
Functional group	Reagent	Chemical Reaction	Observation
Aldehyde -CHO	Fehling's Reagent	Oxidation  Reduction $2Cu(OH)_2 + e \rightarrow Cu_2O + H_2O + [O]$	Red precipitate
Methyl ketone CH_3CO-	Aqueous iodine solution	 yellow precipitate	Yellow precipitate
Methyl alcohol $CH_3CH(OH)$-	Aqueous iodine solution	 yellow precipitate Iodine is a weak oxidant and can oxidize secondary alcohol into ketone. This is what happened in the first step	Yellow precipitate

Infra-red spectrum

Different type of bond shows specific infra-red absorption. We can predict the bond present in the molecule from its infra-red spectrum.

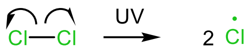
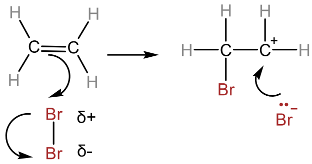
Bond	Functional groups containing the bond	Absorption range (in wavenumbers)/cm^{-1}	Appearance of peak (*s = strong, w = weak*)
C–O	alcohols, ethers, esters	1040–1300	***s***
C=C	aromatic compounds, alkenes	1500–1680	***w*** unless conjugated
C=O	amides ketones and aldehydes esters	1640–1690 1670–1740 1710–1750	***s*** ***s*** ***s***
C≡C	alkynes	2150–2250	***w*** unless conjugated
C≡N	nitriles	2200–2250	***w***
C–H	alkanes, CH_2–H alkenes/arenes, =C–H	2850–2950 3000–3100	***s*** ***w***
N–H	amines, amides	3300–3500	***w***
O–H	carboxylic acids, RCO_2–H H-bonded alcohol, RO–H free alcohol, RO–H	2500–3000 3200–3600 3580–3650	***s*** and very broad ***s*** ***s*** and sharp

The infra-red spectrum of the propanoic acid produced by reaction **2** is shown.



Absorption at 3000 cm^{-1} suggests the presence of O-H in RCOOH
Absorption at 1250 cm^{-1} suggests the presence of O-C
Absorption at 1690 cm^{-1} suggests the presence of O=C

Key terms of Organic Chemistry

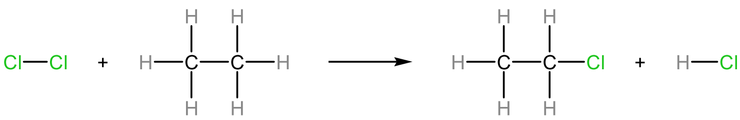
Term	Definitions	Examples
Free radical	Species with unpaired electron	Cl•
Nucleophile	Lone pair donor	OH^-, NH_3, CN^-
Electrophile	Lone pair acceptor	HBr, Br_2, H^+
Homolytic Fission	bonding electrons are equally shared when covalent bond breaks, producing free radicals	
Heterolytic Fission	bonding electrons are unequally shared when covalent bond breaks, producing cation and anion	

Substitution (chlorination, bromination)

Atom or group of atoms in organic molecule replaced by others

e.g.

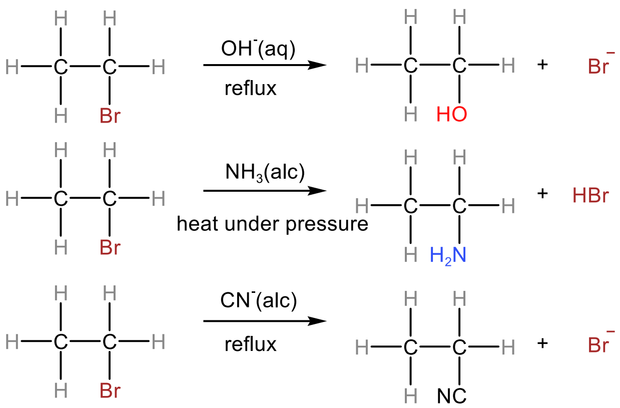
free radical substitution



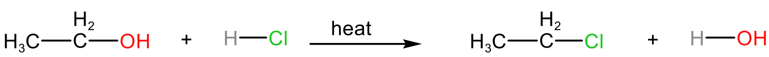
chloromethane

Nucleophilic substitution

Halogenoalkane



Alcohol



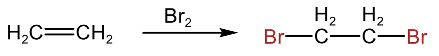
$$CH_3CH_2OH + PCl_5 \rightarrow CH_3CH_2Cl + POCl_3 + HCl$$
$$CH_3CH_2OH + SOCl_2 \rightarrow CH_3CH_2Cl + SO_2 + HCl$$

Addition (hydrogenation, hydration, chlorination, bromination)

One molecule is added to another by breaking a double bond

e.g. Electrophilic Addition

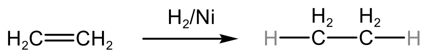
bromination



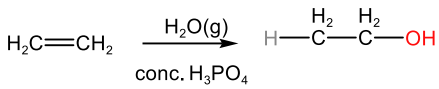
1,2-dibromoethane

bromination

hydrogenation

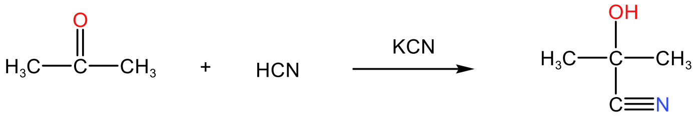


hydration



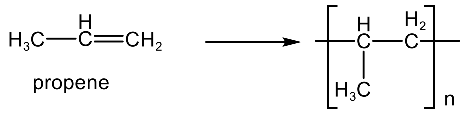
ethanol

e.g. Nucleophilic Addition



Additional Polymerization

Many monomers joint together to form polymer by addition reaction.

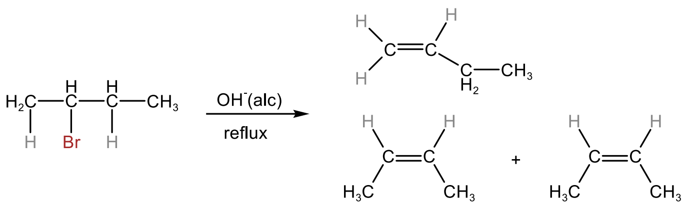


propene

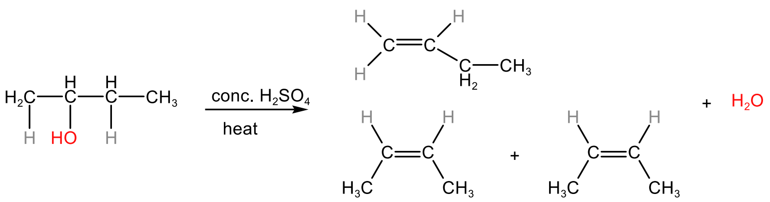
polypropene

Elimination (dehydration)

Small molecule eliminated from an organic compound result in formation of double bond.

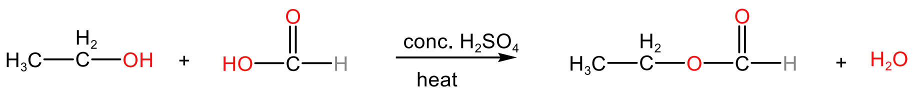


dehydration



Condensation (esterification)

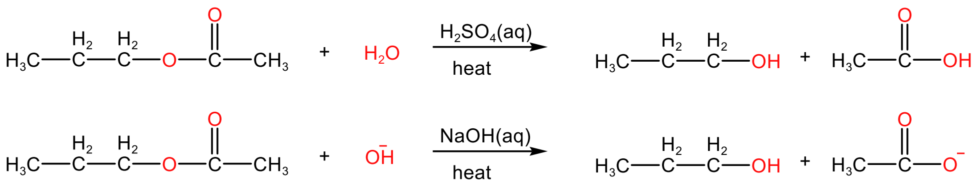
Two molecules join together by elimination of a small molecule.



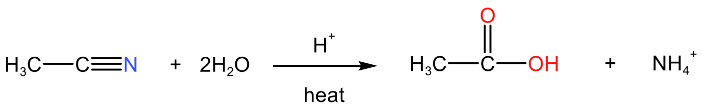
Hydrolysis

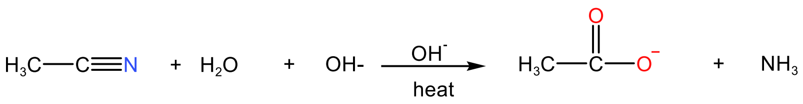
One compound separates into two molecules by a water molecule

e.g. ester

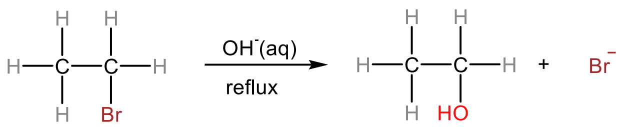


e.g. nitrile





e.g. halogenoalkane

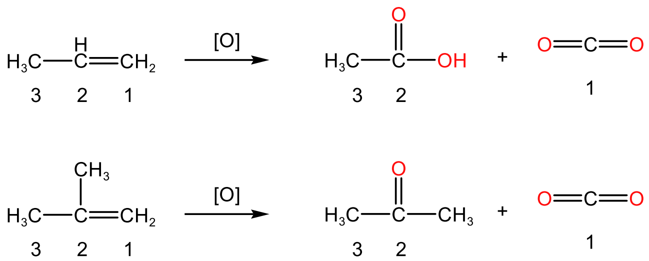


Oxidation (dehydrogenation)

Add oxygen or remove hydrogen from an organic compound.

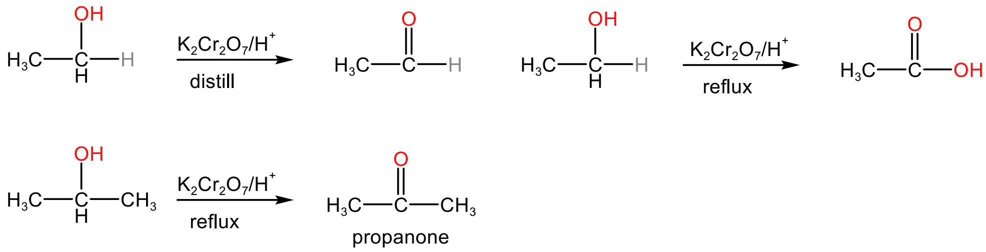
e.g. oxidation of

alkene



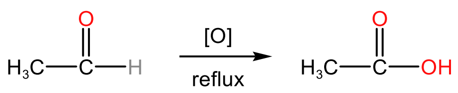
Only $KMnO_4/H^+$ can be used in oxidation of alkene.

alcohol



Both $K_2Cr_2O_7/H^+$ and $KMnO_4/H^+$ can be used in the oxidation of alcohol.

aldehyde



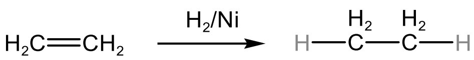
$K_2Cr_2O_7/H^+$, $KMnO_4/H^+$, Tollens's reagent, Fehling's reagent can be used in the oxidation of aldehyde.

Reduction (hydrogenation)

Add hydrogen or remove oxygen from an organic compound.

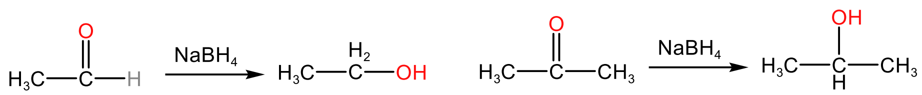
e.g. Reduction of

alkene



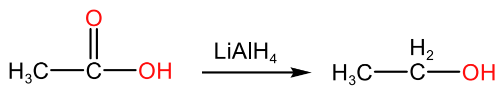
Only H_2/Ni can be used to reduce alkene.

carbonyl compound



$LiAlH_4$, H_2/Ni and $NaBH_4$ can be used to reduce ketone and aldehyde.

carboxylic acid

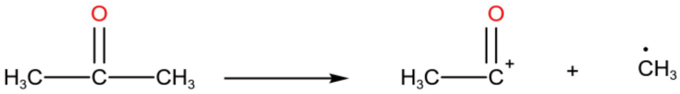


Only $LiAlH_4$ can be used in the reduction of acid

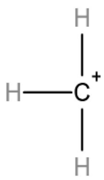
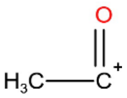
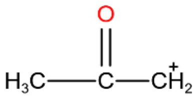
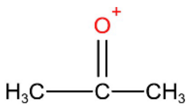
Mass Spectrometry

Principle

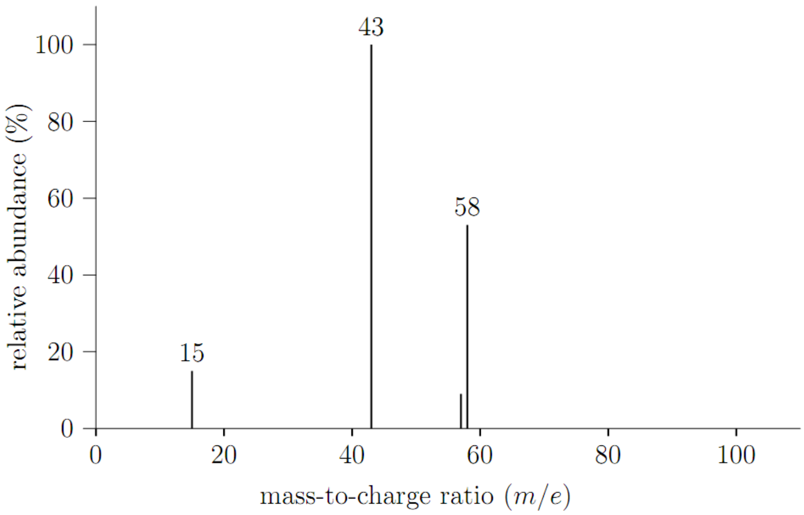
In mass spectrometer the sample is first vaporized. When vapor from the sample enters the machine, it is bombarded by high energy electrons. This knocks electrons from the molecules and breaks covalent bonds, fragmenting the molecules.



Fragments produced by propanone and their mass-to-charge ratio (m/e)

Fragments				
m/e	15	43	57	58

Mass spectrum produced by those fragments



X-axis shows the mass per charge of the fragments, the y-axis shows the relative abundance of each fragment.

The peak at the higher mass-to-charge ratio is caused by the molecular ion (M^+). This ion is formed by the sample molecule with one electron knocked out. It gives us the relative molecular mass of the sample.

Mass Spectrum of Isotopes ^{13}C

There will always be a very small peak just beyond the molecular ion peak at a mass of [M+1]. This is caused by molecules in which one of the carbon atoms is ^{13}C whose chance of occurrence is 1.10%. The abundance of M+1 peak increases as number of carbon increases.

Molecules	Species responsible for		Relative abundance
	M peak	M+1 peak	[M+1]: [M]
HCOOH	$H^{12}COOH$	$H^{13}COOH$	$1.1 : 100$
CH_3COOH	$^{12}CH_312COOH$	$^{13}CH_3{}^{12}COOH$ $^{12}CH_3{}^{13}COOH$	$(1.1 \times 2) : 100$
CH_3CH_2COOH	$^{12}CH_3{}^{12}CH_2COOH$	$^{13}CH_3{}^{12}CH_2{}^{12}COOH$ $^{12}CH_3{}^{13}CH_2{}^{12}COOH$ $^{12}CH_3{}^{12}CH_2{}^{13}COOH$	$(1.1 \times 3): 100$

Thus, the number of carbon atoms (n) in a molecule can be deducted

$$n = \frac{\frac{[M+1]}{[M]}}{\frac{1.1}{100}} = \frac{100}{1.1} \times \frac{\text{abundance of } [M+1]^+ \text{ion}}{\text{abundance of } M^+ \text{ion}}$$

For a molecule whose M peak has relative abundance of 54.5% and M+1 peak of 3.6%, calculate the number of carbon atoms in it.

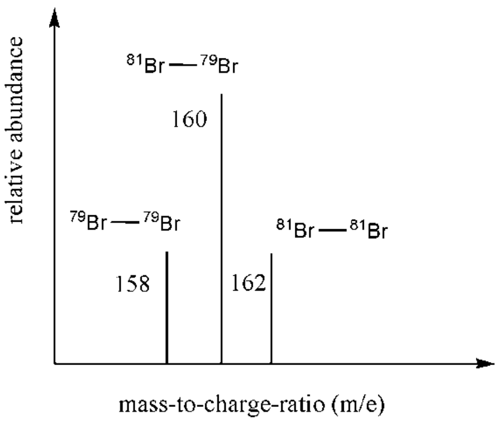
$$n = \frac{100}{1.1} \times \frac{3.6}{54.5} = 6.0$$

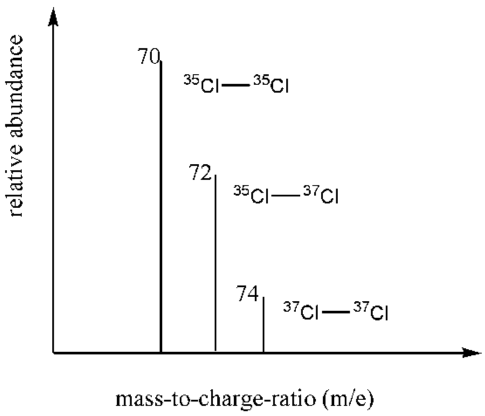
There are 6 carbon atoms in this molecule.

Mass Spectrum of Isotopes Br and Cl

If the sample compound contains chlorine or bromine atoms, we also get peaks beyond the molecular ion peak because of the isotopes of chlorine and bromine.

Element	Isotopes	Approximate %
chlorine	^{35}Cl	75
	^{37}Cl	25
bromine	^{79}Br	50
	^{81}Br	50





Element	number of atoms per molecule	peaks present and their height ration	
Chlorine	1	[M]: [M+2]	= 3:1
	2	[M]: [M+2]: [M+4]	= 9:6:1
Bromine	1	[M]: [M+2]	= 1:1
	2	[M]: [M+2]: [M+4]	=1:2:1

Use the following information to find the molecular formula of compound L.

The three peaks of highest mass in the mass spectrum of organic compound L correspond to masses of 142, 143 and 144. The ratio of the heights of the M: M+1 peaks is 43.3 :3.35, and the ratio of heights of the M: M+2 peaks is 43.3 :14.1.

Because $\frac{[M\ ]}{[M+2]} = \frac{43.3}{14.1} \approx \frac{3}{1}$, there is one chlorine atom in the molecule.

Because $\frac{\frac{[M+1]}{[M]}}{0.11} = \frac{\frac{3.35}{43.3}}{0.11} \approx 7$, there is seven carbon atoms in the molecule.

The molecular peak has mass of 142, in which a chlorine accounts for 35 while seven carbon accounts for 84.

$142 - 35 - 12 \times 7 = 25$

There cannot be twenty-five hydrogen atoms in the molecule, because there are only seven carbon atoms. The maximum number of hydrogen atoms is $2 \times 7 + 2 = 16$

So, we assume there will be at least one oxygen atom in it. $25 - 16 = 7$

The molecular formula is C_7H_7OCl