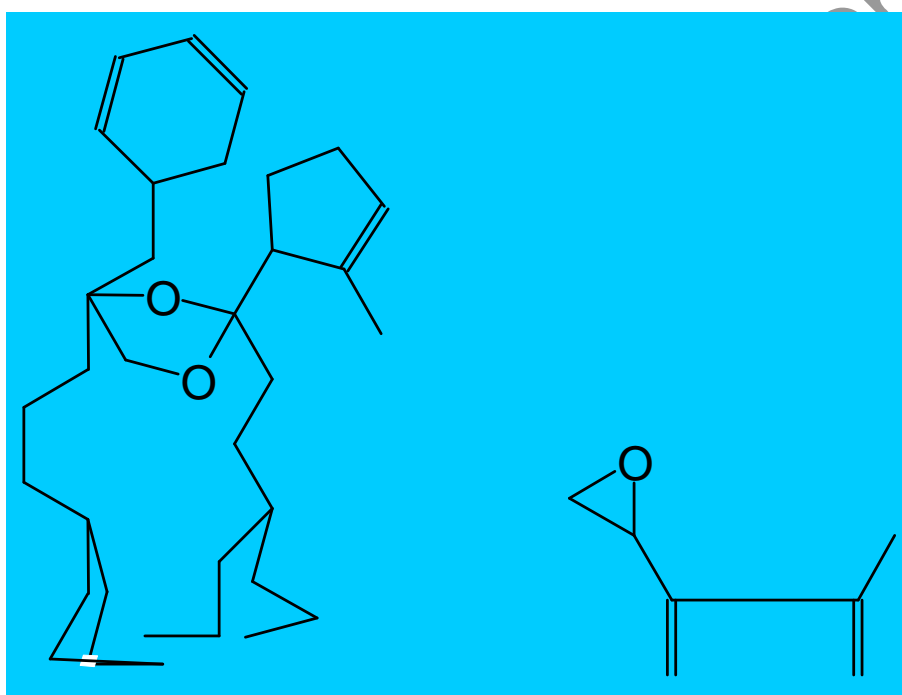


Learn chemistry in 15 days!

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Dr.Prem Vuppalapaty

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BASIC CHEMISTRY

Nature's chemistry vs man-made

Chemistry is a science exploring nature's logic & tools for creating various materials found in solid, liquid and gaseous form on earth. It also predicts various potential new materials which man may make using these laws of nature. In order to understand chemistry, we must understand:

1. Types of building blocks nature uses in creating various compounds which manifest themselves as water, air, food, hormones, blood, tissue, bone, DNA, wood, salt, rock, sand, mud, resin, pigment, perfume, etc.,
2. Laws which govern the formation of such materials in nature,
3. Strategies that will allow man to replicate the process of nature & create man-made materials.

When we examine a natural substance like mud, we may find it to be a mixture of several materials: sand, other inorganic ores, organic matter like tissues & bones. Similarly flesh is made up of water, proteins, fats and others. Living organisms have always been sources of unique chemicals. Millions of chemists have studied & understood chemistry of natural substances and used this knowledge to create numerous man-made substances: polymers, agrochemicals, drugs, colors, fragrances, soaps, solvents, preservatives, stabilizers, nutrients, sweeteners, adhesives, resins, paints, reagents, explosives, fuels, fertilizers, etc.

Nature has created numerous unique substances, both simple and complex. Early chemists broadly classified substances as "organic" and "inorganic".

Questions:

- 1) Name five natural substances each existing in solid, liquid and gaseous forms. Segregate them into "inorganic" and "organic".
- 2) Name five applications of polyethylene. Are there other polymers that you are aware of?
- 3) Name ten chemicals found in nature (e.g., caffeine)

Exercise:

- 1) Learn the composition & complex functions of blood including transportation of oxygen, food, infection-fighting cells, etc. around the body and collecting & dumping wastes at appropriate sites.
- 2) Find out what people really mean by the words "organic", "aromatic", "medicine", "soap", "poison", "color", "fertilizer", "burning".

Atoms, molecules, elements & compounds

A chemist's building blocks are "atoms" or clusters of similar/dissimilar atoms known as "molecules". Atoms are the smallest units of matter man can find, whether they are similar or dissimilar. Atoms of a kind (even if paired) constitute an element, the "purest" substance. There are more than 100 types of atoms of different elements with unique structures/properties known to man, including those created momentarily by man in the laboratory by colliding two different atoms. These atoms of various elements combine in fixed proportions as per certain laws to form new unique substances called compounds where the smallest unit, a molecule, is a cluster of dissimilar atoms in fixed proportion. Sizes of atoms of various elements vary as per certain rules discussed in following pages. Two atoms of certain elements, e.g., oxygen, also combine to give a molecule.

It is necessary to know the structure of atom itself before understanding why elements tend to combine in a particular way. What makes certain combinations more favorable than others? Why a particular proportion? How is the weight related to this proportion? How do you relate solid, liquid and gas phases of the same chemical? How can man build complex molecules? Can we build bigger molecules by attaching smaller ones? What about energy requirements? These are questions we will try to answer in the next 15 days.

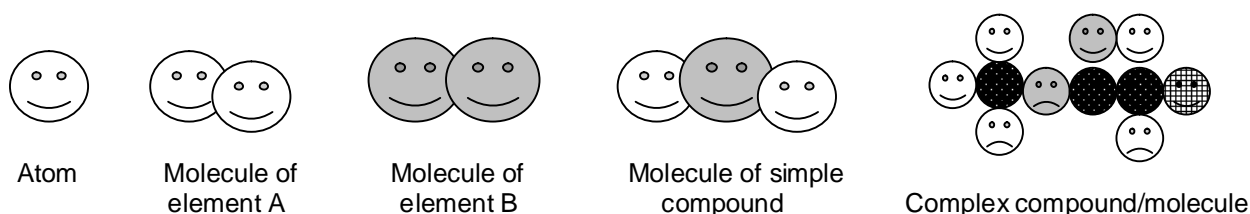


Fig 1: Atoms & molecules

Questions:

- 1) List names of "purest" natural substances known to you.
- 2) Identify natural substances that are mixtures and not "pure".
- 3) What do you think of the composition of a substance known as sodium chloride?
- 4) Predict the shape of carbon dioxide molecule, CO_2 .

Atomic structure: electrons, protons, neutrons & their relative mass

Scientific experiments by renowned scientists have demonstrated that an atom is mostly an empty shell with a heavy, small core (nucleus) containing positive charge while an equivalent negative charge remains scattered over the empty shell in the form of negatively charged particles of negligible mass. These negative particles known as electrons occupy pre-determined spaces called orbitals. Electrons are filled in orbitals of increasing energy levels resulting in bigger atomic size whenever a new higher orbital is occupied. The core of an atom also contains neutral particles called neutrons, which are equal in mass to positively charged protons.

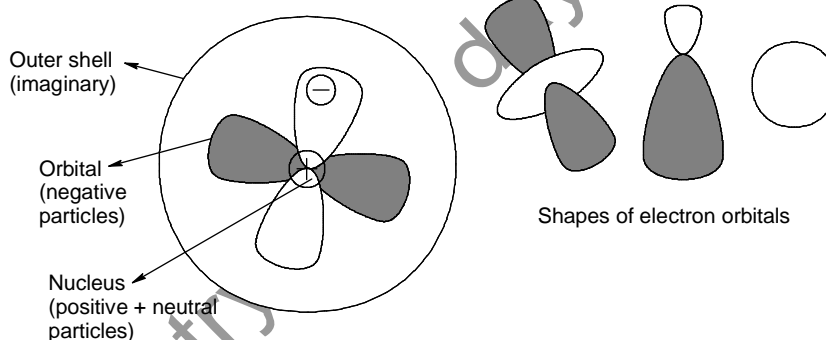


Fig 2: Structure of atom

Mass of electrons, protons and neutrons is measured in atomic mass units (amu) where mass of protons & neutrons is taken as unity (1 amu). Electron has negligible weight though its charge is unity as in proton.

Questions:

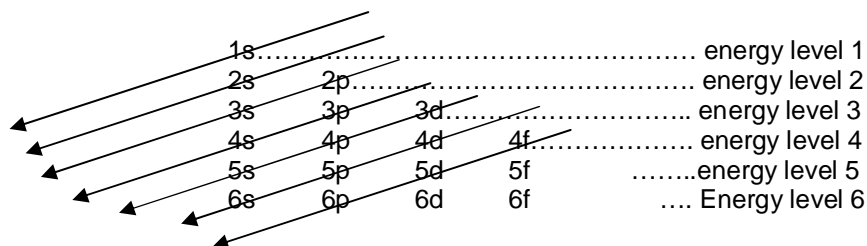
- 1) If an element has 12 neutrons and atom's total weight is 24 amu, how many protons does it have?
- 2) If an element has 15 electrons, how many protons are there?
- 3) Calculate the approximate weight in amu of 10 electrons, 10 protons and 10 neutrons.
- 4) When do you expect an atom to have no neutron at all?
- 5) Where does the centre of gravity of an atom lie?
- 6) Describe an orbital in terms of electron probability/distribution/cloud.

Exercise:

1. Visualize a triple-dumbbell shaped orbital in three dimensions along x, y & z axes.
2. Visualize about 100 different sizes of atoms of various elements. Compare atomic sizes of two elements having 2 and 80 electrons respectively.

Atomic number, atomic weight & electron configuration

Every element has a different number of electrons (equal to protons) starting from 1 for hydrogen. As the mass of hydrogen atom is about 1 amu, it is accounted for mainly by a proton paired with an electron but no neutron. For other elements the difference between atomic mass & number of protons is the number of neutrons, as electrons have negligible mass. Increasing number of electrons are accommodated in orbitals of various sizes & energy levels as shown below:



The order of increasing energy levels of electron orbitals is therefore 1s(2 electrons), 2s(2), 2p(6), 3s(2), 3p(6), 4s(2), 3d(10), 4p(6), 5s(2), 4d(10), 5p(6), 6s(2), 4f(14), 5d(10), etc. This means that sub-orbitals s, p, d, f hold 2, 6, 10, 14 electrons respectively. For bromine, atomic number 35, the electron configuration is written as $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$. We shall see below how this configuration helps us predict the properties of elements with the help of periodic table, an arrangement of elements in groups based on similar electron configurations.

Question:

Given that 115 elements exist (maximum 115 electrons in any atom), how many elements have just a single electron in an outer "d" orbital? How many have single "p" electron?

Periodic table

When some early chemists found interesting similarities among certain elements, they tried to make sense out of it and ultimately prepared a systematic arrangement of elements in the form of a table known as the periodic table. This arrangement, with increasing atomic numbers/atomic weights, places elements of similar electron configurations in vertical groupings (see table). Once elements are arranged like this, we see how easy it is to predict certain characteristics of a given element by simply referring to its place in the periodic table:

- Members of a particular horizontal row called period have electrons in the same energy level, resulting in smaller size as the number of protons/electrons gradually rise (towards right on the same period). This is attributed to greater attraction between electrons and protons within the same size.
- Elements are arranged in 18 vertical groupings of similar electron configurations. Group Ia represents elements having just one "outer orbital" electron. Group VIIa represents 7 outer orbital electrons. The highest is VIII group, as elements tend to either collect or discharge no more than eight electrons.
- Elements fall generally in 3 categories: (1)electron-hungry/electronegative/non-metallic (2)electron-donating/electropositive/metallic (3)electron-sharing/metalloid.
- Elements arranged between metals and non-metals, known as metalloids, tend to share electrons with atoms of other elements and try to avoid ionization.
- Larger atoms of metallic elements tend to lose electron easily due to feebler attraction from nucleus: the most electropositive element, francium, is on the lower left (due to its largest size within the group as well as period). An element trying to lose one electron is more electropositive than one trying to lose two electrons, due to lower energy requirement. Sodium (of vertical Group-Ia) is more electropositive than magnesium (of Group-IIa) and is also larger.
- Smaller atoms of non-metallic elements tend to grab & retain an electron more easily due to stronger attraction from nucleus: the most electronegative element, fluorine, is placed on the top right (indicating its smallest size within the group as well as period). An element trying to grab one electron is more electronegative than one trying to grab two electrons. Fluorine (of vertical Group-VIIa) is more electronegative than oxygen (of Group-VIa) and is also smaller.
- There is one group of elements neither giving nor taking electrons—in fact they rarely react and hence are known as noble elements (Group-0/VIIIa). Scientists figured that other atoms giving/taking electrons are in fact trying to become "noble element-like", i.e., achieve stable electronic configuration.
- Elements keenly giving away electrons have just a few electrons in the outermost orbital so that they tend to have a fully filled lower orbital like noble element by losing extra electrons.
- Elements keenly taking away electrons have just a few electrons short in the outermost orbital so that they tend to have a fully filled orbital like noble element by gaining extra electrons.
- The atomic number in the periodic table immediately lets us write the electron configuration of any element while the atomic weight helps us calculate the number of neutrons present.

11. We may predict how many atoms of a metallic element (say sodium with one electron to spare) would react with how many atoms of a non-metallic element (say sulfur with two electrons to take). The formula of sodium sulfide is therefore Na_2S while that of carbon (di)sulfide is CS_2 . Hydrogen chloride is HCl , aluminium oxide is Al_2O_3 , calcium phosphide is Ca_3P_2 , and so on.

Questions:

- 1) Is it possible for an element to give away electrons in the absence of an acceptor?
- 2) Name the most electropositive & electronegative elements in the periodic table.
- 3) Identify three elements whose atoms become smaller if an electron is lost to form an ion.
- 4) Identify three elements whose atoms become smaller if an electron is gained.
- 5) Is there an element whose atom gets larger when an electron is gained?
- 6) What are differences between second and third period elements of same group?
- 7) Write chemical formulae for silicon chloride, bismuth sulfide and beryllium iodide.
- 8) Calculate percentage by weight of hydrogen in HCl using their atomic weights.
- 9) Analysis of a sample showed 47.9% zinc and 52.1% chlorine. What is the formula of the compound?
- 10) Common sugar was analyzed and found to contain 42.1% carbon and 6.5% hydrogen. Which of the formulae $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ or $\text{C}_6\text{H}_{12}\text{O}_6$ represents the compound better?
- 11) If an element of group Ia reacts with an element of group VIA, what will be the ratio of atoms in the resulting compound?
- 12) Why is fluorine the most electronegative element?
- 13) Why is francium the most electropositive element?
- 14) Why is sodium unable to form covalent compounds? Do you expect covalent bonds formed by fluorine to be ideal sharing?

Sources of elements:

Elements do not always exist in pure form. Gases like oxygen, nitrogen, helium, argon, neon, etc. exist in atmosphere and are separated using physical methods. Solids such as sulfur, carbon, etc. occur in nature. Phosphorus, iodine, boron, silicon, selenium, etc. never occur as elements in nature. Metals, with the exception of precious ones, are usually found as oxides, sulfides, carbonates, chlorides, fluorides, etc. Such ores containing metal compounds are subjected to many types of metallurgical operations to obtain pure metals.

PERIODIC TABLE OF ELEMENTS

Group
Ia Iia IIIb IVb Vb VIb VIIb VIIIb VIII VIII Ib Iib IIIa Iva Va VIa VIIa VIIIa/0

1H 1.008	First period																2He 4.003
3Li 6.941	4Be 9.01	Second period										5B 10.811	6C 12.011	7N 14.007	8O 16.00	9F 19.00	10Ne 20.18
11Na 22.99	12Mg 24.30	Third period										13Al 26.98	14Si 28.086	15P 30.974	16S 32.065	17Cl 35.453	18Ar 39.948
Transition elements (with electrons in 'd' sub-orbital)																	
19K 39.10	20Ca 40.08	21Sc 44.956	22Ti 47.867	23V 50.94	24Cr 51.996	25Mn 54.938	26Fe 55.845	27Co 58.933	28Ni 58.693	29Cu 63.546	30Zn 65.39	31Ga 69.723	32Ge 72.64	33As 74.922	34Se 78.96	35Br 79.904	36Kr 83.80
37Rb 85.468	38Sr 87.62	39Y 88.906	40Zr 91.224	41Nb 92.906	42Mo 95.94	43Tc 97.907	44Ru 101.07	45Rh 102.91	46Pd 106.42	47Ag 107.87	48Cd 112.41	49In 114.82	50Sn 118.71	51Sb 121.76	52Te 127.60	53I 126.90	54Xe 131.29
55Cs 132.90	56Ba 137.33	→	72Hf 178.49	73Ta 180.95	74W 183.84	75Re 186.21	76Os 190.23	77Ir 192.22	78Pt 195.08	79Au 196.97	80Hg 200.59	81Tl 204.38	82Pb 207.2	83Bi 208.98	84Po 208.98	85At 209.99	86Rn 222.02
87Fr 223.02	88Ra 226.02	→	104Rf 261.11	105Db 262.11	106Sg 266.12	107Bh 264.12	108Hs	109Mt 268.14	110Uun	111Uuu 272.15	112Uub		114Uuq		116Uuh		118Uuo

Lanthanides & Actinides (with electrons in 'f' sub-orbital)

→	57La 138.91	58Ce 140.12	59Pr 140.91	60Nd 144.24	61Pm 144.91	62Sm 150.36	63Eu 151.96	64Gd 157.25	65Tb 158.93	66Dy 162.50	67Ho 164.93	68Er 167.26	69Tm 168.93	70Yb 173.04	71Lu 174.97
→	89Ac 227.03	90Th 232.04	91Pa 231.04	92U 238.03	93Np 237.05	94Pu 244.06	95Am 243.06	96Cm 247.07	97Bk 247.07	98Cf 251.08	99Es 252.08	100Fm 257.10	101Md 258.10	102No 259.10	103Lr 262.11

Valency, formulae, formula weight and mole:

Based on the number of electrons an atom of a given element wants to give/take, which is known as valency, its proportion in a chemical compound may be predicted and shown in a chemical formula as in the cases mentioned earlier. Using atomic weights (given in periodic table) it is possible to calculate the relative weights of the two elements required and the weight of compound obtainable. For example, in Ca_3P_2 3x40 grams of calcium (3 gram atoms) will react with 2x31 grams of phosphorus (2 gram atoms) to give 182 grams of Ca_3P_2 (one mole). Here valencies of calcium and phosphorus are 2 and 3 respectively. Ca_3P_2 represents the formula while 182 is the formula weight in atomic mass units, amu. If 182 grams of Ca_3P_2 are taken, it represents one gram formula weight or one mole. One mole of sodium chloride, NaCl, is thus 58.5 grams while a mole of sulfuric acid, H_2SO_4 , is 98 grams.

Avagadro's principle states that one gram atom or mole of any substance contains 6.02×10^{23} atoms or molecules respectively. It has been calculated that one mole of any gas occupies 22.4 liters at standard temperature & pressure (STP). For example, 32 grams of oxygen existing as O_2 contains 6.02×10^{23} molecules and occupies 22.4 liters at STP, though its volume can be compressed by increasing pressure. Behavior of gases is described by following laws of physics:

Boyle's Law: Pressure x Volume = constant (or) $P_1 \times V_1 = P_2 \times V_2$ at constant temperature

Charles' Law: Volume / Temperature = constant (or) $V_1/T_1 = V_2/T_2$ at constant pressure

Gay Lussac's Law: Pressure / Temperature = constant (or) $P_1/T_1 = P_2/T_2$ at constant volume

Combined Gas Equation: Pressure x Volume / Temperature = constant (or) $P_1 V_1/T_1 = P_2 V_2/T_2$

General gas equation: $PV = nRT$, where n = no. of moles & R = 0.082 lit.atm / mole.Kelvin

Dalton's law of partial pressures: Total pressure $P = p_1 + p_2 + p_3 + \dots$ at constant temperature. Partial pressures of component gases are represented by p_1, p_2 , etc.

Questions:

- 1) Given that carbon atoms bond with themselves, suggest a possible structure for ethylene, C_2H_4 .
- 2) Calculate the percentage of hydrogen and carbon in methane, CH_4 . How many liters of hydrogen gas (at STP) will be required to produce 24 grams of methane? How many atoms of hydrogen are there (given that hydrogen gas exists as H_2 molecules)?
- 3) How many grams of sodium will be required to produce 100 grams of sodium hydroxide, NaOH?
- 4) If we want to make 1 kg water H_2O from hydrogen and oxygen gases, how many liters of each are required?

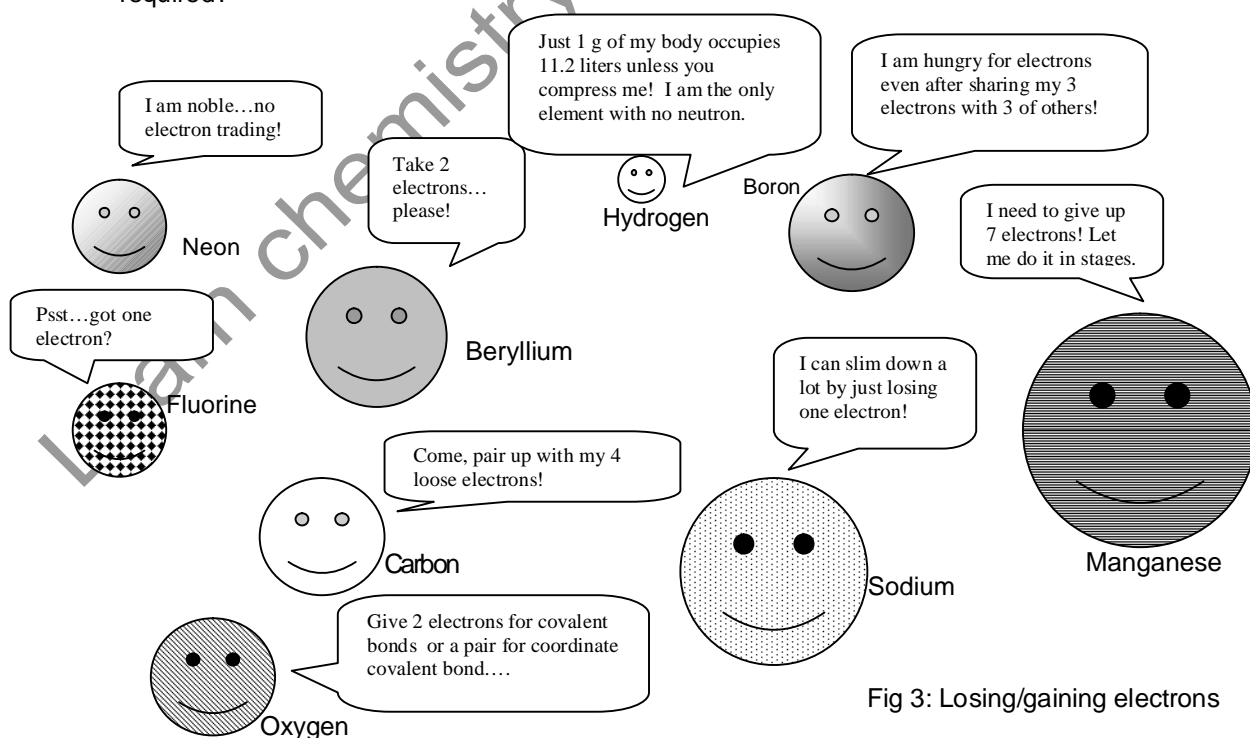


Fig 3: Losing/gaining electrons

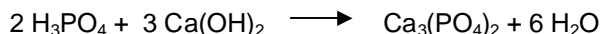
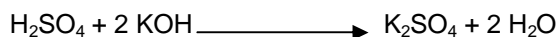
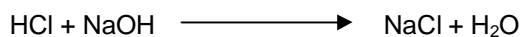
INORGANIC CHEMISTRY

Chemical reactions, balancing, equivalent weights, equilibria and oxidation states:

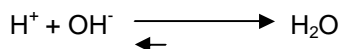
There are chemical reactions between elements as well as compounds. Here the number of electrons "traded" in the reaction is balanced through weights of reactants equivalent to one electron. Equivalent weight is formula weight representing give/take of one electron. Examples:

Acid-base reactions:

Acids are produced when oxides of non-metals (e.g., SO_3 , N_2O_5 , P_2O_5 , Cl_2O) dissolve in water. On the other hand, metallic oxides (e.g., Na_2O , CaO) dissolve in water to produce bases/alkalis. Acids generate hydrogen ions/protons while alkalis generate hydroxide ions. Acids & alkalis neutralize each other to produce water and salt.



In these reactions HCl and NaOH both represent one electron/proton/hydroxide ion each, and therefore have equivalent weights same as formula weights. H_2SO_4 represents 2 protons and hence equivalent weight is one-half of formula weight while in H_3PO_4 equivalent weight is one-third of the formula weight. Similarly, $\text{Ca}(\text{OH})_2$ represents two hydroxide ions and therefore has an equivalent weight one-half of the formula weight. All the above three reactions may be represented by the following equation (leaving out passive ions):



Dissociation of water to give hydrogen & hydroxyl ions is not easy but exists to a very small extent. Such reactions are known to be in equilibrium, which may be disturbed by changing concentration of one or more species. When outside hydrogen ions (protons) are introduced, water becomes an acid while outside hydroxide ions make it a base. Acidity or basicity is measured in pH scale of 0-14 where $\text{pH} = -\log_{10} [\text{H}^+]$. $[\text{H}^+]$ represents concentration of H^+ ion. Range 0-7 indicates acidity while 7-14 indicates alkalinity. Chemicals that change color at specific pH ranges are used as indicators of acid-base reactions, which are fast and useful as analytical methods. An amino compound may be analyzed for purity by titration against a standardized solution of hydrochloric acid in aqueous medium or perchloric acid in non-aqueous medium using appropriate indicators.

In a titration, a known volume of standardized reagent solution is allowed to neutralize a known weight of a substance. Percentage of real substance in that sample weight (called purity) may be calculated as follows:

If X ml of a standard solution (of known concentration Y) is consumed in the titration by W grams of sample having equivalent weight E,

$$X \text{ milliliters} \times Y \text{ eq/liter} = X \times Y \text{ millieq reagent} = X \times Y \text{ millieq substance} = X \times Y \text{ millieq} \times E \text{ grams/eq} = X \times Y \times E \text{ mg contained in W grams or } W \times 1000 \text{ mg of sample.}$$

$$\boxed{\text{Purity as percentage} = \left[\frac{X \times Y \times E}{W \times 1000} \right] \times 100}$$

This procedure may be used to determine equivalent weight of an unknown but pure sample by assuming purity as 98-100% as the case may be and calculating E. This calculation is applicable to all titrations.

Salts formed in acid-base reactions are named by indicating the cation (positively charged ion attracted towards cathode of a cell) first and then the anion (negatively charged ion attracted towards anode of a cell). Thus salt of hydrobromic acid and potassium hydroxide is potassium bromide. Acetic acid and ammonia give ammonium acetate. Sodium bicarbonate and oxalic acid give sodium oxalate. The pH of these salts in solution depends on whether acid or base or neither dominates the pair. Strong acids & strong bases such as

sodium/potassium hydroxide, hydrochloric acid, sulfuric acid dominate over weaker ones like sodium carbonate, ammonia, acetic acid, oxalic acid, etc. It is important to choose the right indicator in a titration based on pH at endpoint and the indicator's color range. For example, in a titration of ammonia against HCl solution, indicators methyl orange (3.1-4.4 pH range) or methyl red (4.4-6.2 pH range) would be more appropriate compared to phenolphthalein (8-9 pH range). On the other hand, the latter indicator would be most appropriate if sodium hydroxide is used against a weak acid. Errors in titrations arise due to inadequate rinsing, reading errors, lack of titrating technique, weighing errors, wrong storage of reagents, etc. Potentiometric titrations using specially designed electrodes allow us to automate this testing to minimize human errors and improve accuracy.

Units for concentration of solutions:

Normality: Number of equivalents of a substance dissolved in 1000mL of solution (N)

Molarity: Number of moles of a substance dissolved in 1000mL of solution (M)

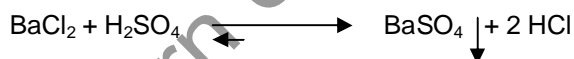
Molality: Number of moles of a substance dissolved in 1000mL of solution (m)

Questions:

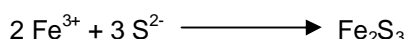
- 1) Write equations for various reactions where water reacts with non-metal oxides to form acids such as H_2SO_4 , H_2SO_3 , HNO_3 , HNO_2 , H_3PO_4 , H_3PO_3 , HClO , H_2CO_3 , H_3BO_3 , HIO_4 .
- 2) Write equations for formation of NaOH , KOH , Ca(OH)_2 , Zn(OH)_2 , Al(OH)_3 , Fe(OH)_3 , Mg(OH)_2 by reaction of corresponding metal oxides with water.
- 3) How are hydrogen halides (generating strong acids when dissolved in water) formed? What commercial applications are possible for etching (corroding) of glass by hydrogen fluoride solution?
- 4) Can we distinguish between pH 7.5 and 9.0 in a solution? How?
- 5) What is the ideal color range of an indicator in a titration of strong acid against strong base?
- 6) Name the salt formed by reaction of ammonia with perchloric acid.
- 7) If 6.82 ml 0.1000 N perchloric acid is consumed in a titration against 0.2132 gram of atropine sample (a naturally occurring alkaloid having equivalent weight 289.37), calculate its percentage purity.
- 8) If 0.1794 gram of a pure sample of unknown substance consumes 16.8 ml of 0.1000 N perchloric acid in a titration, is it likely to be benzylamine or dibenzylamine?
- 9) What is the normality of a solution of 4 grams of sodium hydroxide in 100mL of solution? What will be the molarity of this solution? (Clue: convert 4 grams into number of equivalents/moles and 100mL into number of litres).
- 10) While titrating 0.120 gram of a sample of 99% pure acetic acid against 0.502N sodium hydroxide, what volume of base will be consumed?

Double decomposition reactions:

Ions of two different salts, when dispersed in water or a suitable medium, may pair up differently:



In the above reactions, certain ions combine & precipitate out due to low solubility of the resulting compound. Here low solubility of one product shifts equilibrium towards the right. Such reactions may be written based on the charge on individual ions, e.g., two Fe^{3+} ions require three S^{2-} ions to form a neutral molecule, Fe_2S_3 . This is known as balancing of a chemical reaction. While balancing equations we must account for every atom and charge on both sides representing reactants and products. It may be helpful to omit those ions which do not participate in the reaction and are mute spectators. Example:



Double decomposition reactions are used in analytical chemistry to test for ions such as chloride, sulfate, cyanide, etc. by titration. These ions are titrated against AgNO_3 , BaCl_2 , AgNO_3 respectively (to precipitate AgCl , BaSO_4 , AgCN) till excess titrant shows colour change with indicator. Double decomposition is also used in metallurgy to concentrate ores. Many inorganic chemicals are industrially produced this way.

Questions:

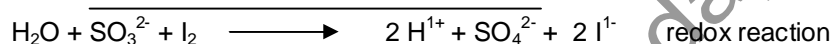
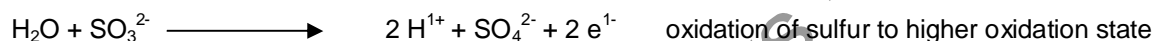
- 1) Can we use a double decomposition reaction to make $\text{Al}(\text{OH})_3$? Explain how.
- 2) How can we use double decomposition reaction to remove cyanide ions from water? [Clue: Find out solubilities of NaCN , CuCN , $\text{Ba}(\text{CN})_2$ in water].
- 3) Can we expel sulfide ions as H_2S gas from a solution of Na_2S ? What ions need to be introduced? Is it possible to precipitate sulfide ions by introducing a different ion?
- 4) Ability of halide ions to precipitate silver ions as silver halides is used in titration method to test for halide content in a solution. What type of an indicator do we require here?

Redox reactions:

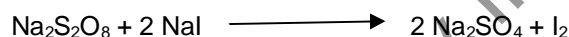
There are reactions where species give/take electrons to form new species. These are called reduction-oxidation or redox reactions.



Reaction 2, for example, may be divided into two half reactions as follows:



Such redox reaction based titrations are useful as analytical tools while testing samples of oxidizing/reducing agents. Iodimetry is based on redox method. It involves reducing iodine to iodide ion or oxidizing the latter to iodine and estimating iodine consumed/liberated through titration. Standard sodium thiosulfate solution is frequently used in this titration, with starch (which gives dark blue colour with iodine) as an indicator:



Oxidation state of an element is always zero while those of hydrogen and oxygen in compounds are generally taken as +1 and -2 respectively. Sulfur in the above reaction is increasing +4 oxidation state to +6. Iodine is getting reduced from 0 to -1. Increase of oxidation state is therefore oxidation while decrease is reduction. Similarly, oxidation states of chlorine in HCl , HClO , HClO_2 , HClO_3 , HClO_4 are -1, +1, +3, +5, +7 respectively. Nitrogen's oxidation states in N_2O , NO , N_2O_3 , N_2O_4 , N_2O_5 are +1, +2, +3, +4, +5 respectively. Oxidation potential is the energy required for an oxidation (half-reaction). The other half-reaction is reduction of another species, by taking electron generated from oxidation. This data for various elements, available in textbooks under "Standard electrode potentials", allows us to determine which reactions are favored naturally and which ones require external energy. Using oxidation potentials we may list metals in the order of their reactivities. Gold/platinum are among the least reactive. A more reactive metal may displace less reactive metal from its compound in a solution. Sodium displaces hydrogen from water. Zinc displaces copper. Copper displaces gold. Using electrical energy it is possible to reverse many of these reactions. For example, sodium chloride may be converted into sodium metal and chlorine gas in an electrolytic cell.

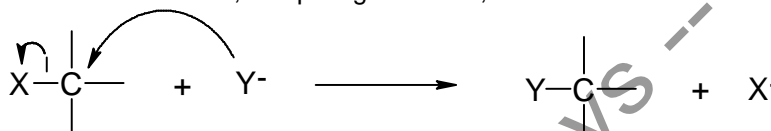
Half-reaction	E^0 , volts
$\text{Li}^+ + \text{e}^- \longrightarrow \text{Li}$	-3.045
$\text{Na}^+ + \text{e}^- \longrightarrow \text{Na}$	-2.714
$\text{Mg}^{++} + 2\text{e}^- \longrightarrow \text{Mg}$	-2.37
$\text{Al}^{+++} + 3\text{e}^- \longrightarrow \text{Al}$	-1.66
$\text{Zn}^{++} + 2\text{e}^- \longrightarrow \text{Zn}$	-0.763
$\text{Cu}^{++} + 2\text{e}^- \longrightarrow \text{Cu}$	+0.337
$\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}$	+0.798
$\text{Br}_2 + 2\text{e}^- \longrightarrow 2\text{Br}^-$	+1.065
$\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Cl}^-$	+1.36
$\text{F}_2 + 2\text{e}^- \longrightarrow 2\text{F}^-$	+2.87

Questions:

- 1) We learnt earlier that Group Ia metals are more electropositive than Group IIa. Explain this in terms of oxidation potentials.
- 2) Double bonds in commercial products like cooking oils are often quantified in terms of iodine value, number of milligrams of iodine consumed by one gram of substance. Explain how this test is done.
- 3) Suggest a way to coat a copper ring with silver or gold.
- 4) Explain how bubbling chlorine gas into a solution of sodium bromide generates bromine vapor.

Bonding—ionic and covalent:

As discussed earlier, certain elements tend to form ions by giving/taking electrons while others tend to share electrons with other atoms. Such sharing may or may not be equal due to differing pulls, but sharing one electron or more each ensures that both atoms get the benefit of filled outer orbitals. Shared bonding is called covalent bonding. Unequal pull from partners often results in polarization of the covalent bond itself, resulting in potential attack by electrophilic (seeking negative charge) or nucleophilic (seeking positive charge) species. This results in substitution over a single covalent bond or addition over a double or triple bond. During substitution many concepts like leaving group stability, activation energy/enthalpy, catalysis, nucleophilicity, reaction kinetics, steric orientation effects, competing reactions, etc. are used to rationalize data.



Carbon can bond with its own atoms. Here we must remember that carbon has a valency of 4, which makes double & triple covalent bonds possible. Diamond is pure carbon in a crystalline lattice. We will read more when we discuss carbon compounds under organic chemistry.

We also find elements like nitrogen, phosphorus, sulfur, chlorine, etc. which have some of their outer sub-orbital electrons already in paired form. They may additionally share these spare pairs unequally with elements like boron, aluminium, oxygen, etc. which are always hungry for an electron pair. This one-sided sharing is known as coordinate covalent bond, where a complete electron pair is offered by one atom only.

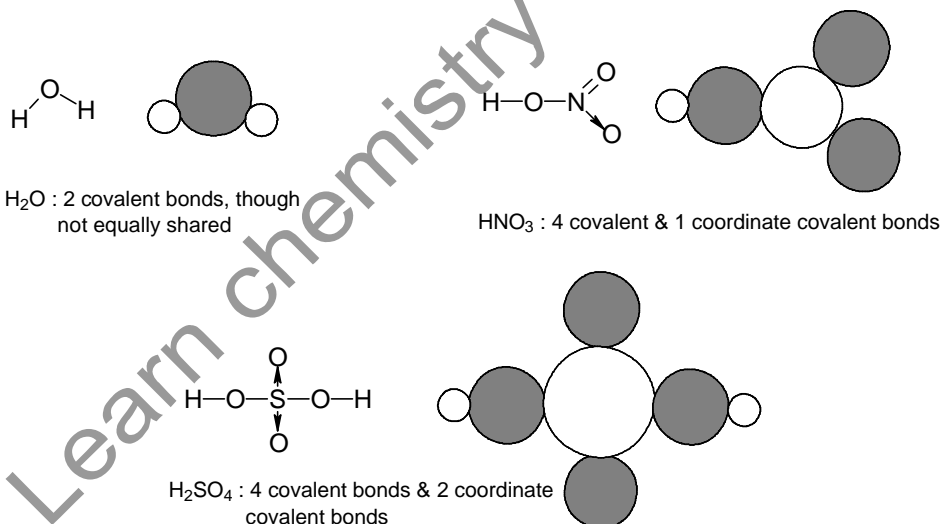


Fig 4: Bonding

Breaking of covalent bonds is governed by energy requirements and reactivities, which are fairly predictable, once we understand various types of chemical reactions, their mechanisms & limitations, critical parameters, other effects including catalysis, etc. Using a combination of these reactions, it is possible to convert plentiful raw materials into a range of commercial products we find in the market today. Each of these in turn offers us more options for making new value-added substances. For example, crude petroleum is fractionated in refineries to get a range of gaseous, liquid and solid products. These clean raw materials are then subjected to

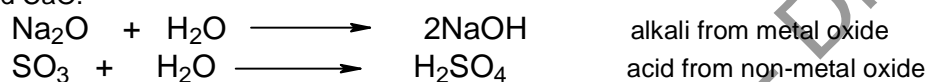
various chemical processes to yield progressively more complex products finding applications in industries as varied as pharmaceuticals, agrochemicals, dyes, pigments, fragrances, cosmetics, toiletries, coatings, inks, lubricants, adhesives, plastics, resins, oils, textiles & leather, paper, surfactants & emulsifiers, optical whiteners, plasticizers, UV absorbers, antioxidants, preservatives, stabilizers, biocides, catalysts, electronic chemicals, warfare agents, fuels, rocket propellants, ceramics, etc.

Questions:

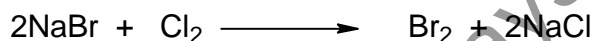
- 1) When does a part of a molecule allow itself to be attacked by electrophilic/nucleophilic group? Which pole of a polarized bond do you expect an electrophilic species to attack?
- 2) How effective is a good leaving group as an attacking species in substitution reaction?

Inorganic compounds:

Oxides: These are most abundant in nature. Alkalis are formed when metallic oxides dissolve in water while acids result from non-metallic oxides and water. Most common oxides are H_2O , SiO_2 , Fe_2O_3 , Al_2O_3 , Cr_2O_3 , TiO_2 , Mn_2O_3 and CaO .

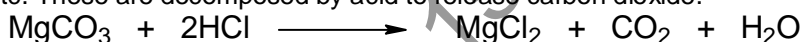


Halides: Chlorine is found abundantly and forms chlorides with most metals. NaCl is present in sea water while KCl is mined. Potassium fluoride is found in nature. Bromine is produced by displacement from sea water using chlorine gas.



Chlorine gas oxidizes bromide ion to bromine. Please note half reaction potentials favouring this. Fluorine, the most electronegative element, is difficult to be generated from fluoride except through electrolysis.

Carbonates: Presence of atmospheric carbon dioxide has created carbonate ores such as MgCO_3 , BaCO_3 , CaCO_3 , ZnCO_3 , etc. These are decomposed by acid to release carbon dioxide.



Sulfides: Heavy metal sulfides are characterized by general insolubility in water and black color. Many natural ores exist as sulfides, e.g., copper, cobalt, zinc, lead, cadmium, arsenic, etc. Na_2S is a reducing agent.

Nitrates: Tendency of nitrates to go back to lower oxidation state of nitrogen has made them a source of oxygen in fireworks and explosives.

Nitrites: Salts of nitrous acid, HNO_2 , which may be regenerated by acidification.

Silicates: Sand and complex silicates are found in nature. Silicon is widely used in electronics. It is made from sand (silicon dioxide, SiO_2). Complex silicates have applications in catalysis.

Phosphates: Used as fertilizers and detergent additives. Many phosphorus compounds are used as agrochemicals. A few find applications in pharmaceuticals.

Phosphites: Salts of phosphorus acid, H_3PO_3 . They are reducing agents.

Sulfates: Na_2SO_4 is found in nature. Ammonium sulfate is a minor fertilizer. Sulfur-based agrochemicals are common.

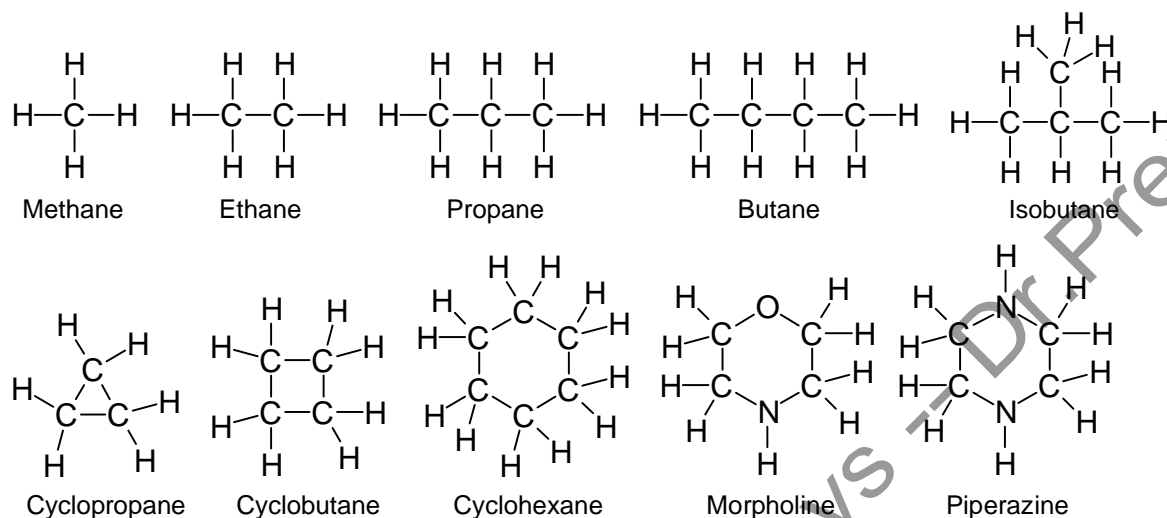
Sulfites: These are salts of sulfurous acid, H_2SO_3 , and are reducing agents.

ORGANIC CHEMISTRY

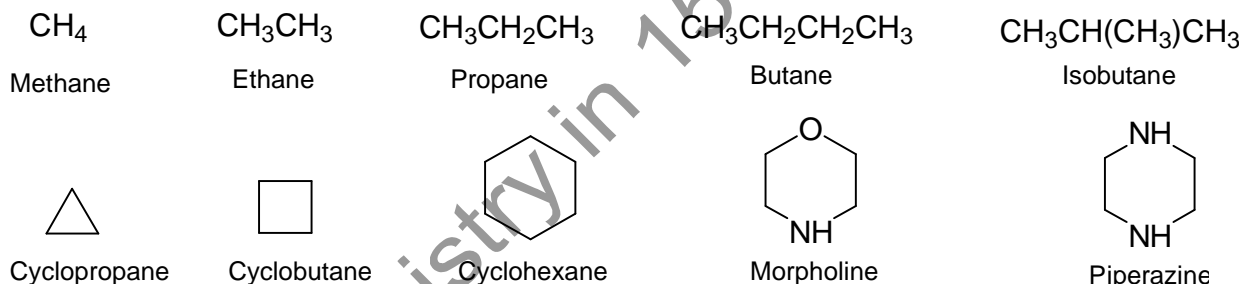
The chemistry of millions of known and unknown covalent compounds of carbon through combination with hydrogen, oxygen, nitrogen, fluorine, chlorine, bromine, sulfur, phosphorus, etc. is known as organic chemistry. Carbon atoms, having a valency of 4, have ability to form infinite number of compounds through linkage with themselves as well as other atoms. Various types of chains and rings are possible among organic compounds. Organic chemical transformations are possible (so as to create millions of compounds) due to the presence of specific functional groups, which are polarized parts of an organic molecule, allowing themselves to be attacked by electron-rich or deficient species. Various functional groups behave differently, but it is easy to understand & predict these reactions if we understand the nature of polarization underlining the reactivity of a given functional group and the type of attacking species. Organic reaction mechanisms have been studied extensively by various researchers and published in most text-books. These help us understand the site of attack and its consequence in a chemical reaction.

Chains, branches, rings and isomers:

Carbon atoms link up to form chains, branches and rings. Sometimes more than one arrangement of a given set of atoms is possible, leading to different compounds having same formula. Such compounds having same empirical formula but different structures are known as isomers.

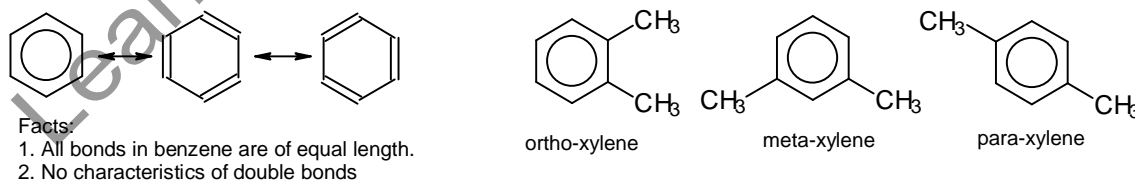


The possibilities are endless with various permutations & combinations involving other elements. In a simpler representation, the above chemical structures may be written as follows:



Benzene & its substituted derivatives:

The most common ring compound is benzene, C_6H_6 , whose structure puzzled chemists till Kekule dreamt of a snake catching its own tail. Numerous permutations with various substituents on the benzene ring have engaged organic chemists till date. Disubstituted benzenes offer various possibilities including ortho-meta-para isomers at 1,2-, 1,3- and 1,4-positions respectively:

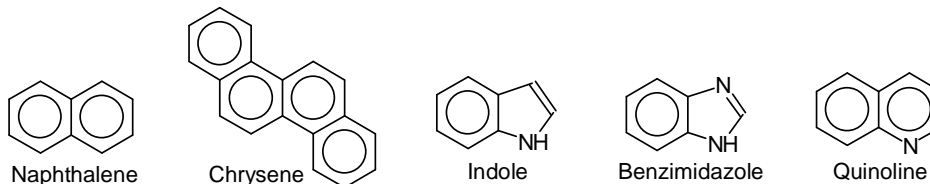


Exercise:

- 1) Write the molecular structure of cyclohexylbenzene, in which one of benzene's hydrogens is replaced by a cyclohexyl group. Ensure every carbon has only four bonds.
- 2) How many isomers of trimethylbenzene are there?
- 3) Write structures of all isomers of dichloroaniline or aminodichlorobenzene.

Fused rings:

Two or more rings may fuse together to produce polycyclic compounds:



Functional groups:

Certain parts of organic molecules have capacity to undergo certain chemical reactions due to polarization of bond(s) within the part, known as a functional group, allowing electrophilic/nucleophilic species to attack. Compounds containing just carbon & hydrogen, saturated (multiple bond absent) or unsaturated (multiple bond present), are called hydrocarbons. Saturated hydrocarbons are presumed to have no functional groups, though it is possible to introduce functional groups in them.

Examples of species capable of attacking functional groups are:

Electrophilic (attracted to negative charge):

1. Hydrogen ion H^+ formed by ionization of acids.
2. Nitronium ion NO_2^+ formed by mixing con. HNO_3 (nitric acid) and con. H_2SO_4 (sulfuric acid).
3. Chlorinium ion Cl^+ formed by reaction of $AlCl_3$ with chlorine molecule
4. Carbonium ions such as $(CH_3)_3C^+$ formed when $(CH_3)_3COH$, tertiary-butanol, is treated with an acid

Nucleophilic (attracted to positive charge):

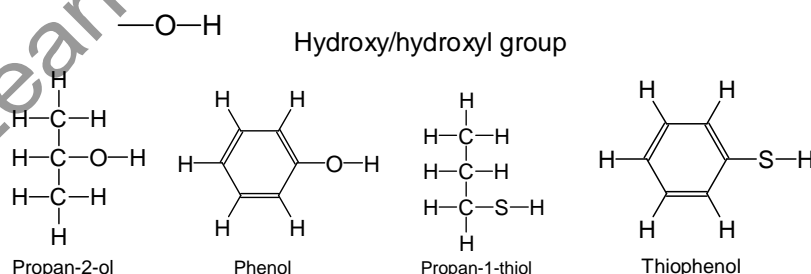
1. Hydroxide ion OH^- formed by ionization of metallic hydroxides
2. Cyanide ion CN^- formed by ionization of metallic cyanides
3. Carbanions such as $NC-CH_2^-$ formed when a polarized C-H bond is split with help of a strong base
4. Amines derived from NH_3 , including those where one or more H is substituted by an alkyl group such as CH_3^- (methyl), $CH_3CH_2^-$ (ethyl), $C_3H_7^-$ (propyl), etc. An electron-rich nitrogen is present in amines.

Bond polarization: driving force for reactions

Polarization of a covalent bond due to differing affinities of elements for a shared electron pair creates a dipole. Fractional negative and positive charges develop. These poles are attacked by oppositely charged poles from another dipole. This is the basis for chemical reactions involving covalent molecules. The only exception is free radical reactions involving equal splitting of a covalent bond.

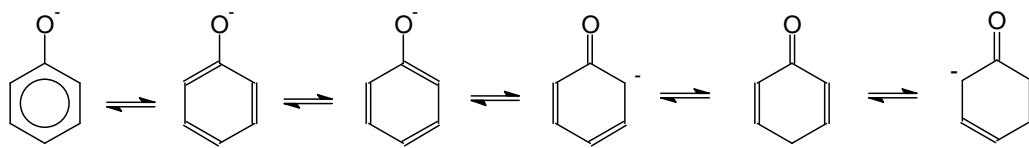
Various types of functional groups

1. Hydroxy/thiol group representing an alcohol/phenol or its sulfur analog mercaptan/thiophenol:

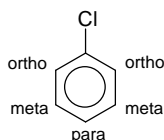


Alcohols and phenols are distinguished by the degree of polarization of the O-H bond. Phenols are acidic enough to dissolve in aqueous NaOH solution (to form sodium phenoxides) unlike alcohols, which require a stronger base such as Na metal to form sodium alkoxides. This increased polarization of O-H bond in

phenols is attributed to the ability of the phenyl ring to stabilize the negative charge on oxygen through delocalization or resonance:

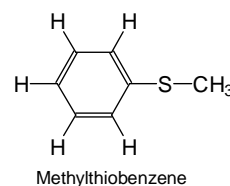
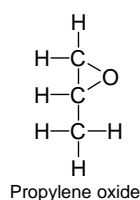
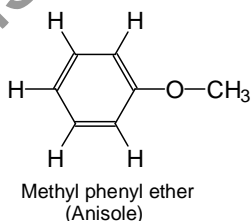
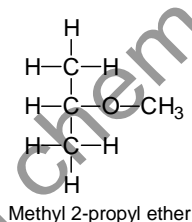


This delocalization in substituted benzenes is influenced by the nature of substituent present. However, the effect is always either increase or decrease of electron density at 2-, 4- & 6-positions relative to substituent. Positions 2- & 6- are known as "ortho" positions while position 4- is "para". Remaining 3- & 5-positions are "meta".



This concept of resonance is used to explain why

- (i) Substituents in which a positively polarized atom is attached to ring decrease its electron density at ortho & para positions and allow electrophilic aromatic substitution mainly at meta (3 and 5) positions, e.g., carbonyl, nitrile, nitro, sulfonic acid, etc. Such electron-withdrawing groups are also called "**meta-directing groups**".
 - (ii) Substituents in which a negatively polarized atom is attached to ring increase its electron density at ortho & para positions and allow electrophilic substitution mainly at ortho (2- & 6-positions) and para (4-) position, e.g., alkyl, alkoxy, phenolic, amino, amido, halogeno, etc. Such electron-releasing groups are also called "**ortho-para directing groups**".
 - (iii) All bonds within the phenyl ring are identical with same bond length, showing no "addition" properties of double bonds.
 - (iv) Carbonium ions or carbanions attached to a phenyl ring are more stable.
2. Alkoxy/aryloxy group representing an ether (including 3-membered ring "epoxides", which are easily broken into, forming a range of derivatives with water, alcohol, acid, amine, phenol, etc.) or its sulfur analog thioether:



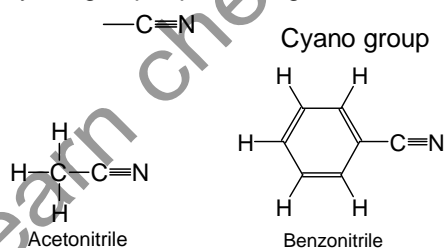
3. Carbonyl group representing aldehyde, ketone, carboxylic acid, ester, acid chloride/halide, amide, acid anhydride and acyl cyanide:



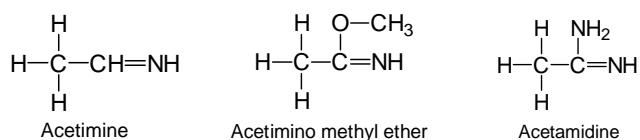
<p>Acetaldehyde</p>	<p>Aldehyde: carbonyl group flanked by hydrogen and alkyl groups</p> <p>In acetaldehyde, the alkyl group is methyl.</p>
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$\begin{array}{c} \text{H} \quad \text{O} \quad \text{H} \\ \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \\ \text{H} \quad \quad \text{H} \end{array}$ <p>Acetone</p>	<p>Ketone: carbonyl group flanked by two alkyl groups</p> <p>In acetone, the alkyl groups are both methyl. A more logical name is dimethylmethanone but acetone is commonly used.</p>
$\begin{array}{c} \text{H} \quad \text{O} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{O}-\text{H} \\ \\ \text{H} \end{array}$ <p>Acetic acid</p>	<p>Carboxylic acid: carbonyl group flanked by alkyl and hydroxyl groups</p> <p>In acetic acid, the alkyl group is methyl. Ethanoic acid is a more logical name, but acetic acid stays.</p>
$\begin{array}{c} \text{H} \quad \text{O} \quad \text{H} \\ \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{O}-\text{C}-\text{H} \\ \quad \quad \\ \text{H} \quad \quad \text{H} \end{array}$ <p>Methyl acetate</p>	<p>Ester: carbonyl group flanked by alkyl and alkoxy groups</p> <p>In methyl acetate, the alkyl group is methyl and alkoxy group is methoxy. Nomenclature starts with the alcohol's alkyl group first.</p>
$\begin{array}{c} \text{H} \quad \text{O} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{Cl} \\ \\ \text{H} \end{array}$ <p>Acetyl chloride</p>	<p>Acid chloride: carbonyl group flanked by alkyl and halide groups</p> <p>In acetyl chloride, the alkyl group is methyl.</p>
$\begin{array}{c} \text{H} \quad \text{O} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{NH}_2 \\ \\ \text{H} \end{array}$ <p>Acetamide</p>	<p>Amide: carbonyl group flanked by alkyl and amino groups</p> <p>In acetamide, the alkyl group is methyl.</p>
$\begin{array}{c} \text{H} \quad \text{O} \quad \text{O} \quad \text{H} \\ \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{O}-\text{C}-\text{C}-\text{H} \\ \quad \quad \\ \text{H} \quad \quad \text{H} \end{array}$ <p>Acetic anhydride</p>	<p>Acid anhydride: carbonyl group flanked by alkyl and acyloxy groups</p> <p>In acetic anhydride, the alkyl group is methyl and acyloxy group is acetyloxy.</p>
$\begin{array}{c} \text{H} \quad \text{O} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{C}\equiv\text{N} \\ \\ \text{H} \end{array}$ <p>Acetyl cyanide</p>	<p>Acyl cyanide: carbonyl group flanked by alkyl and cyano groups</p> <p>In acetyl cyanide, the alkyl group is methyl.</p>

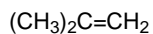
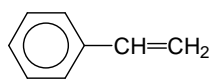
4. Cyano group representing a nitrile:



5. Imino group representing an imine, imino ether, amidine:

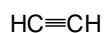


6. Reactive double bond representing an alkene:



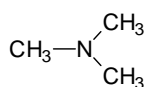
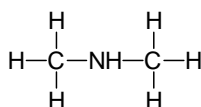
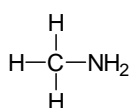
Isobutylene

7. Reactive triple bond representing an alkyne:

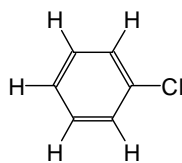
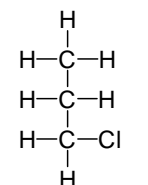


Acetylene

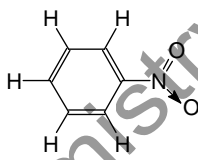
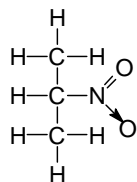
8. Nitrogen containing (electron pair rich) amines:



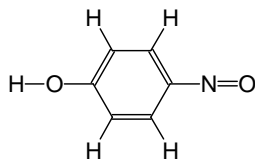
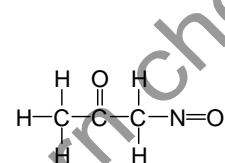
9. Halogen-containing alkyl/aryl halides:



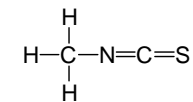
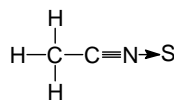
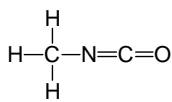
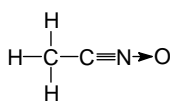
10. Nitro group containing nitroalkanes/nitroarenes:



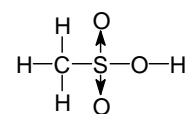
11. Nitroso compounds:



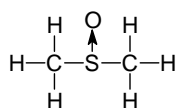
12. Cyanates/isocyanates/thiocyanates/isothiocyanates:



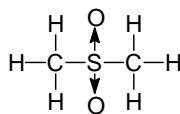
13. Sulfonic acids/sulfones/sulfoxides/sulfonyl chlorides:



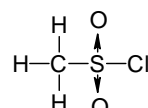
Methanesulfonic acid



Dimethyl sulfoxide

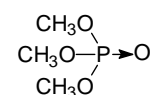


Dimethyl sulfone

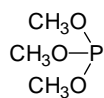


Methanesulfonyl chloride

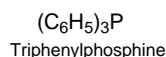
14. Phosphates/phosphites/phosphines:



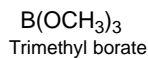
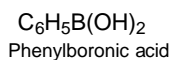
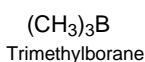
Trimethyl phosphate



Trimethyl phosphite



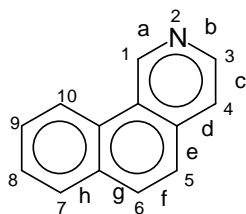
15. Boranes, boronic acids, borates:



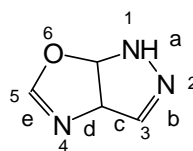
Nomenclature in organic chemistry:

Functional groups, substituents, basic structure and orientation of an organic molecule are expressed through an internationally accepted naming system called IUPAC. The following simple principles may be used in naming organic compounds:

- 1) A basic skeleton of the compound is identified while substituents are indicated by marking various positions.
- 2) Various substituents are marked in alphabetical order.
- 3) Even large fragments may be shown as substituents on a small but convenient skeleton.
- 4) When heteroatoms are present in a ring, that belonging to highest group in periodic table gets priority. If two heteroatoms of the same group are present, then preference is given to lowest atomic number. Prefixes indicate the hetero atom(s) present while suffixes indicate ring size & saturation/unsaturation. Prefixes dihydro, tetrahydro, etc. are used to indicate level of unsaturation. The numbering of positions must ensure lowest numbers.
- 5) In fused ring compounds the ring containing a hetero atom is taken as the parent compound. If more than one heterocyclic ring is present, nitrogen gets highest priority. If other heteroatoms are present, then above system based on periodic group is followed. The fused ring is prefixed to the parent ring, e.g., benzo, naphtho, etc. If more than two rings are fused, the structure is written with maximum rings in horizontal position and other rings preferably on the right side above the horizontal line. Numbering is done clockwise starting from the top rightmost ring & omitting ring junctions. Small letters a, b, etc. are used to indicate peripheral sides 1-2, 2-3, etc. while prefixing with the place of fusion in other ring.



Benzo[h]isoquinoline



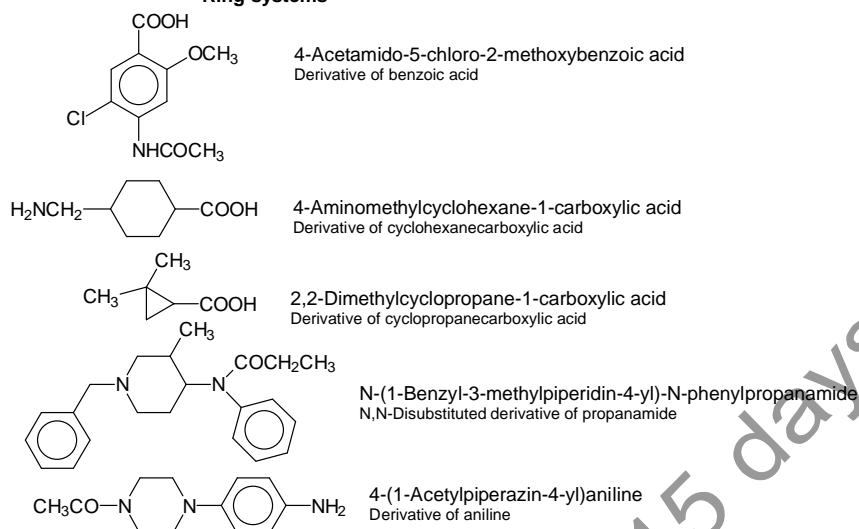
1H-Pyrazolo[4,3-d]oxazole

- 6) If the compound contains one principal functional group, it is indicated in the ending of the name. When more than one functional group is present, the principal function's suffix & others' prefixes are used, e.g., 4-hydroxycyclohexane-1-carboxylic acid.

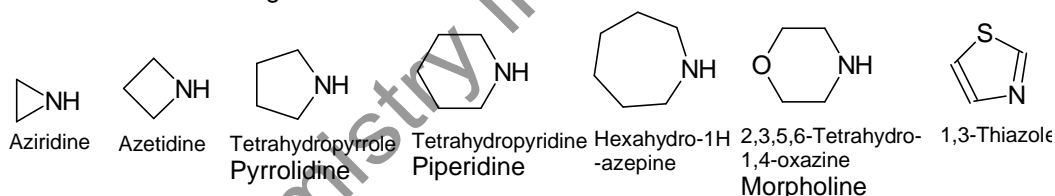
Straight chains

$\text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2$	1-Nitropropane (propane derivative)
$\text{ClCH}_2\text{CH}_2\text{COOH}$	3-Chloropropanoic acid (Propane derivative)
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{OH}$	2-Ethyl-1-hexanol (Hexane derivative)
$\text{CH}_2=\text{CHCOCH}_3$	1-Buten-3-one (Butane derivative)
$\text{CH}_3\text{C}\equiv\text{CHCOOH}$	2-Butynoic acid (Butane derivative)

Ring systems



Size of ring systems is indicated using suitable suffixes while heteroatoms are shown using prefixes. The suffix also indicates whether the ring is saturated or unsaturated.



Organic synthesis:

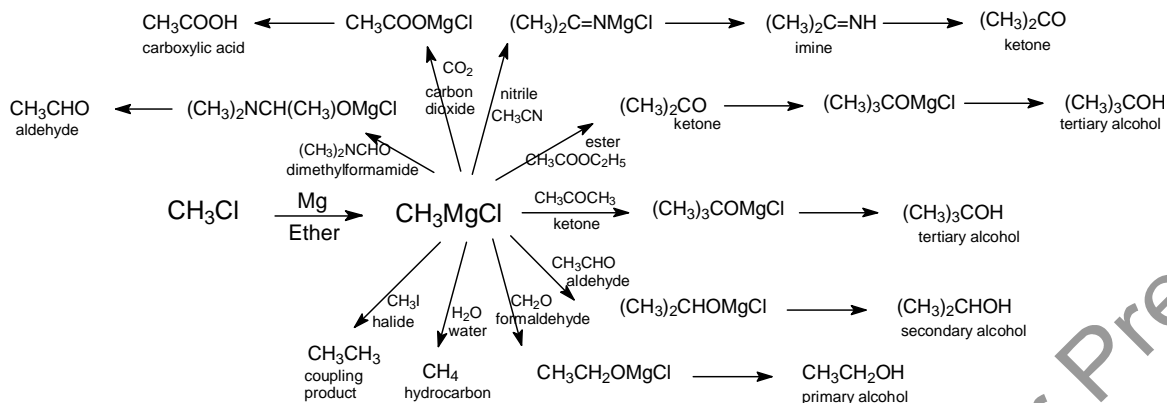
The art of using various combinations of chemical reactions to create man-made organic chemicals is known as organic synthesis. It is a fusion of logic & creativity with deft hands & physical labour. Published data are available in literature, which often give valuable insights regarding the behaviour/controlling parameters of a given chemical reaction. By carrying out simulated small experiments, it is possible to generate sufficient data on desirable sequence of operations, optimum parameters, conversion & yield, material balance, product isolation, process control & testing methods, specifications, safety precautions to be taken, recycle of reagents/solvents, engineering design, pollution control, quality assurance, etc. This data may then be processed to generate operating procedures and other documents such as material safety data sheet (MSDS), material specifications, costing, statutory licences, packing-related certification, shipping documents, methods of analysis, certificates of analysis, etc. An optimized & validated process technology is a pre-condition for commercial production where occupational health & safety and repeatability are of prime concern.

Organic reactions:

Alcohols

In alcohols, the hydroxyl group consists of a polarized $\text{O}^{\delta-}-\text{H}^{\delta+}$ bond in which the hydrogen has acquired a slight positive charge while oxygen has acquired a slight negative charge. Any element more electropositive

Reactions of Grignard reagent, e.g., methyl magnesium chloride



Starting material	Grignard reaction product
Formaldehyde	Primary alcohol
Other aldehyde	Secondary alcohol
Ketone	Tertiary alcohol
Nitrile	Ketone
Ester	Tertiary alcohol (usual)
α,β -Unsaturated ester	1,4-Addition (Cu catalyst)
N,N-Dialkylformamide	Aldehyde
Acid chloride	Ketone (very low temp.) Tertiary alcohol (usual)
Carbon dioxide	Carboxylic acid
Reactive halide	Hydrocarbon
Ethylene oxide	Primary alcohol
Water	Hydrocarbon

Nitro/nitroso compounds

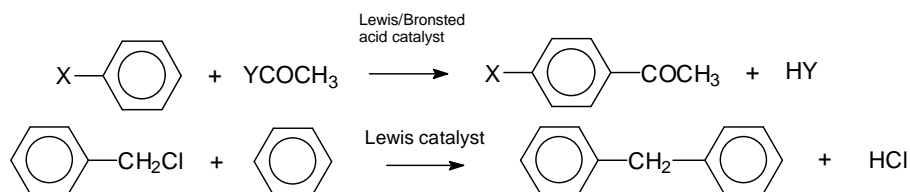
Nitro compounds are derived from nitric acid while nitroso compounds are derivatives of nitrous acid. Aliphatic nitro compounds are characterized by the presence of acidic α -hydrogens while nitroso compounds generally equilibrate to form oximes. Aromatic nitro compounds are usually made by direct nitration using nitric acid with/without sulfuric acid. Activated aromatic compounds such as phenols undergo direct nitrosation with nitrous acid. Nitro/nitroso compounds are easily converted to the corresponding amines using reduction with hydrogen.

Name reactions:

Various chemists have discovered generalized but unique organic reactions that are named after them. These name reactions let us recall specific techniques for specific jobs in a complex array of reactions. They also help us apply each of these generalized techniques to prepare a large range of compounds having similar functional groups. Some of the most common name reactions besides Grignard reaction (discussed earlier) are:

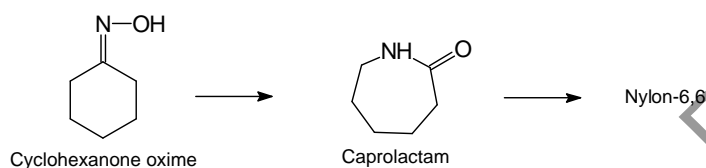
Friedel-Crafts reaction

This reaction allows us to generate an acyl carbonium ion $-\text{C}^+=\text{O}$ from acid chlorides & anhydrides, but some reagents/catalysts may work even with carboxylic acids & esters. It also generates an alkyl carbonium ion $-\text{CR}_2^+$ with compounds containing good leaving groups (such as halides, sulfonates, etc.). Originally Friedel-Crafts reactions were carried out using anhydrous AlCl_3 catalyst (Lewis acid: electron-deficient species seeking coordinate covalent bonding), which is powerful enough to be applicable in most such reactions. Today a range of catalysts from H_2SO_4 , HF , F_3CCOOH , $\text{CH}_3\text{SO}_3\text{H}$, BF_3 , ZnCl_2 , clays, alumina as well as reusable acidic resin granules is available for various applications.



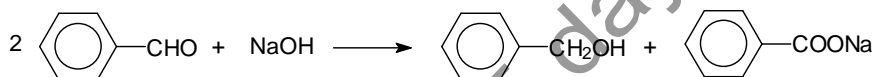
Beckmann rearrangement

Acid-catalyzed isomerization of oxime to amide is possible by this reaction. Oximes of cyclic ketones give enlarged cyclic amides.



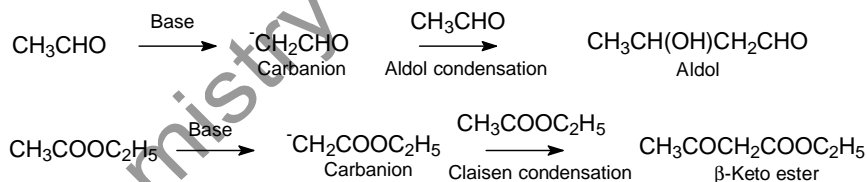
Cannizzaro reaction

Aliphatic aldehydes with no α -hydrogen and aromatic aldehydes which do not undergo aldol condensation disproportionate in the presence of base to corresponding acid and alcohol.



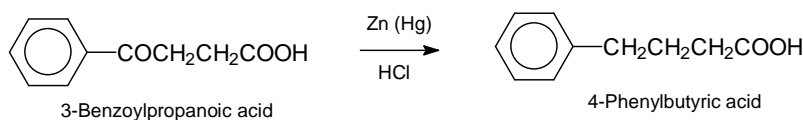
Claisen condensation

It is a type of aldol condensation restricted to esters, involving a carbanion generated from the active methylene group adjacent to a carbonyl group attacking the positively polarized carbonyl carbon of another ester molecule. The product is a β -keto ester.



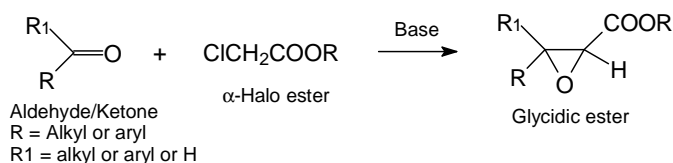
Clemmensen reduction

Reduction of an aldehyde or ketone with zinc amalgam and hydrochloric acid to give deoxygenated methylene groups is known as Clemmensen reduction.



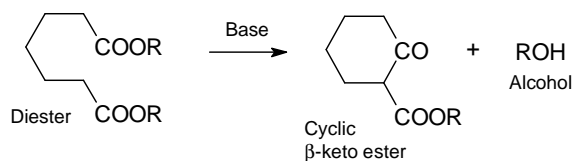
Darzens condensation

Condensation of aldehydes or ketones with α -haloesters in the presence of alkoxide base to get α,β -epoxy esters is called Darzens glycidic ester condensation.



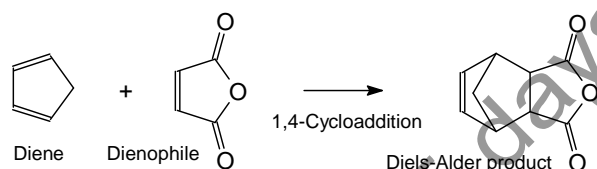
Dieckmann cyclization

A special case of Claisen condensation involving two ester groups of the same chain to get a cyclic β -keto ester is known as Dieckmann cyclization.



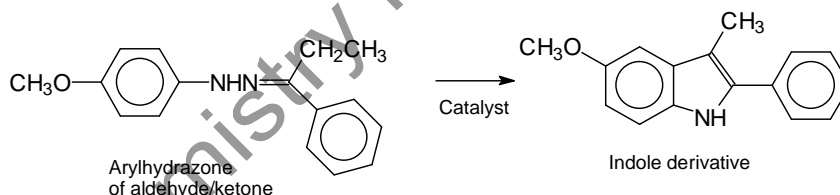
Diels-Alder reaction

Certain double bonds undergo 1,4-cycloaddition over a diene, usually under light, to give a six-membered ring.



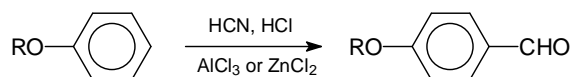
Fischer indole synthesis

Acid-catalyzed cyclization (with rearrangement) of arylhydrazones of aldehydes/ketones to indoles is known as Fischer indole synthesis.



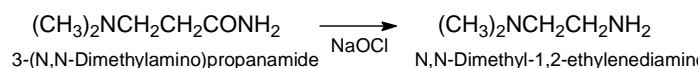
Gattermann aldehyde synthesis

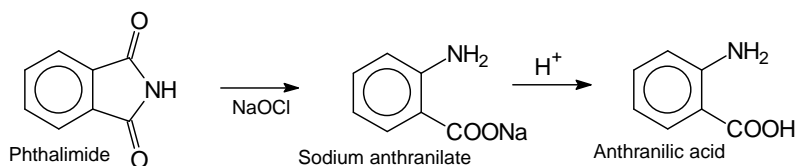
Phenols/phenol ethers undergo reaction with hydrogen cyanide and hydrogen chloride in the presence of Lewis acid catalysts to give aromatic aldehydes.



Hofmann reaction

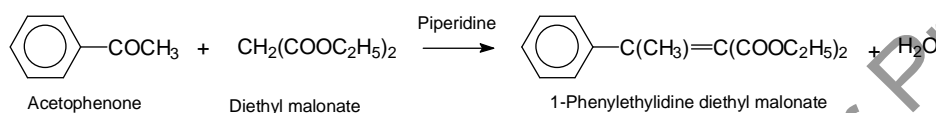
Decarbonylation of primary and secondary amides using hypohalite and base to get an amine with one carbon less is known as Hofmann reaction.





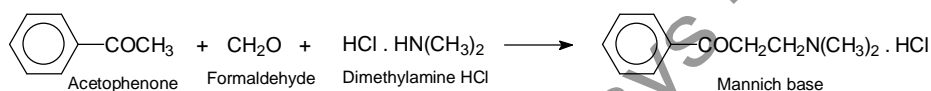
Knovenagel condensation

Aldehydes and ketones condense with active methylene compounds when catalyzed by amines to give α,β -unsaturated compounds.



Mannich reaction

Active methylene compounds condense with non-enolizable aldehydes and primary/secondary amines/ammonia to give aminomethylated products known as Mannich bases.



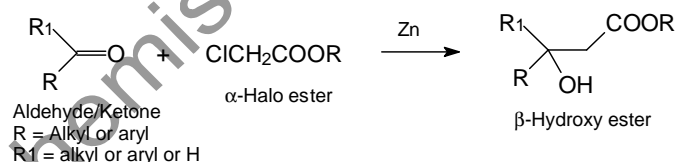
Michael reaction

Base-catalyzed 1,4-addition of a carbanion to activated α,β -unsaturated compounds is known as Michael reaction.



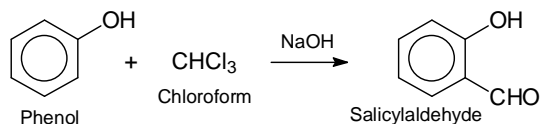
Reformatsky reaction

Organozinc derivatives of α -haloesters react with aldehydes and ketones to give β -hydroxy esters.



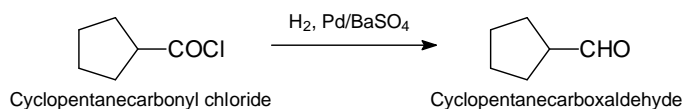
Reimer-Tiemann reaction

Phenols react with chloroform and alkali to give phenolic aldehydes.



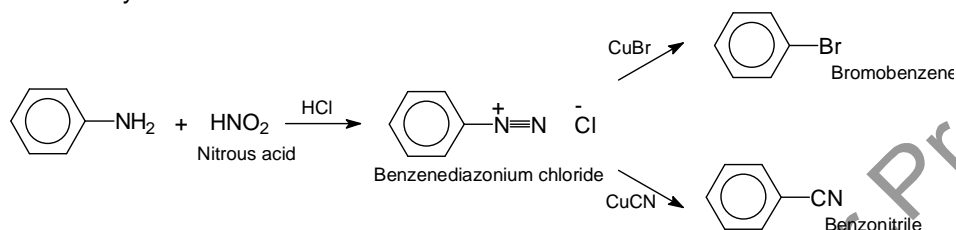
Rosenmund reduction

Stopping catalytic hydrogenation (reduction reaction using hydrogen gas in presence of catalyst) of acid chlorides at aldehyde stage (which can further get reduced to alcohol) through deliberate poisoning of palladium catalyst using BaSO_4 is known as Rosenmund reduction.



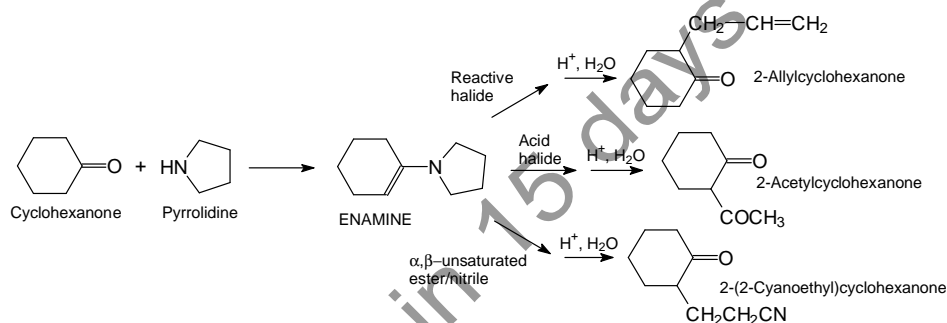
Sandmeyer reaction

Replacement of an aromatic primary amine group through diazotization by halo or cyano groups using cuprous salts is known as Sandmeyer reaction.



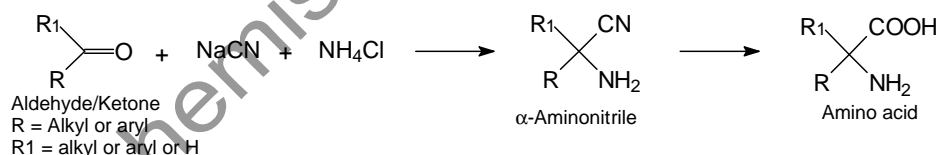
Stork enamine reaction

Reactive alkyl & acyl halides as well as α,β -unsaturated esters/nitriles react with enamines (a type of Schiff's base derived from cyclic secondary amine and a cyclic ketone) to give α -alkyl or α -acyl ketone.



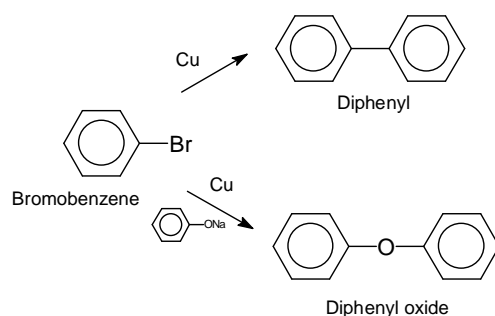
Strecker amino acid synthesis

Aldehydes, ammonia and hydrogen cyanide react to form α -aminonitriles, which are easily hydrolyzed to the corresponding amino acids.



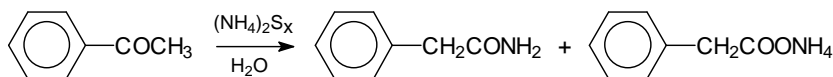
Ullmann reaction

Biphenyl is obtained through copper catalyzed coupling of aryl halides. Diaryl ethers are also obtained by reaction of aryl halide with phenol.



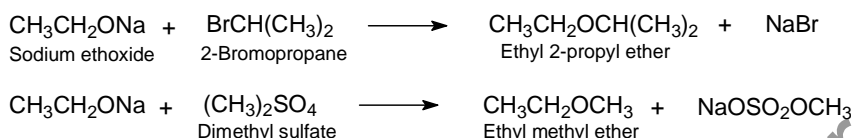
Willgerodt-Kindler reaction

Conversion of aryl alkyl ketones to amides and/or the ammonium salts of corresponding acids by sulfur and amine is called Willgerodt-Kindler reaction.



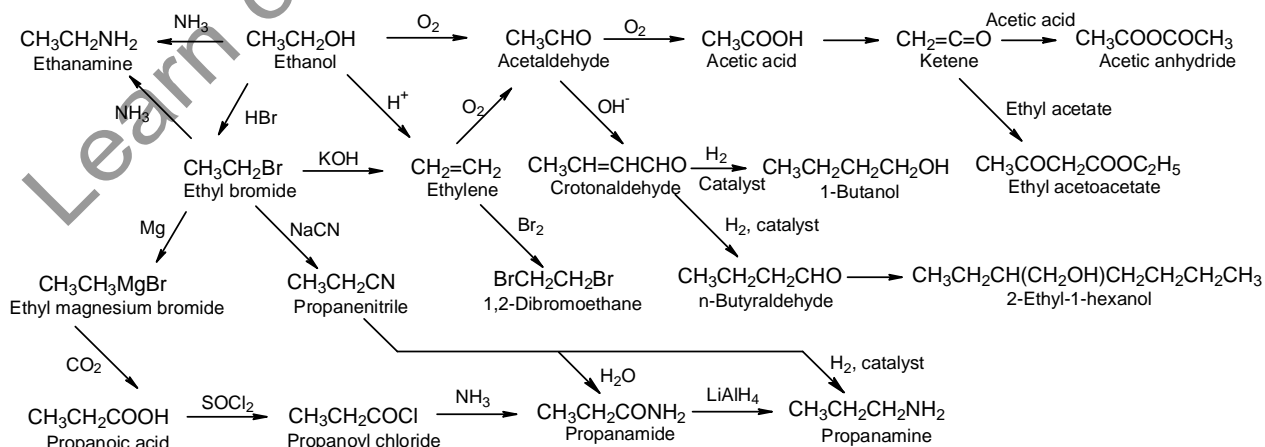
Williamson synthesis

Alkoxide base reacts with alkyl halide/sulfate to give aliphatic ethers.



Organic functional group preparations:

- Alcohols are generally made by (1) reduction of aldehydes, ketones and esters, (2) hydration of double bonds, (3) direct oxidation of hydrocarbon with oxygen, (4) Grignard reaction
- Aldehydes are generated by (1) mild oxidation of primary alcohols or hydrocarbons, (2) halogenolysis of acid chlorides with hydrogen, (3) Darzens reaction, (4) Grignard reaction, (5) hydroformylation, (5) Sommerlet reaction, (6) Gattermann reaction, (7) Reimer-Tiemann reaction, (8) Stephen reaction
- Ketones are made by (1) Friedel-Crafts reaction, (2) direct oxidation of hydrocarbon or alcohol, (3) Claisen/Dieckmann condensation, (4) Grignard reaction, (5) pyrolysis of carboxylic salts, (6) hydrolysis of imines
- Carboxylic acids are made by (1) direct oxidation of hydrocarbon, alcohol or aldehyde, (2) hydrolysis of esters, amides or nitriles, (3) carbonylation of alcohols/halides, (4) Grignard reaction
- Esters are made by (1) direct reaction of carboxylic acid/acid chloride/another ester with alcohol, (2) hydrolysis of imino ethers, (3) alkoxy carbonylation with dialkyl carbonate
- Acid chlorides are made by reaction of carboxylic acid with SOCl_2 , SOCl_2 , PCl_3
- Amides are made by (1) reaction of amines with acid chlorides, carboxylic acids, esters or other amides, (2) hydration of nitriles, (3) Beckmann rearrangement
- Nitriles are made by (1) cyanation of halides, (2) industrial vapor-phase ammoxidations, (3) dehydration of primary amides and aldoximes, (4) Sandmeyer reaction
- Halides are obtained by (1) direct halogenation of hydrocarbons, (2) reaction of alcohols with hydrogen halides, (3) cleavage of ethers, (4) Sandmeyer reaction
- Amines are made by (1) direct alkylation of ammonia with alcohols in vapor phase or with alkyl halides in presence of base, (2) reduction of imines, nitriles or nitro compounds, (3) LiAlH_4 reduction of amides, (4) Hoffmann degradation of amides.



Reaction mechanisms:

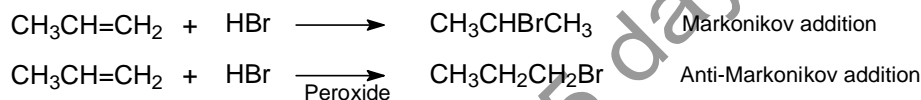
Reactions may be classified into three categories:

1. Reactions where one bond is replaced by another bond through ion pair formation
2. Reactions where one bond is replaced by another bond without ion pair formation
3. Reactions involving free radicals formed by equal splitting of a bond.

When ion pair formation is involved, this becomes the rate-controlling step, irrespective of the concentration of the attacking species. Such reactions are called unimolecular, giving substitutions (S_N1) or eliminations (E1). Reactions involving stable carbonium ions may be unimolecular.

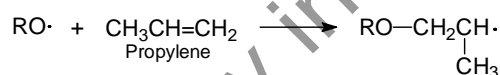
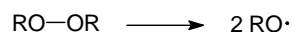
When ion pair formation does not take place, bond-breaking and bond-formation may take place simultaneously, and the rate of reaction is dependent on concentration of both reactants. This is a bimolecular reaction and may also lead to substitution (S_N2) or elimination (E2). When an unstable primary carbonium ion formation needs to be avoided, the reaction may prefer bimolecular route. It is common for unstable carbonium ions to rearrange to most stable carbonium ions, which are tertiary.

Free radicals are involved in reactions such as halogenation of alkanes. Certain polymerization reactions are carried out using free radical initiators which link up millions of monomer units containing double bonds. Using such initiators Markonikov's rule can be overcome in certain addition reactions to produce least substituted rather than most substituted derivatives.

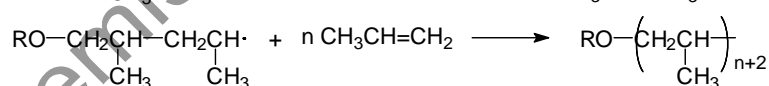
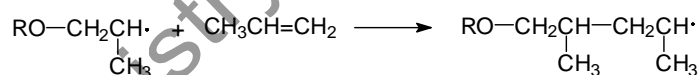


Polymerization using free radical initiators:

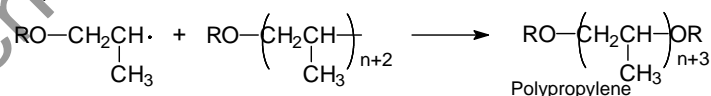
Step 1: Chain initiation



Step 2: Chain propagation



Step 3: Chain termination



Techniques in organic synthesis:

Synthesis route selection

Identifying data to be generated & designing experiments for this

Monitoring reaction through suitable tests/measurements

Sampling methodology & analytical method development

Extraction/solvent stripping

Filtration/phase separation

Distillation

Crystallization

Derivatization

ANALYTICAL CHEMISTRY

Testing forms an integral part of organic synthesis, as it is not possible to visually monitor most chemical reactions. There are test methods based on

1. Physical measurements such as pH, solubility, density, melting point, boiling point, refractive index, loss on drying, spectroscopy involving infrared, NMR, UV, atomic absorption, mass, etc.
2. Titrations involving acid-base reaction, double decomposition, redox reaction, etc.
3. Assisted separation & quantification of various components of a sample through gas chromatography (GC), high performance liquid chromatography (HPLC), thin layer chromatography (TLC), etc. These techniques rely on a mobile neutral phase to move the sample over a stationary phase, which causes different adsorbed components to move at different rates to achieve separation & detection.
4. Chemical techniques such as derivatization, elemental analysis, qualitative analysis of inorganic ions & organic functional groups.

Inorganic tests:

Qualitative:

Inorganic ions are identified using a series of reagents, which precipitate certain insoluble salts. Lack of precipitate lets us eliminate certain possibilities in a particular sequence. These tests are based on insolubility of following salts from cations:

- 1) Halides of silver, mercury(I), copper (I) and lead
- 2) Sulfides of mercury(II), bismuth, copper(II), arsenic, antimony, cadmium, tin, lead, manganese, zinc, nickel, cobalt
- 3) Hydroxides of aluminium, iron, chromium, cobalt, nickel, zinc
- 4) Sulfates of calcium, barium, strontium
- 5) Phosphate of magnesium

Anions are tested by a series of specific tests. For example, halides are precipitated as silver halides but yellow color as well as solubility in ammonia solution increases from chloride to bromide to iodide. Sulfate is precipitated by barium while nitrate has a "brown ring test". When these tests are performed in a particular order, it is possible to detect more than one salt in a mixture. Certain characteristic flame tests (colors shown by specific cations when a crystal is exposed to a flame) are also used. White salts are characteristic of sodium, potassium, ammonium, calcium, barium, magnesium, etc. (Groups IA & IIA). Only ammonium salts have characteristic odour.

Quantitative:

Inorganic compounds are tested by

1. Titrations for estimate of acid, alkali, chloride, bromide, iodide, cyanide, sulfite, peroxide, etc.
2. Atomic absorption spectroscopy to determine the percentage of specific metals
3. Gravimetric analysis to determine the content of specific ions such as sulfate.
4. Karl-Fischer titrator for moisture content
5. Manual drying for loss on drying
6. pH meter for pH measurement.

Questions:

- 1) If an inorganic salt solution gives a black precipitate with H_2S and also a rose-red precipitate with NaOH , which ion's presence is indicated? (Clue: find out which metal hydroxide is pink in color)
- 2) If a salt solution forms no precipitate with solutions of HCl , H_2S , NaOH and H_2SO_4 , what cation is indicated?
- 3) What test method would you recommend while testing BaBr_2 for its purity?

Organic tests:

Qualitative:

Organic functional groups are identified using reagents that are specific to certain functional groups:

- Aldehydes reduce Ag^+ to metallic silver, precipitating a silver mirror
- Aldehydes & ketones form solid derivatives such as phenylhydrazone, semicarbazone and oxime with phenylhydrazine, semicarbazide and hydroxylamine respectively.
- Carboxylic acids evolve carbon dioxide gas & dissolve when treated with NaHCO_3 solution. On addition of acid, the carboxylic acid is liberated.
- Phenols dissolve in NaOH but not NaHCO_3 solution. Acidification liberates free phenols. They also give dark colors with a solution of neutral FeCl_3 .
- Amines are soluble in HCl solution and are liberated on addition of base. Toluenesulfonyl chloride reacts with primary and secondary amines (in the presence of base) to form solid sulfonamides, which are soluble and insoluble respectively in NaOH solution. Tertiary amines do not form sulfonamides.
- Nitriles and amides are hydrolyzed by water in the presence of acid/base to liberate carboxylic acid and amine. Primary amides and nitriles evolve ammonia when heated with base.
- Double & triple bonded compounds undergo addition reactions with bromine water and potassium permanganate solutions leading to disappearance of colour.
- Aromatic compounds & those having high carbon content generally burn with a sooty flame compared to aliphatic compounds.
- Esters generally have sweet smell. On heating with KOH solution, they are broken down to carboxylic acid salt and alcohol and the sweet smell vanishes.
- Fusing the compound with sodium metal and dissolving in water allows us to test for halides, sulfur, and nitrogen using inorganic reagents.

A sample's pH indicates whether it is an acidic compound such as carboxylic acid/phenol or basic like amine. There are instrumental techniques known as spectroscopy based on absorption of specific energy radiation. Such spectroscopic methods are extensively used to identify functional groups and elucidate molecular structures of unknown compounds. These spectra generate unique fingerprints.

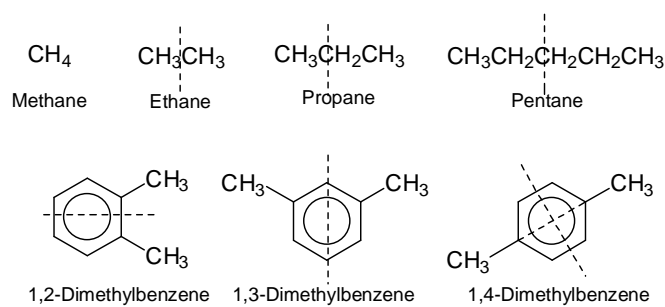
Quantitative:

Elemental analysis gives us precise percentages of carbon, hydrogen, nitrogen, etc. in a given organic sample. This is tallied with calculated percentages to see if the structure is matching. Halogens may be quantitatively estimated by fusing sample with Na and titrating the resultant aqueous solution with AgNO_3 standard solution. Gas and liquid chromatography are commonly used these days to quantify substances (a) practically using area percent method, and (b) precisely using internal standard method, which cancels differences in peak responses for different compounds. An inert standard compound of known purity & quantity is introduced into the sample and percentage purity of sample is calculated from peak areas and sample weights.

SPECTROSCOPY

Infrared spectroscopy shows fingerprints of various functional groups at specific wavelengths. For example, carbonyl groups of aldehydes, ketones, carboxylic acids, amides and esters show characteristic absorption band at wavenumber $1800\text{-}1700\text{ cm}^{-1}$, while nitriles show a characteristic band at 2300 cm^{-1} instead. Alcohols and phenols have a broad band at $3550\text{-}2700\text{ cm}^{-1}$ but they may be distinguished by phenol's aromatic hydrogens at 1500 cm^{-1} while aliphatic hydrogens show band at 3000 cm^{-1} . Amines have a strong to medium band at 800 cm^{-1} while alcohols lack this band, even though they both show weak and broad bands respectively above 3000 cm^{-1} . Alcohols and ethers may be distinguished by a characteristic band of ethers at $1300\text{-}1000\text{ cm}^{-1}$. Alkynes show a strong band at 3200 cm^{-1} which alkanes & alkenes lack. If two samples show identical IR spectra, they are likely to be the same or very similar.

Ultraviolet spectroscopy indicates the presence of UV-absorbing "chromophore" functional groups such as aromatic rings, carbonyl groups, etc. involving multiple bonds. Nuclear Magnetic Resonance (NMR) gives the relative numbers of different types of hydrogen, carbon, etc. atoms enabling us to tally with the structure on hand. For example, methane & ethane have only one type of hydrogen & carbon while propane has 2 types and pentane has 3. Similarly, 1,2-dimethylbenzene has 3 different types of aromatic carbon but 1,3-dimethylbenzene has 4 while 1,4-dimethylbenzene has just 2 owing to double symmetry.



Planes of symmetry indicating the different types of hydrogens & carbons in NMR

Mass spectroscopy gives the mass of various fragments of a given molecule, giving us valuable clues about its skeleton. Often it is possible to determine the molecular weight of an organic compound using this technique. Atomic absorption lets us identify metals & their concentrations present in a sample.

INDUSTRIAL CHEMISTRY

Tools & decisions:

Monitoring a chemical reaction is the most basic element of chemical technology. It involves mainly instrumental analysis but observations & measurements give valuable insights. Instruments are used today to generate reliable data about the progress of a chemical reaction. Based on this decisions may be taken in laboratory as well as production plant.

Routine production requires foolproof process control so that processes produce desired results consistently & safely every time. These include in-process tests, monitoring devices indicating temperature & pressure wherever required, valves at right points, audits & regular maintenance including calibration of measuring devices. Most important is presence of people who fully understand the process being carried out. Gas chromatograph has revolutionized chemical testing through fast, cheap and efficient analysis. Liquid chromatograph complements this tool and often fills in where GC is incompatible with a sample. Certain samples may require infrared and NMR spectra for further examination. Mass spectroscopy (MS) also helps in cases where minor components need to be identified. GC-MS and LC-MS are new tools available to organic/analytical chemists. These instruments separate components of a given sample and provide MS of each component in minimum time. Atomic absorption helps to keep content of metals within limits. Titration allows us to test for ions like chloride, sulfate, cyanide, etc. Simpler ready-made reagent-based test kits are also available today. Blood sugar level may be checked quickly this way with the help of a simple instrument.

Technology development:

Technology development may be defined as a series of activities that lead to a standardized reproducible process. Each of these activities such as literature survey, laboratory experiments, analytical method development, documentation, optimization, validation, sample generation, customer evaluation & fine tuning, engineering, scale-up, etc. may require repeated trials to deliver the standardized process that will pose no occupational & health risk in commercial production.

Industrial operations:

Industrial chemistry involves handling chemicals of various hazards safely and bringing about chemical reactions in specially designed reaction vessels (including those whose interiors are coated with corrosion-resistant materials such as glass/ceramic, Teflon, etc.). These reaction vessels are serviced by

- Utilities such as steam, hot oil, raw water, chilled water, chilled brine, etc., which are circulated through outer jacket of the reactor for controlling temperature
- Stirrer of appropriate design if the reaction mixture requires to be agitated to keep it homogeneous

- Distillation column, condenser and receiver if a liquid needs to be distilled out of the vessel
- Filtration devices in case solid-liquid separation is involved
- Drying systems to evaporate volatile impurities in the product
- Vacuum systems for sucking materials into vessels, facilitating filtration/distillation, etc.
- Scrubbing systems for trapping any gaseous by-product that may be released from the vessel
- Addition tanks for introducing liquid materials into reaction vessel at specific rates
- Storage tanks which hold raw materials & solvents required to be charged into reactors
- Pipelines that transport heat transfer fluids as well as process streams
- Pumps which help transfer liquids/slurries
- Various measuring devices such as temperature and pressure gauges at critical points.

There are batch wise and continuous operations. Certain processes may involve very routine operations while others may require continuous monitoring & decision-making. Liquid phase reactions as well as vapour phase reactions are employed. There are numerous designs to suit the occasion, including pressure reactors (such as hydrogenators), tubular reactors, photolytic reactors, crackers, fermentors, rotary kilns, etc. Petrochemical complexes are engineering intensive whereas pharmaceutical manufacture is human resource intensive. This means that petrochemical plants are highly automated & precision engineered to handle energy input/output as well as volumes while pharmaceutical plants focus on controls, reproducibility, documentation and quality in a technology-intensive business.

Human skills may add value to an industrial product through unmatched & consistent quality, timely delivery, excellent technical support, customization, ethical business culture, accurate documentation, flexible output, high safety and pleasant & efficient communication. Such high standards are achieved through harmony, motivation, training, technology and professional management, which smart customers always take note of.

Questions:

- 1) Identify ways to make a chemical plant spark-free and thus flame-proof.
- 2) A chemical reaction at 150 deg C under inert nitrogen atmosphere in a large reactor needs to be sampled for testing. Outline a stepwise procedure for this, including provisions in reactor and safety precautions.
- 3) If a chemical process mandates an accuracy of one degree in temperature, what should be the minimum readability of temperature indicator?
- 4) Why is it important to record every decision/operation in a chemical production batch?
- 5) What are the moral obligations of a supplier while accepting an order?
- 6) What may be the consequence if technology development does not ensure that a process is repeated & reproduced safely every time using reliable controls?
- 7) Most HPLC systems use UV detector for detecting UV-absorbing components of samples. If refractive index (RI) detector is available, what additional benefit may we get?
- 8) If samples often contain resinous impurities not eluting from GC column during analysis, what limitation does it cause? How can we overcome it?
- 9) If one of the impurities and main component merge in a GC graph, what does it mean? What needs to be done?
- 10) If a sample of acetic acid shows 99.8% purity by GC but 96.5% by NaOH titration, what may be our next test?
- 11) Why is it difficult to deliver consistent quality product in every batch unless systems are introduced?
- 12) Give reasons why international markets value ethical suppliers.

ENVIRONMENT

Purification & clean chemistry:

Purification of products is required in order to remove impurities which may enter through (1) raw materials already containing these impurities, (2) side reactions during processing, (3) incomplete conversion of raw materials, and (4) inappropriate processing including human errors & contamination. Techniques available for purification include crystallization, distillation, extraction, salt formation, and certain combination techniques

like zone refining, sublimation, freeze-drying, spray-drying, steam distillation, etc. The best technique, however, is to develop a process technology which gives complete conversion with no unwanted side product using fool-proof process control & operating procedures to deliver products safely & consistently every time. It may appear to be a dream to most humans, but nature is apparently just doing this through plants and animals. Microorganisms' tiny bodies may safely be considered capable of synthesizing many complex molecules without waste generation.

Questions:

- 1) Under what circumstances is purification of a chemical product not required after production?
- 2) What is the best way to avoid an impurity in a raw material? (Clue: buyer is a king)
- 3) Mention possible R&D goals for a product being newly produced by a company.

Pollution and sources:

Pollution from chemical industries may be contained through green chemistry, which requires that (1) wastes are eliminated through efficient conversions & zero spillages, (2) every "by-product" is treated as a product to be utilized, (3) reaction media, such as water & organic solvents, are recovered and recycled, (4) no chemical substance is allowed to get into the atmosphere in gaseous form without permission from authorities, (5) clean raw materials are used, and (6) safe methods such as incineration are employed to destroy organic residues.

Atmospheric pollution, on the other hand, is caused due to:

- Automobile exhaust gases containing carbon dioxide (which humans are generating much more than our forests can handle) and other minor but harmful pollutants
- Ozone-depleting gases released into the environment by industries such as refrigeration, polyurethane foams, aerosol sprays, etc.
- Huge quantities of chemicals dumped in the environment through toiletries, cosmetics, detergents, pest control agents, plant growth regulators, non-biodegradable plastics (often inappropriately used as packing materials), hospital wastes, etc.
- Wastes dumped by chemical and other industries due to improper treatment & accidental release
- Huge releases of pollutants through volcanic eruptions, nuclear leaks and fires in oil & gas wells, spillage of crude oil & chemicals during transportation including ruptures of pipelines, etc.
- Accumulation of chemical residues through used batteries, paints, household insecticides, cleaning agents, etc.
- Improper treatment & release of huge quantities of sewage from various cities.

Questions:

- 1) Are the basic principles of green chemistry outlined above achievable? Do they imply that clean chemistry means big investment on pollution control?
- 2) Is the present human generation justified in pumping huge quantities of carbon dioxide into environment? What clean alternatives do we have?

MANUFACTURING ETHICS & OCCUPATIONAL SAFETY

Good manufacturing practices:

Prevention of contamination during production and achieving consistent performance & traceability with safety & efficiency are major focus areas of good manufacturing practices (GMP). It requires total commitment to contractual obligations, continual improvement of processes, foolproof operating procedures, clear documentation & record keeping, calibration & validation of measuring devices as well as processes, etc. These standards are well elaborated under ISO guidelines.

Safety & systems:

Chemicals have a wide range of biological effects on our bodies. Chemical manufacturing involves many occupational hazards, which only an experienced individual/company may be able to foresee and prevent. These hazards include fire accidents, runaway exothermic reactions/explosions, equipment failure, ruptures of pipelines/equipment, spillages & accidental exposure, allergies & other biological effects, human errors leading to injury, contamination, generation of non-salable goods, etc. Every chemical can be handled safely if the hazards are well documented and sincere efforts are made. Chemical plant construction should take into account various requirements of material handling & transfer without exposing human beings to occupational hazards. It should be designed to avoid fire accidents due to mechanical as well as electrical (including static) sparks. In addition to flammability, hazards also arise out of high pressures, powered mechanical devices, inadequate process controls, improper engineering and failure of staff to react in time. For best safety an organization requires systematic working, controls, people, equipment, records, training, incentives, opportunities, drills, written instructions & documents, audits, etc. which are mandated under ISO guidelines.

Questions:

- 1) Explain why contamination of a chemical production batch is considered inexcusable.
- 2) What benefits come from good records & reviews?
- 3) Describe the knowledge profile of a Safety Manager in a large chemical plant.
- 4) Describe the knowledge profile of a Technical Head in a large chemical plant.

Exercise:

Consider the following steps in an organization for executing a new order: (1) order negotiation, (2) raw material procurement & production planning, (3) receipt of material at the gate, (4) testing, (5) transfer to store, (6) issue & use in production, (7) generating batch records & in-process test reports, (8) finishing & blending records, (9) packing, labeling, storing, shipping, documenting & communicating.

Suggest suitable records to trace every production & quality problem at the least to providing the customer a delightful experience at best.