A.D. M COLLEGE FOR WOMEN (A)., NAGAPATTINAM

PG & RESEARCH DEPARTMENT OF CHEMISTRY

STUDY MATERIAL

GENERAL CHEMISTRY - IV

II-B.SC CHEMISTRY

SEMESTER – IV

BY

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SYLLABUS

UNIT I - d-BLOCK & f-BLOCK ELEMENTS

General characteristics of d-block elements, comparative study of zinc group elements. Extraction of Mo and Pt – Alloys of copper, amalgams and galvanization. Evidences for the existence of Hg2+ ions

General characteristics of f-block elements – Lanthanides Electronic configuration – oxidation states – ionic radii, lanthanide contraction. Colour and magnetic properties. Extraction of mixture of lanthanides from monazite sand and separation of lanthanides. Uses of lanthanides. Actinides Sources of actinides – preparation of transuranic elements - electronic configuration – oxidation states – ionic radii – colour of ions – comparison with lanthanides. Extraction of thorium from monazite sand. Production and uses of plutonium.

UNIT II - CHEMISTRY OF ORGANOMETALLIC COMPOUNDS

Introduction – Preparation of organomagnesium compounds – physical and chemical properties – uses. Organozinc compounds – general preparation, properties and uses.

Organolithium, Organocopper compounds – Preparation, properties and uses. Organolead, Organophosphorous and organoboron compounds – Preparation, properties and uses.

UNIT III - CHEMISTRY OF ALCOHOLS, PHENOLS AND ETHERS

Nomenclature – Individual source of alcohols – preparation of alcohols: hydration of alkenes, oxymercuration, hydroboration, Grignard addition, reduction – Physical, chemical properties and uses- Glycols from dihydroxylation, reduction, substitution reactions and glycerols and their uses.

Preparation of Phenols including di- and trihydroxy phenols – Physical and chemical properties – uses- aromatic electrophilic substitution mechanism – theory of orientation and reactivity.

Preparation of ethers: dehydration of alcohols, Williamsons synthesis – silyl ether, epoxide from peracids – Sharpless asymmetric epoxidation – reactions of epoxides – uses – introduction to crown ethers – structures – applications.

UNIT IV - THERMODYNAMICS I

Definitions – System and Surround – isolated, closed and open system – state of the system- intensive and extensive variables. Thermodynamic processes – reversible and irreversible, isothermal and adiabatic processes – state and path functions.

Work of expansion at constant pressure and at constant volume, First law of thermodynamics – statement – definition of internal energy (E), enthalpy (H) and heat capacity. Relationship between Cp and Cv.

Calculation of w, q, dE and dH for expansion of ideal and real gases under isothermal and adiabatic conditions of reversible and irreversible processes.

Thermo chemistry – relationship between enthalpy of reaction at constant volume (qv) and at constant pressure (qp) – temperature dependence of heat of reaction – Kirchoff's equation – bond energy and its calculation from thermo chemical data- integral and differential heats of solutions and dilution.

UNIT V - CHEMICAL KINETICS

Rate of reaction -rate equation, order and molecularity of reaction. Rate laws – rate constants – derivation of first order rate constant and characteristics of zero order, first order and second order reaction – derivations of time for half change (t1/2) with examples.

Methods of determination of order of reactions – experimental methods – determination of rate constant of a reaction by volumetry, colorimetry and polarimetry.

Effect of temperature on reaction rate – concept of activation energy, energy barrier. Arrhenius equation. Theories of reaction rates – collision theory – derivation of rate constant of bimolecular reaction – failure of collision theory – Lindemann's theory of unimolecular reaction.

Theory of absolute reaction rate – derivation of rate constant for a bimolecular reaction – significance of entropy and free energy of activation. Comparison of collision theory and Absolute Reaction Rate Theory (ARRT).

UNIT I

d-BLOCK & f-BLOCK ELEMENTS

GENERAL CHARACTERISTICS OF d-BLOCK ELEMENTS

1. Introduction

d-block elements are present from fourth period onwards. There are mainly three series of the transition metals – 3*d* series (Sc to Zn), 4*d* series (Y to Cd) and 5*d* series (La to Hg, omitting Ce to Lu).

d-block elements are known as transition elements because their position in the periodic table is between the s-block and p-block elements. Electronic configuration of the *d*-block elements is $(n-1)d^{1-10}ns^{o-2}$ but Cu^+, Zn, Cd, Hg etc. $[(n-1)d^{10}]$ are *d*-block elements, but not transition metals because these have completely filled *d*-orbitals.

Transition Metals of *d*-block Elements

3rd group ns^2	**4th group** $d^1\ ns^2d^2$	**5th group** ns^2d^3	**6th group** ns^2d^5	**7th group** ns^2d^5	**8th group** ns^2d^6	**9th group** ns^2d^7	**10th group** ns^2d^8	**11th group** ns^2d^{10}	**12th group** ns^2d^{10}
$(n-1)$	$(n-1)$	$(n-1)$	$(n-1)$	$(n-1)$	$(n-1)$	$(n-1)$	$(n-1)$	$(n-1)$	$(n-1)$
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

2. General Properties of the Transition Elements

(i) Atomic and Ionic Radii

In transition metals, left to right net nuclear charge increases due to poor shielding effect. Due to this, the atomic and ionic radii for transition elements for a given series show a decreasing trend for first five elements and then becomes almost constant for next five elements of the series.

(ii) Enthalpies of Atomisation

Transition elements exhibit higher enthalpies of atomization because of large number of unpaired electrons in their atoms. They have stronger interatomic interaction and hence, stronger bond.

(iii) Ionisation Enthalpies

- In a series from left to right, ionization enthalpy increases due to increase in nuclear charge.

- The irregular trend in the first ionization enthalpy of the 3*d* metals, though of little chemical significance, can be accounted for by considering that the removal of one electron alters the relative energies of 4*s* and 3*d* orbitals.

(iv) Oxidation States

- Transition metals shows variable oxidation state due to two incomplete outermost shells. Only stable oxidation states of the first row transition metals are Sc(+ 3), Ti(+ 4), V(+ 5), Cr(+ 3, + 6), Mn(+ 2, + 7), Fe(+ 2, + 3), Co(+ 2, +3), Ni(+ 2), Cu)+ 2), Zn(+ 2)

- The transition elements in their lower oxidation states (+ 2 and + 3) usually forms ionic compounds. In higher oxidation state compounds are normally covalent.

- Only Os and Ru show + 8 oxidation states in their compounds.

- Ni and Fe in $Ni(CO)_4$ and $Fe(CO)_5$ show zero oxidation state.

(v) Trends in the Standard Electrode Potentials

- Transformation of the solid metal atoms to M^{2+} ions in solution and their standard electrode potentials.

- If sum of the first and second ionization enthalpies is greater than hydration enthalpy standard potential ($E^\circ_{M^{2+}/M}$) will be positive and reactivity will be lower and vice-versa.

(vi) Trends in Stability of Higher Oxidation States

The higher oxidation numbers are achieved in TiX_4, VF_5 and CrF_6. The + 7 state for Mn is not represented in simple halides but MnO_3F is known and beyond Mn no metal has a trihalide except FeX_3 and CoF_3 and increasing order of oxidizing power in the series $VO_2^{+} < Cr_2O_7^{2-} < MnO_4^{-}$.

(vii) Magnetic Properties

- When a magnetic field is applied to substances, mainly two types of magnetic behavior are observed : diamagnetism and paramagnetism. Paramagnetism due to presence of unpaired electrons, each such electron having a magnetic moment associated with its spin angular momentum.
- The magnetic moment is determined by the number of unpaired electrons.

Magnetic moment = $\sqrt{n(n+2)}$

where, n = number of unpaired electrons.

If all electrons are paired, substance will be diamagnetic and magnetic moment will be zero.

(viii) Formation of Coloured Ions

- The *d*-orbitals are non-degenerated in presence of ligands. When an electron from a lower energy *d*-orbital is excited to a higher energy *d*-orbital, the energy of required wavelength is absorbed and rest light is transmitted out. Therefore, the colour observed corresponds to the complementary colour of the light absorbed.
- In V_2O_5, V is in + 5 oxidation state. It is coloured due to defects in crystal lattice.

(ix) Formation of Complex Compounds

- Transition metals have small size high nuclear charge which facilitates the acceptance of lone pair of electron from ligands.
- They have vacant *d*-orbitals of appropriate energy in order to accommodate the lone pair of electrons.

(x) Catalytic Properties

- Transition metals have two outermost shells incomplete and ability to adopt multiple oxidation states and to form complexes, therefore used as a catalyst.
- Transition metals also provide larger surface area for the reactant to be adsorbed.

(xi) Formation of Interstitial Compounds

- Small size of non-metals (H, C, N) fit into the voids of crystalline solid of transition metals and form interstitial compounds.
- The principal physical and chemical characteristics of these compounds are as follows :

(i) They have high melting points, higher than those of pure metals.
(ii) They are very hard, some borides approach diamond in hardness.
(iii) They retain metallic conductivity.
(iv) They are chemically inert.

(xii) Alloy Formation

Alloy is the homogeneous mixture of two or more metals. Transition metals have approximate same size therefore, in molten form they can fit to each other crystalline structure and form homogeneous mixture and form the alloy.

E.g., Brass (copper-zinc) and bronze (copper-tin) etc.

COMPARATIVE STUDY OF ZINC GROUP ELEMENTS

Zinc group element, any of the four chemical elements that constitute Group 12 (IIb) of the periodic table—namely, zinc (Zn), cadmium (Cd), mercury (Hg), and copernicium (Cn). They have properties in common, but they also differ in significant respects. Zinc, cadmium, and mercury are metals with a silvery-white appearance and relatively low melting points and boiling points.

Mercury is the only common metal that is liquid at room temperature, and its boiling point is lower than that of any other metal.

Zinc, cadmium, and mercury can lose the two electrons in the outermost shell to form dipositive ions, M^{2+} (in which M represents a generalized metal element), thereby exposing the next innermost shell with a stable configuration in each case of 18 electrons.

These three elements tend to use the two outer electrons for covalent bonding.

Zinc exhibits only the +2 oxidation state. It can give up two electrons to form an electrovalent compound; e.g., zinc carbonate ZnCO3. It may also share those electrons, as in zinc chloride, ZnCl2, a compound in which the bonds are partly ionic and partly covalent.

Cadmium compounds are mainly ionic, but cadmium also forms complex ions with ligands (atoms, ions, or molecules that donate electrons to a central metal ion); e.g., the complex ion with ammonia NH3, having the formula $[Cd(NH3)4]^{2+}$, or with the cyanide ion, the formula $[Cd(CN)4]^{2-}$.

Mercury in its +2 and +1 oxidation states forms the ions Hg^{2+} and $[Hg2]^{2+}$, respectively. In the latter, two electrons are shared in a covalent bond between the two metal atoms. The $[Hg2]^{2+}$ ion shows little tendency to form complexes, whereas the Hg^{2+} ion does form them. In contrast to compounds of mercury in the +2 state, which are usually covalent, all the common salts of mercury in the +1 state are ionic, and the soluble compounds—e.g., mercurous nitrate, Hg2(NO3)2—show normal properties of ionic compounds, such as ease of dissociation or breakup into separate ions in solution.

Mercury is exceptional in that, unlike zinc or cadmium, it does not react easily with oxygen on heating, and mercuric oxide does not show the acid property of forming salts (mercurates), whereas zinc oxide does this readily.

Extraction of Mo:

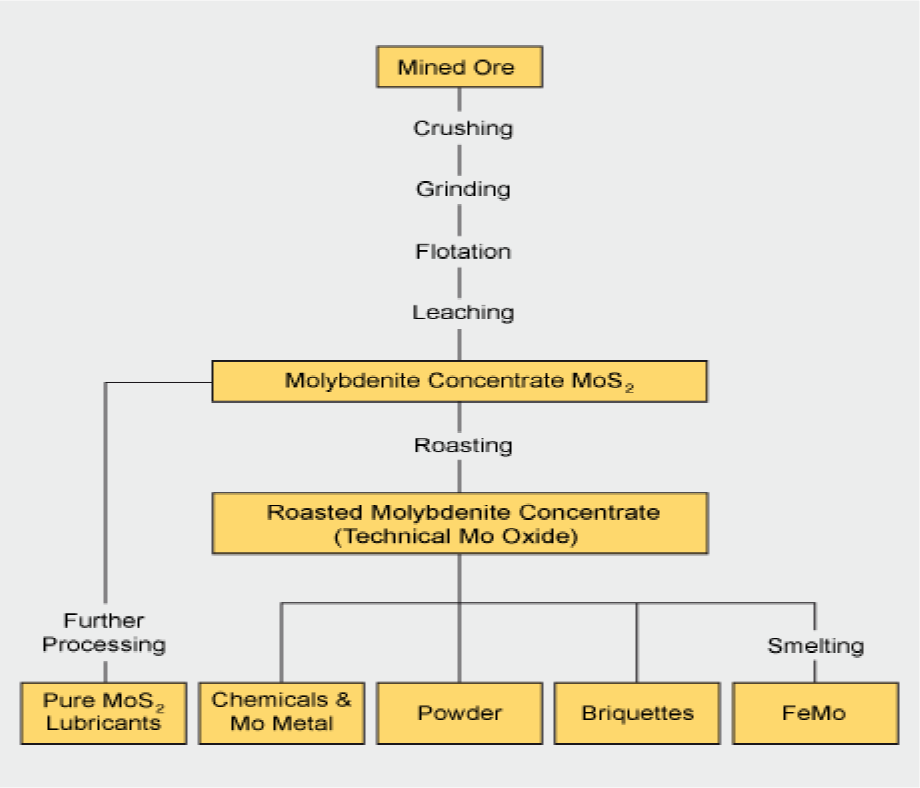
- Molybdenum can be found in a number of minerals, but only molybdenite is suitable for the industrial production of marketable molybdenum products. Molybdenite can occur as the sole mineralization in an ore body, but is usually associated with the sulphide minerals of other metals, mainly copper. Molybdenum mines are classified into three groups according to the minerals contained in the ore body and their quality:

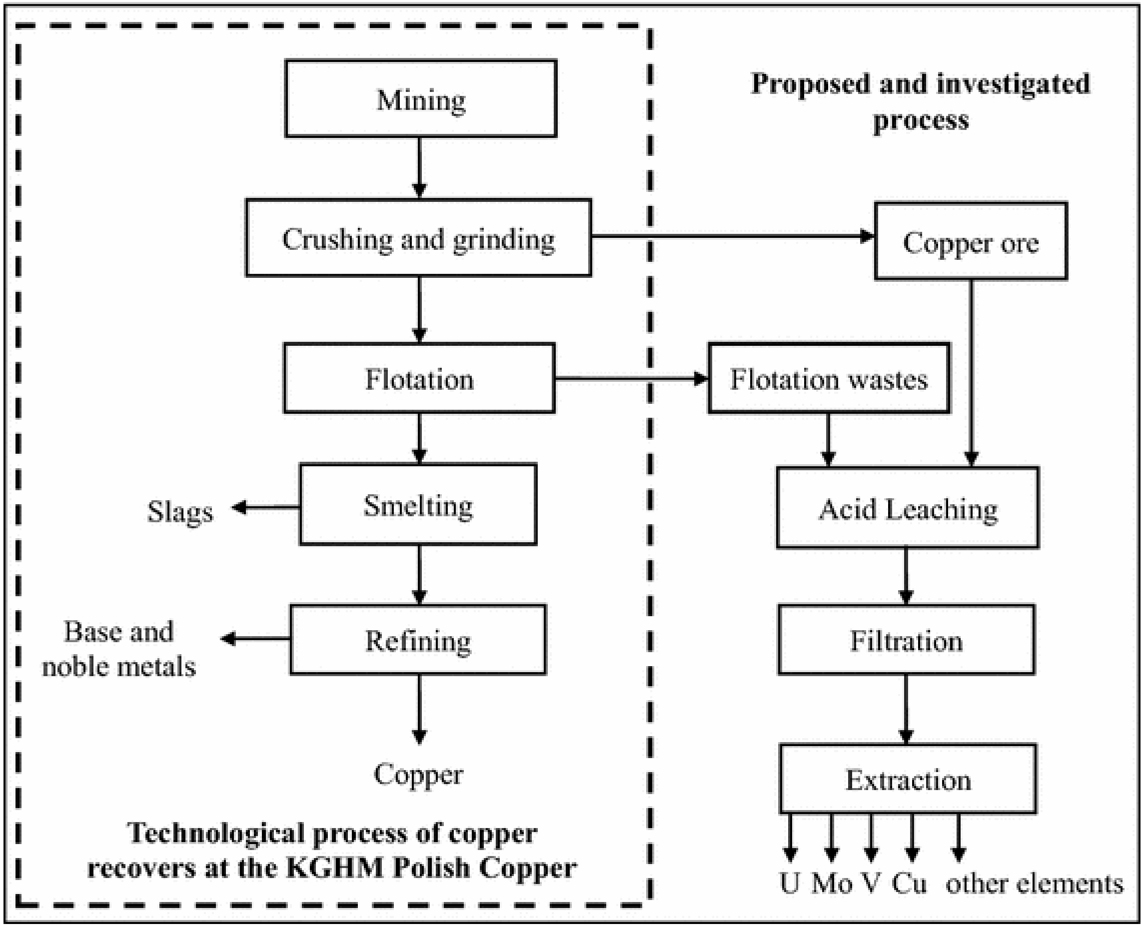
Primary mines, where the extraction of molybdenite is the sole aim.

By-product mines, where the extraction of copper-bearing ores is the primary aim, and molybdenite extraction provides additional economic value.

Co-product mines, where both molybdenite and copper-bearing minerals are extracted.

- Roughly 40 percent of molybdenum comes from primary mines, with the other 60 percent a by-product of copper or, in some cases, tungsten.
- If the ore lies close to the surface, open-pit technology will be used, and if the ore lies deep underground, the underground method will be used.





Extraction of Pt:

Alloys of copper:

Copper alloys are metal alloys that have copper as their principal component. They have high resistance against corrosion. The best known traditional types are bronze, where tin is a significant addition, and brass, using zinc instead. Both of these are imprecise terms, having both been commonly referred to as lattens in the past. Today the term *copper alloy* tends to be substituted, especially by museums.

Classification of copper and its alloys

Family	Principal alloying element	UNS numbers
Copper alloys, brass	Zinc (Zn)	C1xxxx–C4xxxx,C66400–C69800
Phosphor bronze	Tin (Sn)	C5xxxx
Aluminium bronzes	Aluminium (Al)	C60600–C64200
Silicon bronzes	Silicon (Si)	C64700–C66100
Cupronickel, nickel silvers	Nickel (Ni)	C7xxxx

Amalgams:

An **amalgam** is an alloy of mercury with another metal. It may be a liquid, a soft paste or a solid,depending upon the proportion of mercury.

These alloys are formed through metallic bonding,with the electrostatic attractive force of the conduction electrons working to bind all the positively charged metal ions together into a crystallattice structure.

Almost all metals can form amalgams with mercury, the notable exceptions being iron, platinum,tungsten, and tantalum. Silver-mercury amalgams are important in dentistry, and gold-mercury amalgam is used in the extraction of gold from ore. Dentistry has used alloys of mercury with metals such as silver, copper, indium, tin and zinc.

Important amalgams:

Zinc amalgam

Zinc amalgam finds use in organic synthesis (e.g., for the Clemmensen reduction).[3] It is the reducing agent in the Jones reductor, used in analytical chemistry. Formerly the zinc plates of dry batteries were amalgamated with a small amount of mercury to prevent deterioration in storage. It is a binary solution (liquid-solid) of mercury and zinc.

Potassium amalgam:

For the alkali metals, amalgamation is exothermic, and distinct chemical forms can be identified, such as KHg and KHg_2.KHg is a gold-coloured compound with a melting point of 178 °C, and KHg_2 a silver-coloured compound with a melting point of 278 °C. These amalgams are very sensitive to air and water, but can be worked with under dry nitrogen.

Sodium amalgam:

Sodium amalgam is produced as a byproduct of the chloralkali process and used as an important reducing agent in organic and inorganic chemistry.

With water, it decomposes into concentrated sodium hydroxide solution, hydrogen and mercury, which can then return to the chloralkali process anew. If absolutely water-free alcohol is used instead of water, an alkoxide of sodium is produced instead of the alkali solution.

Aluminium amalgam:

Aluminium can form an amalgam through a reaction with mercury. Aluminium amalgam may be prepared by either grinding aluminium pellets or wire in mercury, or by allowing aluminium wire or foil to react with a solution of mercuric chloride.

This amalgam is used as a reagent to reduce compounds, such as the reduction of imines to amines.

Tin amalgam:

Tin amalgam was used in the middle of the 19th century as a reflective mirror coating.

Other amalgams:

- Thallium amalgam has a freezing point of −58 °C, which is lower than that of pure mercury (−38.8 °C) so it has found a use in low temperature thermometers.
- Gold amalgam: Refined gold, when finely ground and brought into contact with mercury where the surfaces of both metals are clean, amalgamates readily and quickly to form alloys ranging from $AuHg_2$ to Au_8Hg.

Lead forms an amalgam when filings are mixed with mercury and is also listed as a naturally occurring alloy called leadamalgam in the Nickel–Strunz classification.

Dental amalgam:

Dentistry has used alloys of mercury with metals such as silver, copper, indium, tin and zinc. Amalgam is an "excellent and versatile restorative material" and is used in dentistry for a number of reasons. It is inexpensive and relatively easy to use and manipulate during placement; it remains soft for a short time so it can be packed to fill any irregular volume, and then forms a hard compound.

Galvanization:

Galvanization or **galvanizing** (also spelled **galvanisation** or **galvanising**) is the process of applying a protective zinc coating to steel or iron, to prevent rusting. The most common method is hot-dip galvanizing, in which the parts are submerged in a bath of molten hot zinc.

Protective action:

Galvanizing protects the underlying iron or steel in the following main ways:

- The zinc coating, when intact, prevents corrosive substances from reaching the underlying steel or iron.
- The zinc protects iron by corroding first. For better results, application of chromates over zinc is also seen as an industrial trend.
- In the event the underlying metal becomes exposed, protection can continue as long as there is zinc close enough to be electrically coupled. After all of the zinc in the immediate area is consumed, localized corrosion of the base metal can occur.

Evidences for the existence of Hg_2^{2+} ions

- Most common oxidation states: +1, +2
- M.P. -38.87°

- B.P. 356.57°
- Density 13.546 g/cm^3
- Characteristics: Mercury is one of the few liquid elements. It dissolves in oxidizing acids, producing either Hg2+ or Hg2+2, depending on which reagent is in excess. The metal is also soluble in aqua regia (a mixture of hydrochloric and nitric acids) to form $HgCl2^{-4}$

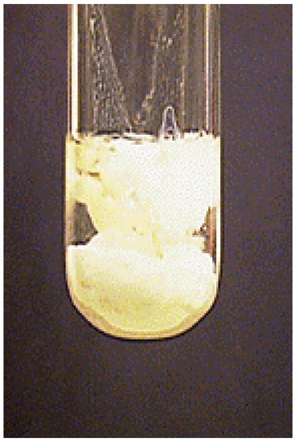
Mercury(I) Ion: Hg_2^{2+}

Mercury(I) compounds often undergo disproportionation, producing black metallic mercury and mercury(II) compounds.

Chloride Ion

Soluble chlorides, including hydrochloric acid, precipitate white mercury(I) chloride, also known as calomel:

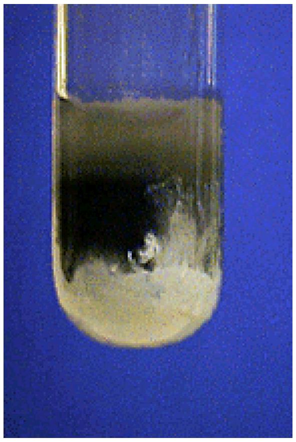
$Hg2+2(aq)+2Cl-(aq) \rightleftharpoons Hg2Cl2(s)$



Aqueous ammonia reacts with Hg2Cl2

to produce metallic mercury (black) and mercury(II) amidochloride (white), a disproportionation reaction:

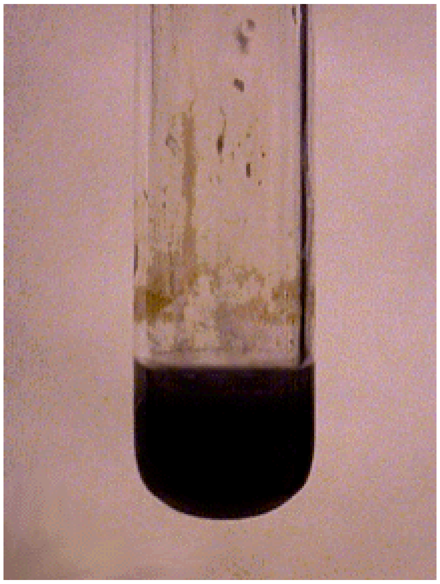
$Hg2Cl2(s)+2NH3(aq) \longrightarrow Hg(l)+HgNH2Cl(s)+NH+4(aq)+Cl-(aq)$



Aqueous Ammonia

Aqueous ammonia produces a mixture of a white basic amido salt and metallic mercury:

2Hg2+2(aq)+4NH3(aq)+NO−3(aq)+H2O(l)⟶2Hg(l)+Hg2ONH2NO3(s)+3NH+4(aq)

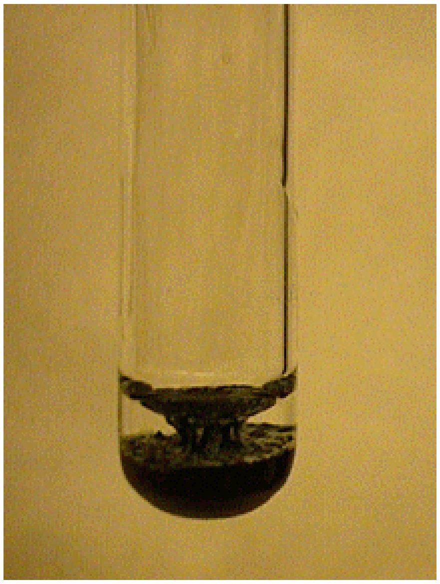


The precipitate is not soluble in excess aqueous ammonia.

Sodium Hydroxide

Black finely divided mercury metal and yellow mercury(II) oxide (HgO) are precipitated by NaOH:

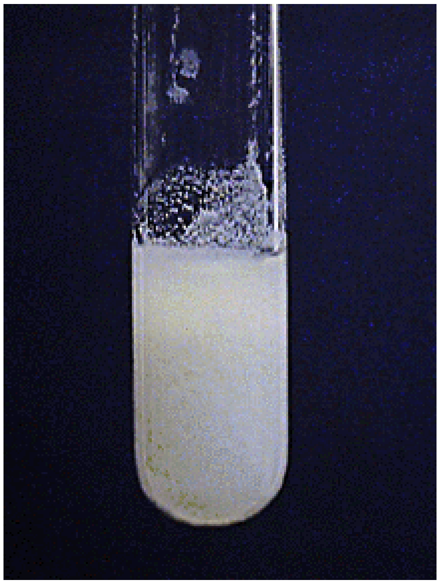
Hg2+2(aq)+2OH−(aq)⟶Hg(l)+HgO(aq)+H2O(l)



Reducing Agents

Reducing agents, such as Sn2+ and Fe2+, reduce mercury(I) to the metal:

Hg2+2(aq)+2Fe2+(aq)⟶2Hg(l)+2Fe3+(aq)



Consult an activity series or a table of reduction potentials for other possible reducing agents.

No Reaction

$SO2^{-4}$

(unless solutions are concentrated; solubility of mercury(I) sulfate is 0.06 g per 100 mL of water at 25^{oC})

Mercury(II) Ion: Hg^{2+}

Characteristic reactions of Hg^{2+}

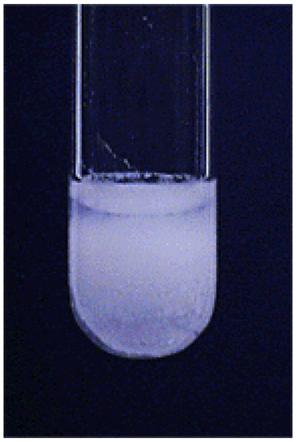
Chloride Ion

No reaction is visible, but Hg(II) will be present as $[HgCl_4]^{2-}$.

Aqueous Ammonia

Aqueous ammonia produces white amido salts whose composition depends on the mercury(II) salt present in the solution:

$HgCl_2(aq)+2NH_3(aq) \rightleftharpoons HgNH_2Cl(s)+2NH_4^+(aq)+Cl^-(aq)$



These salts are not soluble in excess aqueous ammonia, but do dissolve in acids:

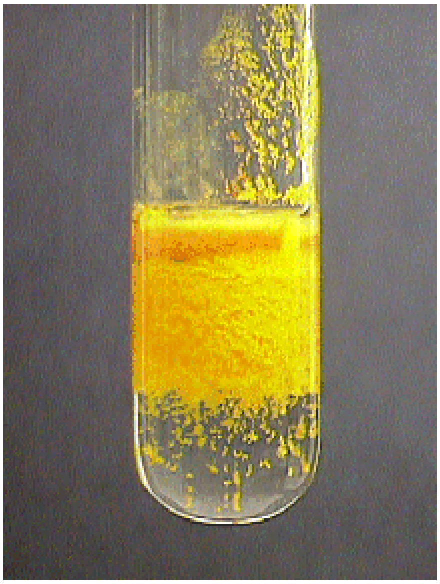
$HgNH_2Cl(s)+2H^+(aq)+Cl^-(aq) \rightleftharpoons HgCl_2(aq)+NH_4^+(aq)$

Sodium Hydroxide

A yellow precipitate of HgO is produced by NaOH:

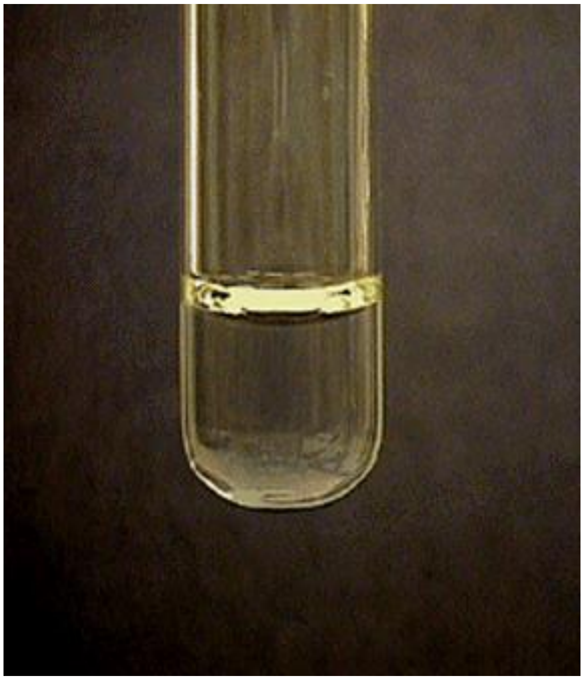
$Hg^{2+}(aq)+2OH^-(aq)\longrightarrow HgO(s)+H_2O(l)$

$HgCl_2(s)+2OH^-(aq)\longrightarrow HgO(s)+H_2O(l)+2Cl^-(aq)$



The mercury(II) oxide precipitate is insoluble in excess hydroxide but is soluble in acids:

$HgO(s)+2H^+(aq)\rightleftharpoons Hg^{2+}(aq)+H_2O(l)$

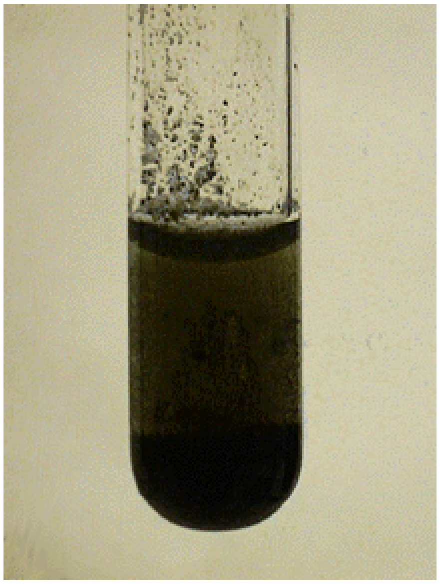


Hydrogen Sulfide

Hydrogen sulfide precipitates black mercury(II) sulfide, the least soluble of all sulfide salts.

$Hg^{2+}(aq)+H_2S(aq) \rightleftharpoons HgS(s)+2H^+(aq)$

$[HgCl_4]^{2-}(aq)+H_2S(aq) \rightleftharpoons HgS(s)+2H^+(aq)+4Cl^-(aq)$



Mercury(II) sulfide is insoluble in 6 M HNO_3

or 12 M HCl, even if heated. However, it is soluble in aqua regia (3:1 HCl:HNO_3) and in hot dilute NaOH containing excess sulfide.

$$3HgS(s)+12Cl^-(aq)+2NO_3^-(aq)+8H^+(aq)\longrightarrow 3[HgCl_4]^{2-}(aq)+2NO(g)+3S(s)+4H_2O(l)$$

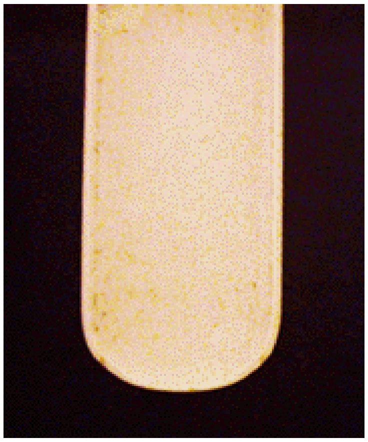
$$HgS(s)+S^{2-}(aq)\rightleftharpoons [HgS_2]^{2-}(aq)$$

Tin(II) Chloride

Tin(II) chloride reduces Hg(II) to Hg(I) or to metallic Hg

, giving a white or gray precipitate:

$$2[HgCl_4]^{2-}(aq)+[SnCl_4]^{2-}(aq)\rightleftharpoons Hg_2Cl_2(s)+[SnCl_6]^{2-}(aq)+4Cl^-(aq)$$



No Reaction

SO_4^{2-}

(may precipitate as a mixed sulfate-oxide - a basic sulfate - $HgSO_4\cdot 2HgO$)

General characteristics of f-block elements

The *f*-block consists of the two series, lanthanoids and actinoids. Lanthanoids are known as rare earth metals and actinoids are known as radioactive elements (Th to Lr).

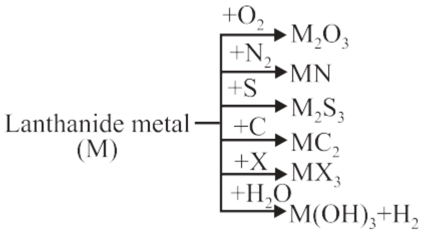
Lanthanoids

General characteristics

- General configuration [Xe] $4f^{1-14}$, $5d^{0-1}$, $6s^2$.
- Atomic and ionic size from left to right, decreases due to increase in nuclear charge. This is known as lanthanoid contraction.
- All the lanthanoids are silvery white soft metals and tarnish rapidly in air.
- Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions. Neither La^{3+} nor Lu^{3+} ion shows any colour but the rest do so.
- The lanthanoid ions other than the f^0 type (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic. The paramagnetism arises to maximum in neodymium.
- Oxidation states □ Ce^{4+}; (Some elements) is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common + 3 state. The E^{o}_{value} for Ce^{4+}/Ce^{3+} is + 1.74 V, the reaction rate is very slow and hence, Ce(IV) is a good

analytical reagent. Pr, Nd, Tb and Dy also exhibit + 4 state but only in oxides. Eu^{2+} is formed by losing the two s-electrons and its f^7 configuration accounts for the formation of this ion. However, Eu2+ is a strong reducing agent changing to the common + 3 state. Similarly, Yb^{2+} which has f^{14} configuration is a reductant, Tb^{4+} has half-filled f-orbitals and is an oxidant.

- Lanthanoid are very reactive metals like alkaline earth metals.



- Misch metals, contain lanthanoids about 90-95% (Ce 40-5%, Lanthanum and neodymium 44%) iron 4.5%, calcium, carbon and silicon, used in cigarette and gas lighters, toys, tank and tracer bullets.

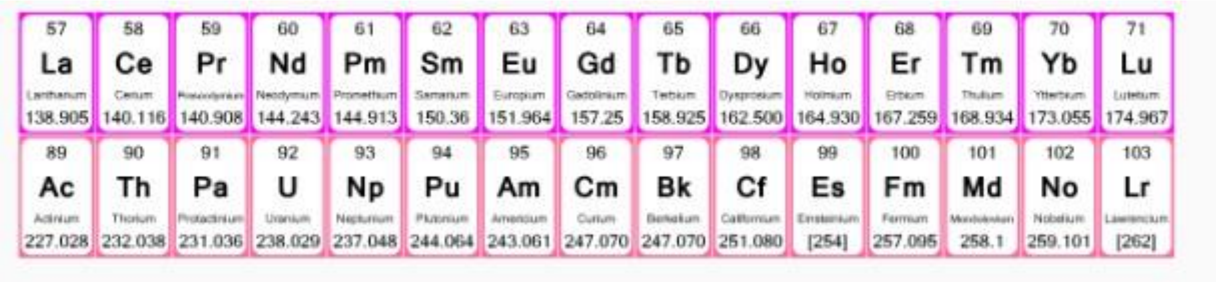
Actinoids

- Genral configuration [Rn] $5f^{1-14}$, $6d^{0-2}$, $7s^2$.
- Actinoids exhibit a range of oxidation states due to comparable energies of $5f$, $6d$ and $7s$ orbitals. The genral oxidation state of actinoids is + 3.
- All the actinoids are strong reducing agents and very reactive.

- Actinoids also react with oxygen, halogen, hydrogen and sulphur, etc. like lanthanoids.
- Actinoids are radioactive in nature and therefore, it is difficult to study their chemical nature.

F block elements are divided into two series, namely lanthanoids and actinoids. These blockof elements are often referred to as **inner transition metals** because they provide a transition in the6th and 7th row of the periodic table which separates the s block and the d block elements.

Elements whose f orbital getting filled up by electrons are called **f block elements**. Theseelements have electrons, (1 to 14) in the f orbital, (0 to 1) in the d orbital of the series.



57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

Properties of Lanthanide:

- Lanthanide Series
- Lanthanide Contraction
- Electronic Configuration
- Oxidation State of Lanthanides
- Chemical Reactivity
- Ionization Energy
- Physical Properties
- Formation of Coloured Ions
- Uses of Lanthanides

Lanthanides are highly dense metals with even higher melting points than d-block elements. They form alloys with other metals. These are the f block elements that are also referred to as the inner transition metals. The inner transition elements/ions may have electrons in s, d and f- orbitals.

In the periodic table like transition metal if we consider lanthanides and actinides series the table will be too wide. These two series are present in the bottom of the periodic table and they are called

4f series (Lanthanods series) and 5f series (Actanoids series). The 4f and 5f series together called inner transition elements.

All of the elements in the series closely resemble lanthanum and each another in their chemical and physical properties. Some of the key characteristics and properties are:

- They have a lustre and are silvery in appearance.
- They are soft metals and can even be cut with a knife
- The elements have different reaction tendencies depending on basicity. Some are very reactive while some take time to react.
- Lanthanides can corrode or become brittle if they are contaminated with other metals or non-metals.
- They all mostly form a trivalent compound. Sometimes they can also form divalent or tetravalent compounds.
- They are magnetic.

Lanthanide Contraction:

The atomic size or the ionic radii of tri positive lanthanide ions decrease steadily from La to Lu due to increasing nuclear charge and electrons entering inner (n-2) f orbital. This gradual decrease in the size with an increasing atomic number is called **lanthanide contraction.**

Consequences of Lanthanide Contraction:

Following points will clearly depict the effect of lanthanide contraction:

- Atomic size
- Difficulty in the separation of lanthanides

- Effect on the basic strength of hydroxides
- Complex formation
- The ionization energy of d-block elements

1. **Atomic size:** Size of the atom of third transition series is nearly the same as that of the atom of the second transition series. For example: radius of Zr = radius of Hf & radius of Nb = radius of Ta etc.

2. **Difficulty in the separation of lanthanides**: As there is an only small change in the ionic radii of Lanthanides, their chemical properties are similar. This makes the separation of elements in the pure state difficult.

3. **Effect on the basic strength of hydroxides**: As the size of lanthanides decreases from La to Lu, the covalent character of the hydroxides increases and hence their basic strength decreases. Thus, La(OH)3 is more basic and Lu(OH)3 is the least basic.

4. **Complex formation**: Because of the smaller size but higher nuclear charge, tendency to form coordinate. Complexes increases from La3+ to Lu3+.

5. **Electronegativity:** It increases from La to Lu.

6. **Ionization energy:** Attraction of electrons by the nuclear charge is much higher and hence Ionization energy of 5d elements are much larger than 4d and 3d. In 5d series, all elements except Pt and Au have filled s-shell.

Elements from Hafnium to rhenium have same Ionization Energy and after Ionization Energy increases with the number of shared d-electrons such that Iridium and Gold have the maximum Ionization Energy.

Mercury – the liquid metal: Mercury is the only metal that exists in its liquid state at room temperature. 6s valence electrons of Mercury are more closely pulled by the nucleus (lanthanide contraction) such that outer s-electrons are less involved in metallic bonding.

7. **Formation of Complex:** Lanthanides exhibiting 3+ oxidation state is the larger and hence low charge to radius ratio. This reduces the complex-forming ability of lanthanides compared to d-block

elements. Still they, form complexes with strong chelating agents like EDTA, β-diketones, oximeetc. They do not form Pπ-complexes.

Electronic Configuration of Lanthanides:

Lanthanides of first f-block have a terminal electronic configuration of [Xe] 4f1-14 5d 0-16s2 of thefourteen lanthanides, promethium (Pm) with atomic number 61 is the only synthetic radioactive element. The energy of 4f and 5d electrons are almost close to each other and so 5d orbital remains vacant and the electrons enter into the 4f orbital.

Exceptions are in the case of gadolinium, Gd (Z = 64) where the electron enters the 5d orbital due tothe presence of half-filled d-orbital and lutetium (Z = 71) enters the 5d orbital.

Oxidation State of Lanthanides:

All the elements in the lanthanide series show an oxidation state of +3. Earlier it was believed thatsome of the metals (samarium, europium, and ytterbium) also show +2 oxidation states. Further studies on these metals and their compounds have revealed that all the metals in lanthanide series exhibit +2 oxidation state in their complexes in solutions.

A few metals in the lanthanide series occasionally show +4 oxidation states. This uneven distribution of oxidation state among the metals is attributed to the high stability of empty, half-filled or fully filled f-subshells.

The stability of f-subshell affects the oxidation state of lanthanides in such a way that the +4 oxidation state of cerium is favoured as it acquires a noble gas configuration but it reverts to a +3oxidation state and thus acts as a strong oxidant and can even oxidize water, although the reactionwill be slow.

The +4 oxidation state is also exhibited by the oxides of:

- Praseodymium (Pr)
- Neodymium (Nd)
- Terbium (Tb)

- Dysprosium (Dy)

Europium (atomic number 63) has the electronic configuration [Xe] $4f^7$ $6s^2$, it loses two electrons from 6s energy level and attains the highly stable, half-filled $4f^7$ configuration and hence it readily forms Eu^{2+}ion. Eu^{2+} then changes to the common oxidation states of lanthanides (+3) and forms Eu^{3+}, acting as a strong reducing agent.

Ytterbium (atomic number 70) also has similar reasons for being a strong reducing agent, in the Yb^{2+} state; it has a fully filled f-orbital.

The presence of f-subshell has a great influence on the oxidation state exhibited by these metals and their properties. New developments and findings continue to add information on lanthanides.

The energy gap between 4f and 5d orbitals is large and so the number of oxidation states limited, unlike the d-block elements.

Energy level and in the outermost's orbital:

There are two series in the f block corresponding to the filling up of 4f and 5f orbitals. The elements are 4f series of Ce to Lu and 5f series of Th to Lw. There are 14 elements filling up the 'f' orbital in each series.

- Lanthanides
- Actinides

The lanthanides, also known as the f-block elements, are a group of 15 metallic elements from lanthanum (La) to lutetium (Lu) in the periodic table. They are known for their unique and fascinating properties, including vibrant colors and interesting magnetic behavior.

COLOUR AND MAGNETIC PROPERTIES IN LANTHANIDE

The colors of the lanthanides arise from the electronic transitions within their f-orbitals. These transitions absorb specific wavelengths of light, resulting in the observed colors. Here's a breakdown of the colors of some key lanthanides:

- **Lanthanum (La):** Silvery white (no f-electrons)

- **Cerium (Ce):** Pale yellow or grey (one f-electron)
- **Praseodymium (Pr):** Pale green (two f-electrons)
- **Neodymium (Nd):** Purple or lavender (three f-electrons)
- **Promethium (Pm):** Silvery white (radioactive, difficult to observe)
- **Samarium (Sm):** Silvery white or pale yellow (four f-electrons)
- **Europium (Eu):** Pale pink or white (six f-electrons)
- **Gadolinium (Gd):** Silvery white (seven f-electrons)
- **Terbium (Tb):** Pale pink or lilac (nine f-electrons)
- **Dysprosium (Dy):** Silvery white or pale yellow (ten f-electrons)
- **Holmium (Ho):** Pale pink or orange (eleven f-electrons)
- **Erbium (Er):** Pale pink or rose (twelve f-electrons)
- **Thulium (Tm):** Silvery white or pale green (thirteen f-electrons)
- **Ytterbium (Yb):** Silvery white (fourteen f-electrons)
- **Lutetium (Lu):** Silvery white (fifteen f-electrons)

As you can see, the colors of the lanthanides vary widely depending on the number of f-electrons present. This makes them particularly interesting for applications in decorative coatings, lasers, and other optical technologies.

Magnetic Properties:

The magnetic properties of the lanthanides are also influenced by their f-electrons. Most lanthanides have unpaired electrons in their f-orbitals, which makes them paramagnetic. This means that they are weakly attracted to a magnetic field. However, some lanthanides, such as lanthanum (La) and lutetium (Lu), have all their f-electrons paired and are therefore diamagnetic, meaning they repel a magnetic field.

The magnetic properties of the lanthanides have important applications in data storage, superconductors, and other technologies. For example, the strong magnetic moments of gadolinium (Gd) are used in magnetic resonance imaging (MRI) machines.

Here's a summary of the magnetic properties of some key lanthanides:

- **Lanthanum (La):** Diamagnetic (no unpaired f-electrons)
- **Cerium (Ce):** Paramagnetic (one unpaired f-electron)
- **Praseodymium (Pr):** Paramagnetic (two unpaired f-electrons)
- **Neodymium (Nd):** Paramagnetic (three unpaired f-electrons)
- **Promethium (Pm):** Paramagnetic (four unpaired f-electrons)

- **Samarium (Sm):** Paramagnetic (five unpaired f-electrons)
- **Europium (Eu):** Paramagnetic (six unpaired f-electrons)
- **Gadolinium (Gd):** Paramagnetic (seven unpaired f-electrons)
- **Terbium (Tb):** Paramagnetic (nine unpaired f-electrons)
- **Dysprosium (Dy):** Paramagnetic (ten unpaired f-electrons)
- **Holmium (Ho):** Paramagnetic (eleven unpaired f-electrons)
- **Erbium (Er):** Paramagnetic (twelve unpaired f-electrons)
- **Thulium (Tm):** Paramagnetic (thirteen unpaired f-electrons)
- **Ytterbium (Yb):** Paramagnetic (fourteen unpaired f-electrons)
- **Lutetium (Lu):** Diamagnetic (fifteen f-electrons)

The unique combination of colorful and magnetic properties makes the lanthanides a truly fascinating group of elements. They continue to be a subject of active research and development, with the potential for even more exciting discoveries in the future.

I hope this explanation gives you a good understanding of the colors and magnetic properties of the lanthanides. Please let me know if you have any other questions.

EXTRACTION OF MIXTURE OF LANTHANIDES FROM MONAZITE SAND

Monazite sand is a rich source of various lanthanides, elements with diverse and valuable applications. Extracting these valuable metals, however, is a complex process due to their similar chemical properties and intimate presence within the sand. Let's break down the key steps involved:

1. Preprocessing the Sand:

- **Concentration:** Gravity separation techniques using tables or spirals enrich the monazite content by removing lighter materials like quartz.
- **Magnetic separation:** Monazite is weakly magnetic, allowing for further separation from strongly magnetic minerals like ilmenite.
- **Grinding:** The concentrated monazite sand is finely ground to increase surface area for subsequent chemical processing.

2. Extraction of Lanthanides:

- **Acid digestion:** Concentrated sulfuric acid or caustic soda breaks down the monazite, forming soluble lanthanide salts and insoluble residues.

- **Solution purification:** Impurities like silica and iron are removed through filtration and precipitation techniques.

3. Separation of Individual Lanthanides:

This is the most challenging step due to the lanthanides' near-identical properties. Several methods are employed:

- **Liquid-liquid extraction:** Lanthanides form complexes with specific organic solvents, selectively removing them from the aqueous solution.
- **Ion exchange chromatography:** Lanthanide ions bind to different resins with varying strengths, allowing their separation as they flow through the column.
- **Solvent extraction with ligands:** Specific ligands can selectively complex with certain lanthanides, enabling their extraction and separation.

4. Recovery and Purification:

- **Precipitation:** Lanthanide ions are precipitated as hydroxides, carbonates, or oxalates, followed by filtration and drying.
- **Calcination:** Precipitates are converted to their corresponding oxides, the final lanthanide products.

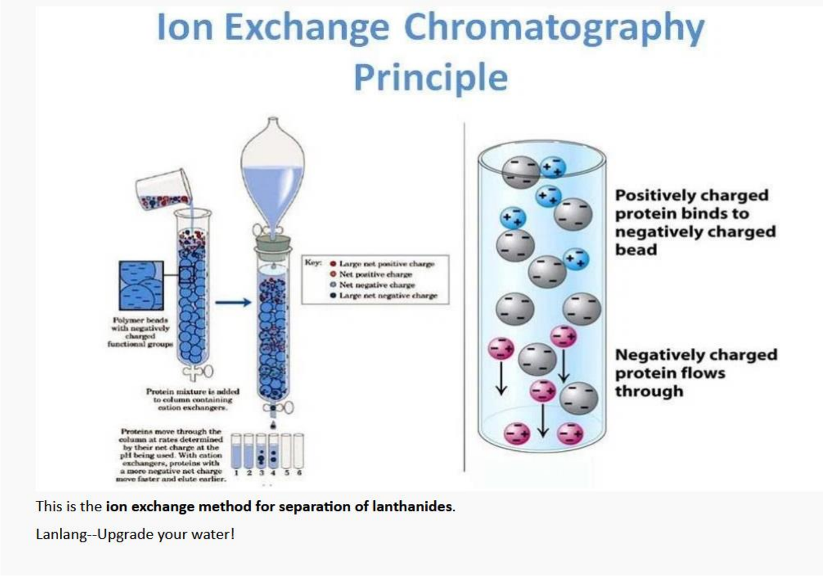
Additional Considerations:

- **Environmental impact:** The extraction process generates hazardous waste and requires careful management to minimize environmental damage.
- **Sustainability:** Monazite often contains thorium, a radioactive element. Safe handling and proper disposal of thorium-containing residues are crucial.

SEPARATION OF LANTHANIDES

Separating lanthanides, those silvery-white metals with similar properties that often give chemists a headache, is no easy feat. But fear not, science has some cool tricks up its sleeve! Here are two main methods used to crack this separation code:

1. Ion Exchange Chromatography: Imagine a long, skinny tube packed with a special resin that acts like a picky bouncer at a nightclub. Lanthanide ions, dressed in their hydrated coats, try to squeeze through. But the bouncer (resin) is size-conscious! Smaller lanthanide ions, like lanthanum (La), slip through easily, while the larger ones, like lutetium (Lu), get stuck for a while. By carefully controlling the flow of liquids and the strength of the bouncer (using different solutions), chemists can coax the lanthanides out one by one, like a VIP line at the coolest club in town.

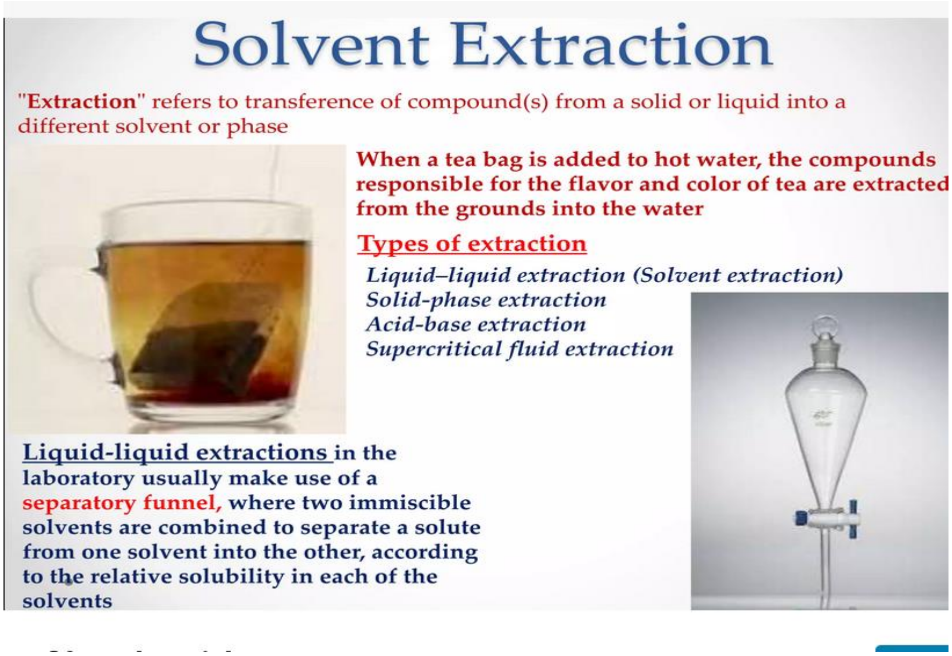


This is the **ion exchange method for separation of lanthanides**.

Lanlang--Upgrade your water!

Ion exchange chromatography for lanthanides separation

2. Solvent Extraction: This method involves a liquid-liquid dance party. The lanthanides are dissolved in one solution, then shaken up with another immiscible solvent (think oil and water) containing special chelating agents. These agents act like matchmakers, grabbing specific lanthanides and whisking them away to the other solvent, like couples disappearing onto the dance floor. By using different chelating agents and controlling the pH of the solutions, chemists can separate the lanthanides based on their varying attractions to the dance partners.



Solvent Extraction

"**Extraction**" refers to transference of compound(s) from a solid or liquid into a different solvent or phase

When a tea bag is added to hot water, the compounds responsible for the flavor and color of tea are extracted from the grounds into the water

Types of extraction

Liquid–liquid extraction (Solvent extraction)
Solid-phase extraction
Acid-base extraction
Supercritical fluid extraction

Liquid-liquid extractions in the laboratory usually make use of a separatory funnel, where two immiscible solvents are combined to separate a solute from one solvent into the other, according to the relative solubility in each of the solvents

Solvent extraction for lanthanides separation

Both methods have their own strengths and weaknesses, and the choice depends on the specific lanthanides being separated and the desired purity. It's like choosing the right tool for the job

USES OF LANTHANIDES

Lanthanides, also known as the rare earth elements, are a group of 15 metallic elements with unique and versatile properties. They're found in various applications across diverse fields, from technology and medicine to energy and materials science. Here are some fascinating uses of lanthanides:

Technology:

- **Magnets:** Lanthanides like neodymium and samarium are crucial components of high-strength magnets used in electric vehicles, hard drives, wind turbines, and even medical imaging devices like MRI machines.
- **Lasers:** Lanthanide-doped crystals play a key role in producing powerful and efficient lasers for applications like medical diagnostics, material processing, and even scientific research.
- **Electronics:** Lanthanides like cerium and lanthanum are used in catalytic converters for cars, while others find their way into electronic components like transistors and capacitors.

Medicine:

- **Gadolinium:** This lanthanide is used as a contrast agent in MRI scans, helping to enhance the visibility of internal organs and tissues.
- **Bone-targeting drugs:** Lanthanides can be attached to drugs for targeted delivery to bones, improving treatment efficacy for conditions like osteoporosis and cancer.
- **Luminescent probes:** Lanthanides with their unique light-emitting properties are used in bioassays and medical imaging to study biological processes at the cellular level.

Energy:

- **Fuel cells:** Lanthanides like lanthanum and cerium are used in solid oxide fuel cells, a promising clean energy technology that converts chemical energy directly into electricity.
- **Batteries:** Lanthanide-based batteries are being developed for electric vehicles and grid storage, offering high energy density and potentially longer lifespans.
- **Hydrogen production:** Lanthanide-based catalysts are being explored for efficient hydrogen production from water, a crucial step in the transition to a hydrogen-based economy.

Materials Science:

- **Glass and ceramics:** Lanthanides are used to improve the strength, durability, and optical properties of glass and ceramics used in various applications, from cookware to architectural elements.
- **Phosphors:** Lanthanides are essential components of phosphors used in fluorescent lamps and LEDs, making them more efficient and energy-saving.
- **Polishing compounds:** Lanthanide-based polishing compounds are used in the precision finishing of optical lenses and other delicate surfaces.

These are just a few examples of the diverse and impactful uses of lanthanides. As research and development continue, we can expect even more exciting applications of these fascinating elements to emerge in the future.

ACTINIDES SOURCES OF ACTINIDES

Actinides, a fascinating group of elements encompassing thorium (Th) through lawrencium (Lr), have diverse sources depending on their rarity and stability:

Natural occurrences:

- **Abundant:** Only two actinides, **thorium (Th)** and **uranium (U)**, exist in significant quantities in Earth's crust. They are found in mineral deposits like pitchblende and monazite and are extracted for various applications.
- **Traces: Actinium (Ac)** and **protactinium (Pa)** occur naturally in trace amounts as decay products of thorium and uranium. **Neptunium (Np)** also appears in minimal quantities within uranium ore due to transmutation reactions.

Synthetic production:

- **Reactor breeding:** Elements heavier than thorium, like **plutonium (Pu)**, are primarily produced through neutron capture and subsequent decay processes within nuclear reactors fueled by uranium.
- **Bombardment:** Elements beyond plutonium, known as transuranium elements, are synthesized in particle accelerators by bombarding heavier elements with neutrons or other charged particles.

Additional sources:

- **Nuclear fallout:** Past nuclear weapons tests have dispersed minute amounts of transuranium elements like **americium (Am)** and **curium (Cm)** into the environment.
- **Nuclear fuel reprocessing:** Reprocessing spent nuclear fuel can recover and purify various actinides like plutonium and neptunium for further use.

Here's a quick summary of the main sources:

Element	**Main Source**
Thorium & Uranium	Natural deposits
Actinium & Protactinium	Decay products of Th & U
Neptunium	Traces in U ore & reactor breeding
Plutonium	Reactor breeding
Transuranium elements	Particle accelerator bombardment
Americium & Curium	Nuclear fallout
Reprocessed actinides	Nuclear fuel reprocessing

PREPARATION OF TRANSURANIC ELEMENTS

The preparation of transuranic elements, elements with atomic numbers higher than uranium (92), involves a fascinating blend of nuclear physics and sophisticated chemical techniques. Here's a glimpse into the world of transuranic element synthesis:

Reactors and Bombardment:

- **Neutron Capture:** One common method involves irradiating target nuclei with neutrons in nuclear reactors. The neutrons can be absorbed by the nucleus, leading to the formation of heavier isotopes or even new elements. For example, bombarding plutonium-239 with neutrons can create plutonium-240, which then decays into americium-240.
- **Charged Particle Bombardment:** In other cases, scientists use accelerators to bombard target nuclei with charged particles like protons, deuterons, or alpha particles. These collisions can induce nuclear reactions that create transuranic elements. For example, bombarding curium-244 with alpha particles can produce californium-248.

Chemical Separation:

Once the desired transuranic element is formed, it needs to be separated from the target material and other reaction products. This is a complex process because transuranic elements are often present in minute quantities and have similar chemical properties to other elements. Techniques like solvent extraction, ion exchange chromatography, and precipitation are used to achieve this separation.

Challenges and Applications:

The preparation of transuranic elements is challenging due to their radioactive nature, requiring specialized facilities and equipment to handle them safely. However, these elements have important applications in various fields, including:

- **Nuclear Medicine:** Some transuranic elements, like americium-241, are used in smoke detectors. Others, like curium-244, are used in cancer treatment as radiation sources.
- **Space Exploration:** Plutonium-238 is used as a heat source in radioisotope thermoelectric generators (RTGs) that power spacecraft in deep space.

- **Scientific Research:** Studying the properties of transuranic elements helps us understand nuclear physics and the evolution of elements in the universe.

The field of transuranic element research is constantly evolving, with new elements and production methods being discovered. It's a testament to human ingenuity and scientific curiosity that we can create and study these exotic elements from the heart of the atom.

LANTHANIDES: ELECTRONIC CONFIGURATION, OXIDATION STATES, IONIC RADII, AND COLOR OF IONS

The lanthanides are a group of 14 elements in the periodic table from Lanthanum (La) to Lutetium (Lu). They're known for their unique properties due to their electronic configuration and incompletely filled 4f orbitals. Here's a breakdown of the key points you mentioned:

Electronic Configuration:

- General form: [Xe] $4f^{0-14}$ $5d^0$ $6s^2$
- Electrons filling the 4f orbitals give rise to their unique properties and characteristics.
- Exceptions: Gadolinium (Gd) and Lutetium (Lu) have electrons in the 5d orbital due to specific stability factors.

Oxidation States:

- Most common: +3
- +2 and +4 states also exist, but less stable than +3.
- The +3 state arises from losing three electrons from the outermost $6s^2$ orbital.

Ionic Radii:

- Decrease steadily from La to Lu due to the phenomenon called "lanthanide contraction."
- Electrons filling the inner 4f orbitals don't effectively shield the nuclear charge, resulting in a stronger pull on outer electrons and a smaller size.

Color of Ions:

- Many lanthanide ions are colored due to d-f transitions within the 4f orbitals.
- The specific color depends on the element and its oxidation state.

- Examples: Ce^{3+} (colorless), Pm^{3+} (pink-yellow), Pr^{3+} (green), Nd^{3+} (reddish), Tm^{3+} (green), Ho^{3+} (pink-yellow).

Additional Points:

- Lanthanide contraction has various consequences, including influencing bond strengths, ionic radii, and chemical properties.
- Lanthanides have a wide range of applications in various fields, including catalysis, metallurgy, lasers, and electronics.

COMPARISON WITH LANTHANIDES

Lanthanides vs. Actinides: A Tale of Two Inner Transition Series

Both lanthanides and actinides are fascinating groups of elements nestled within the f-block of the periodic table. They share some intriguing similarities, yet key differences set them apart. Let's delve into their unique characteristics:

Electronic Configuration:

- **Lanthanides:** These elements have electrons filling the 4f orbitals. As we move across the series, the number of 4f electrons increases from 1 (cerium) to 14 (lutetium).
- **Actinides:** Here, the electrons fill the 5f orbitals. Similar to lanthanides, the number of 5f electrons increases from 1 (actinium) to 14 (lawrencium).

Chemical Properties:

- **Oxidation states:** Both series exhibit a variety of oxidation states, but lanthanides typically prefer +3, while actinides can display a wider range, including +2, +3, +4, +5, and even +7.
- **Reactivity:** Lanthanides are generally less reactive than actinides due to their stronger inner 4f orbitals. Actinides, with their more exposed 5f orbitals, readily participate in chemical reactions.
- **Radioactivity:** All naturally occurring actinides are radioactive, some with extremely short half-lives. In contrast, most lanthanides are stable, with the exception of promethium.

Similarities:

- Both series exhibit the **lanthanide contraction** and **actinide contraction**, where the ionic radii steadily decrease due to the increasing nuclear charge and poor shielding by the f-electrons.
- Both form colorful complexes due to their f-electrons' involvement in bonding.
- Both play crucial roles in various technological applications, such as magnets, lasers, and catalysts.

Applications:

- **Lanthanides:** Used in super magnets, ceramics, phosphors for fluorescent lamps, and catalysts for petroleum refining.
- **Actinides:** Primarily used in smoke detectors (americium), nuclear reactors (uranium and plutonium), and medical imaging (technetium).

In a nutshell:

- **Lanthanides:** Think of them as the more stable and subdued f-block elements, with their inner 4f orbitals keeping them less reactive.
- **Actinides:** Imagine them as the energetic and flamboyant cousins, readily engaging in reactions with their exposed 5f orbitals and often exhibiting radioactivity.

EXTRACTION OF THORIUM FROM MONAZITE SAND

Monazite sand is the primary source of commercially extracted thorium. This black or reddish-brown sand contains a variety of minerals, including monazite, zircon, rutile, and ilmenite. Monazite itself is a phosphate mineral rich in rare earth elements (REEs) and, of course, thorium.

Here's an overview of the process for extracting thorium from monazite sand:

1. Concentration:

The first step involves physically concentrating the monazite from the other minerals in the sand. This is often done using gravity separation, magnetic separation, or flotation techniques.

2. Digestion:

The concentrated monazite is then treated with either a strong acid (like sulfuric acid) or a strong base (like sodium hydroxide) to break down the mineral and dissolve the thorium and other valuable elements.

3. Separation:

The resulting solution is then treated to selectively separate the thorium from the other elements. This can involve various techniques, such as:

Precipitation: Adding specific chemicals to the solution causes the thorium to precipitate out as a solid, while other elements remain dissolved.

Solvent extraction: The solution is passed through a series of immiscible liquids, where the thorium preferentially dissolves into one liquid while other elements remain in the other.

Ion exchange: The solution is passed through a column containing a material that selectively binds to thorium ions, allowing other elements to pass through.

4. Purification:

The separated thorium is then further purified to remove any remaining impurities. This may involve additional precipitation, solvent extraction, or ion exchange steps.

5. Conversion:

Finally, the purified thorium is converted into the desired form, typically thorium oxide (ThO_2). ThO_2 is a white, high-melting-point powder that can be used for various purposes, including nuclear fuel.

It's important to note that thorium extraction is a complex and environmentally sensitive process. The chemicals used can be hazardous, and the process generates radioactive waste that must be managed safely. Therefore, it's crucial to follow strict environmental regulations and best practices throughout the extraction process.

PRODUCTION AND USES OF PLUTONIUM

Production of Plutonium

Plutonium is not found naturally in significant quantities. It is primarily produced through the irradiation of uranium-238 in nuclear reactors. When neutrons bombard uranium-238 atoms, they absorb neutrons and undergo a series of nuclear transformations, eventually resulting in the formation of plutonium-239.

The specific process involves several steps:

Neutron capture: A neutron is absorbed by a uranium-238 nucleus, forming uranium-239.

Beta decay: Uranium-239 undergoes beta decay, emitting an electron and an antineutrino and transforming into neptunium-239.

Beta decay: Neptunium-239 undergoes another beta decay, emitting another electron and antineutrino and transforming into plutonium-239.

The plutonium-239 produced in this way can be separated from the spent nuclear fuel and used for various purposes.

Uses of Plutonium

Plutonium has a number of important uses, including:

Nuclear fuel: Plutonium-239 is a highly fissile material, meaning it readily undergoes nuclear fission when struck by neutrons. This makes it a valuable fuel for nuclear reactors, where it can be used to generate electricity.

Nuclear weapons: Plutonium-239 is also the fissile material used in the cores of nuclear weapons. Its high fissile cross-section and relatively small critical mass make it ideal for this purpose.

Spacecraft power: Plutonium-238, another isotope of plutonium, is a powerful heat source due to its radioactive decay. This heat can be used to generate electricity for spacecraft through radioisotope thermoelectric generators (RTGs). RTGs have been used to power many deep-space missions, including the Voyager probes and the New Horizons spacecraft.

Medical applications: Plutonium-238 has also been used in some medical devices, such as pacemakers. However, its use in medical applications has largely been discontinued due to concerns about its radioactivity.

It is important to note that plutonium is a highly radioactive and toxic material. It must be handled with extreme care to avoid exposure, which can cause serious health problems.

UNIT II

CHEMISTRY OF ORGANOMETALLIC COMPOUNDS

Introduction:

Organometallic Compounds are chemical compounds which contain at least one bond between a metallic element and a carbon atom belonging to an organic molecule. Even metalloid elements such as silicon, tin, and boron are known to form organometallic compounds which are used in some industrial chemical reactions.

The catalysis of reactions wherein the target molecules are polymers or pharmaceuticals can be done with the help of organometallic compounds, resulting in an increase in the rate of the reactions.

Generally, the bond between the metal atom and the carbon belonging to the organic compound is covalent in nature. When metals with relatively high electropositivity (such as sodium and lithium) form these compounds, a carbanionic nature is exhibited by the carbon which is bound to the central metal atom.

Organometallic compounds are a unique class of molecules that bridge the gap between the seemingly separate worlds of organic and inorganic chemistry. They contain at least one **covalent bond** between a **metal atom** and a **carbon atom** belonging to an organic group or molecule. This bond creates a special relationship where the metal's properties get intertwined with the organic group's characteristics, leading to a whole new range of fascinating behaviors and applications.

Types and Properties:

The types of organometallic compounds are diverse, encompassing a wide variety of structures and properties. Some key examples include:

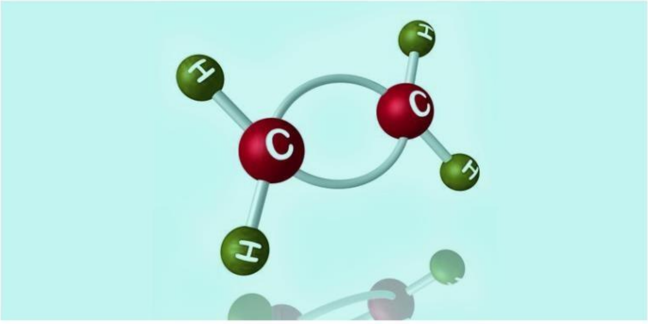
- **Metal carbonyls:** These compounds feature metal atoms surrounded by carbon monoxide (CO) molecules, exhibiting remarkable stability and unique reactivity.
- **Metal alkyls:** These involve direct metal-carbon bonds with alkyl groups (like $CH3$ or $C2H5$), often used as catalysts in industrial processes.

- **Cyclopentadienyl complexes:** Here, the metal atom forms a sandwich-like structure with a five-membered ring called cyclopentadiene, demonstrating exceptional stability and catalytic activity.
- **π-complexes:** These involve weaker bonds between metal atoms and unsaturated organic molecules like alkenes or alkynes, offering fascinating insights into metal-ligand interactions.

Importance and Applications:

Organometallic compounds play a crucial role in various fields:

- **Catalysis:** They act as efficient catalysts for numerous reactions, enabling the production of countless everyday products like plastics, pharmaceuticals, and agrochemicals.
- **Medicine:** Certain organometallic compounds exhibit promising anti-cancer and anti-microbial properties, with some already used in chemotherapy treatments.
- **Materials Science:** They are employed in the development of new materials with tailored properties, such as high-performance polymers and luminescent materials.
- **Energy:** Organometallic research contributes to the development of clean and efficient energy technologies like solar cells and fuel cells.



An example of an organometallic compound wherein carbons belonging to a benzene molecule bond with chromium is illustrated above. A few more examples of these types of compounds are Grignard reagents, tetracarbonyl nickel, and dimethyl magnesium.

Preparation of Organomagnesium Compounds:

The general the synthesis of a Grignard reagent involves the reaction of an alkyl halide (RX, where X = Cl, Br, I) with magnesium metal in a suitable ether solvent, Equation.

$$RX + Mg \rightarrow RMgX$$

While diethyl ether (Et_2O) and tetrahydrofuran (THF) are commonly used as solvents, other polar non-protic solvents are suitable, including: triethylamine (NEt_3), dimethylsulphide (Me_2S), dimethylselenide (Me_2Se), and dimethyltelluride (Me_2Te).

Organomagnesium compounds, also known as Grignard reagents, are incredibly useful tools in organic synthesis. Their preparation, however, requires careful consideration of various factors and methods. To provide you with the most relevant information, I need a bit more context. What specific aspect of organomagnesium compound preparation are you interested in?

Here are some potential areas I can guide you on:

- **General methods:** The most common method involves reacting an alkyl or aryl halide with magnesium metal in an ethereal solvent like diethyl ether. However, variations like Schlenk techniques and alternative activating agents exist.
- **Choice of starting materials:** Different types of alkyl and aryl halides have varying reactivity, and their selection depends on the desired organomagnesium compound and your synthetic goals.
- **Reaction conditions:** Controlling factors like temperature, solvent purity, and presence of additives can significantly impact the yield and efficiency of the reaction.
- **Safety considerations:** Organomagnesium compounds are air and moisture sensitive, and their preparation requires proper safety protocols and handling techniques.

The relative order of reactivity of the alkyl halide follows the trend:

$$I > Br > Cl > F$$

In fact alkyl fluorides are sufficiently inert that highly coordinating polar solvents such as THF or dimethylformamide (DMF) must be used.

If the reaction is allowed to get too hot then several possible side reactions can occur. In THF reaction with the solvent occurs:

$$RMgX + THF \rightarrow RH + H_2C{=}CH_2 + H_2C{=}C(H)MgX$$

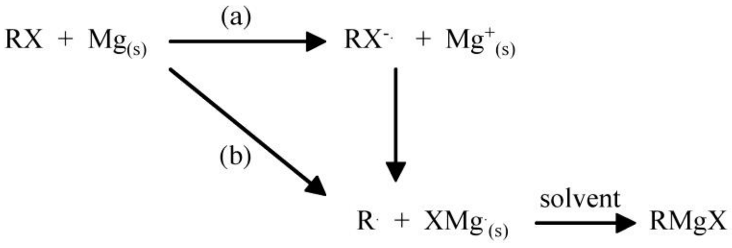
Alternatively, a transition metal catalyzed radical coupling between the Grignard and unreacted alkyl halide is observed irrespective of the identity of the solvent, Equation.

$$RMgX + RX \rightarrow R\text{-}R + MgX_2$$

The mechanism for Grignard formation is thought to be radical in nature; however, a study of the surface of the magnesium during the reaction has shown the presence of corrosion pits. It is generally agreed that initiation occurs at surface dislocations, but the major reaction occurs at a polished surface.

The kinetics of the reaction is 1st order with respect to the alkyl halide concentration, but it has also been claimed to be 1st order with respect to the solvent concentration. It has therefore been concluded that the rate-determining step involves the metal solvent interface.

The reaction of magnesium with aryl bromides has been studied and is proposed to occur by two reactions. The first involves electron transfer between the aryl halide and the metal, while the second involves aryl radical formation.



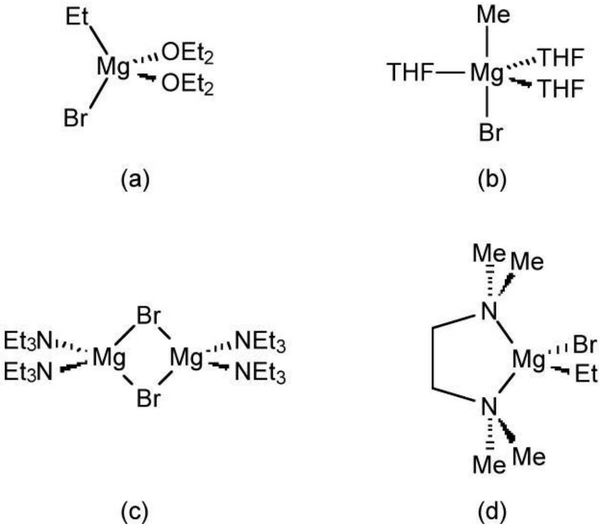
A number of alternative synthetic routes are used with polyhalogenated hydrocarbons, Equation and Equation, and where the alkyl radical is unstable, Equation.

$$X_3CH + {}^{i}PrMgX \rightarrow (X_3C)MgX + {}^{i}PrH$$

$C_6Br_6 + EtMgX \rightarrow (C_6Br_5)MgX + EtBr$

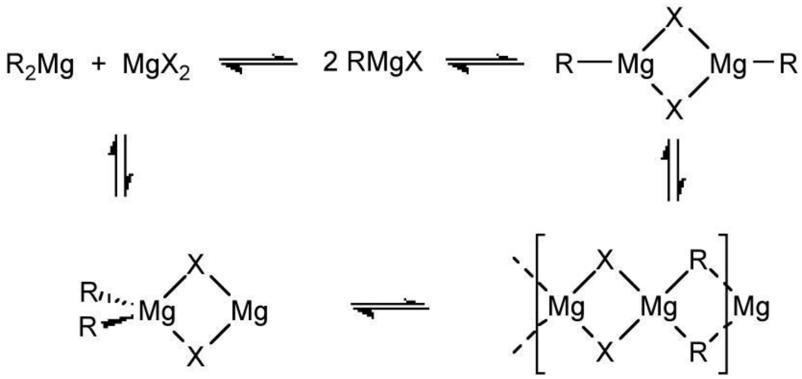
$RX + R'MgX' \rightarrow RMgX' + R'X$

The solid state structure of Grignard reagents is controlled by the presence and identity of the solvent used in the synthesis. In this regard the size and the basicity of the solvent is important. For example, the structure of EtMgBr crystallized from diethyl ether exists as a 4-ccordinate monomer (Figure a), while the use of the sterically less demanding THF results in a 5-coordinate monomeric structure (Figure b). In contrast, the use of triethylamine yields a dimeric bromide bridged structure (Figure c), and the use of a chelate bidentate amine gives a structure (Figured) similar to that observed with diethyl ether (Figure a).



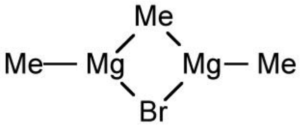
Molecular structure of EtMgBr in (a) diethyl ether, (b) THF, (c) triethyl amine, and (d) tetramethyletheylenediamine (TMED).

In solution, Grignards are fluxional such that no single defined structure is present. The series of exchange reactions are known as an extended Schlenk equilibrium (Figure).



Schematic representation of the extended Schlenk equilibrium observed for Grignard compounds in solution.

It is observed that Grignard solutions are also slightly conducting, and magnesium is deposited at both the anode and cathode suggesting the formation of RMg^+ and $[RMgX2]^-$. The alkyl/halide exchange is thought to occur through a bridging intermediate (Figure).



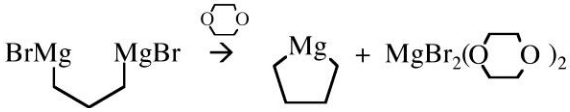
Dialkyl magnesium (R2Mg)

Dialkyl magnesium compounds are involatile white solids. They generally have similar reactivity to their Grignard analogs.

Synthesis

The most common synthesis of R2Mg is by the reaction of a Grignard with dioxane (C4H8O2), Equation, where the precipitation of the dihalide is the reaction driving force.

This method is useful for the synthesis of cyclic compounds, Equation.



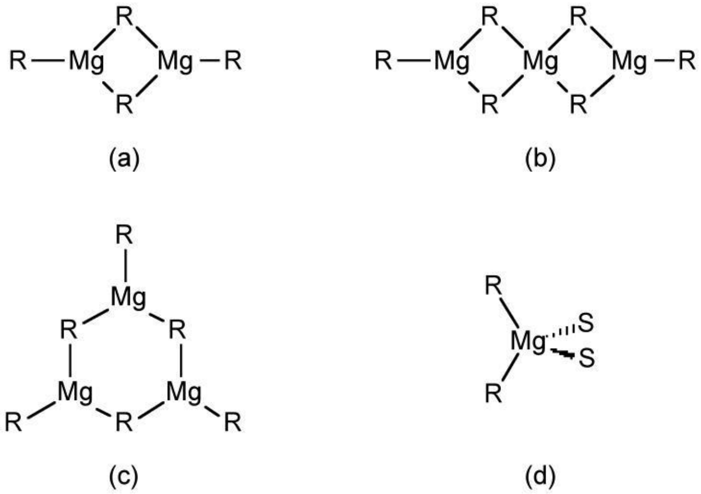
n alternative synthesis that does not require dioxane involves the metal exchange reaction between magnesium metal and a dialkyl mercury compound.

$$R_2Hg + Mg \rightarrow R_2Mg + Hg$$

Finally, in selected cases, magnesium will react with acidic hydrocarbons such as cyclopentadienyl at high temperatures (600 °C).

Structure

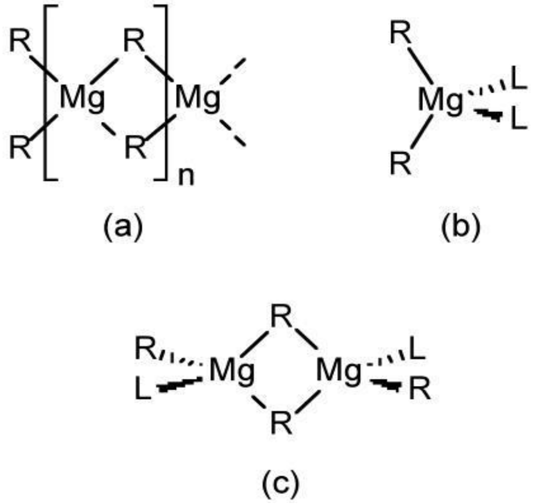
In the vapor phase dialkyl magnesium compounds are generally monomeric linear compounds. In solution, in the absence of coordinating solvents R2Mg form a variety of oligomers (Figurea-c) in solution as determined by molecular weight measurements. In the presence of coordinating solvents 4-coordinate monomers predominate (Figure d).



(a) (b) (c) (d)

Solution structure of R2Mg (R = Me, Et) in (a – c) non-coordinating solvents, and (d) diethyl ether.

As similar trend is observed in the solid state, where polymers have been characterized in the absence of coordinating solvents (Figurea), while monomers or dimmers are generally observed when crystallized from a coordinating solvent Figure b and c).



(a) (b) (c)

Solid state structure of R_2Mg (R = Me, Et) crystallized in (a) the absence and (b and c) the presence of a coordinating solvents.

Physical and Chemical Properties of Organomagnesium Compounds:

Organomagnesium compounds, also known as magnesium-carbon bonds, are a fascinating class of chemicals with unique properties and diverse applications. Here's a breakdown of their key physical and chemical characteristics:

Physical Properties:

- **State:** Most organomagnesium compounds are **solids** at room temperature, especially those with aromatic or cyclic hydrocarbon groups.
- **Reactivity:** Generally, they are **highly reactive** towards air and moisture due to the polarity of the Mg-C bond.
- **Solubility:** They are typically **soluble in polar solvents** like ethers (diethyl ether, tetrahydrofuran) and some non-protic solvents like triethylamine.
- **Volatility:** Their volatility varies depending on the specific compound and the size of the hydrocarbon groups. Smaller alkyl groups tend to be more volatile.

Chemical Properties:

Bonding: The Mg-C bond is primarily **covalent polar**, with some ionic character. This polarity contributes to their reactivity.

- **Structure:** In solution, many organomagnesium compounds exist as **dimers or higher aggregates**, due to their tendency to associate through Lewis acid-base interactions with solvent molecules.
- **Reactions:** They are known for their diverse reactivity, including:
  - **Nucleophilic addition:** They readily react with carbonyl compounds (aldehydes, ketones) to form alcohols.
  - **Grignard reaction:** With alkyl halides, they form new carbon-carbon bonds via nucleophilic substitution.
  - **Hydrolysis:** They react readily with water and protic solvents, releasing methane and forming the corresponding magnesium hydroxide.
  - **Oxidation:** They are readily oxidized by air and various oxidizing agents.
  - **Acid-base:** They can act as weak Brønsted-Lowry acids due to the slightly acidic Mg-H bond in some cases.

Types of Organomagnesium Compounds:

Two main types exist:

- **Grignard reagents (RMgX):** These have one Mg-C bond and one Mg-halide (X) bond. They are widely used in organic synthesis for carbon chain extension and functional group additions.
- **Dialkylmagnesium compounds (R2Mg):** These have two Mg-C bonds and are less common than Grignard reagents. They find applications in specialized organic reactions and as precursors to other organometallic compounds.

Applications:

Organomagnesium compounds, particularly Grignard reagents, are incredibly valuable tools in synthetic organic chemistry. They are used to:

- **Synthesize alcohols, amines, and other organic compounds.**
- **Form carbon-carbon bonds for chain extension and ring synthesis.**
- **Functionalize molecules with various groups like hydroxyls, amines, etc.**

Act as nucleophilic intermediates in various organic transformations.

Hydrolysis and related reactions

Grignard compounds react with water to give the hydrocarbon, Equation, they also react with other hydroxylic compounds such as alcohols and carboxylic acids. One important use of the hydrolysis reaction is specifically deuteration, Equation.

Equation.

$$CH_3MgBr + H_2O \rightarrow CH_4 + BrMgOH$$

$$CH_3CH_2(CH_3)_2CMgBr + D_2O \rightarrow CH_3CH_2(CH_3)_2CD + BrMgOD$$

The hydrogen atom on a terminal alkyne is sufficiently acidic that the reaction with Grignard soccurs in an analogous manner to that of hydrolysis.

$$C_6H_5C{\equiv}CH + C_2H_5MgBr \rightarrow C_6H_5C{\equiv}CMgBr + C_2H_6$$

Once formed the alkynyl Grignard undergoes the same hydrolysis reaction.

$$C_6H_5C{\equiv}CMgBr + D_2O \rightarrow C_6H_5C{\equiv}CD + BrMgOD$$

Reaction with CO2

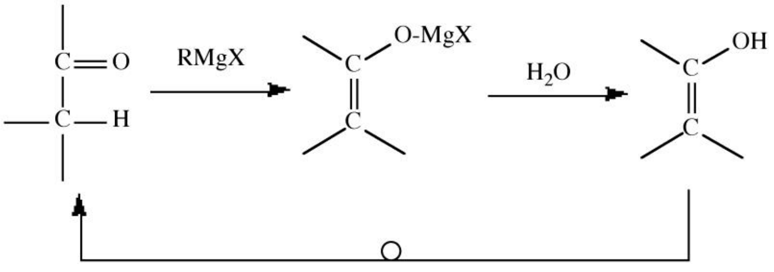
Grignards react readily with carbon dioxide to form the carboxylate, which yields the associated carboxylic acid upon hydrolysis, Equation.

$$RMgX + CO_2 \rightarrow RCO_2MgX \xrightarrow{H_2O} RCO_2H + HOMgX$$

Reaction with carbonyls

Organomagnesium compounds react with organic carbonyls (aldehydes, ketones, and esters) to yield the alcohol on hydrolysis, Equation. This synthetic route is useful for the formation of primary, secondary and terminal alcohols.

$$RMgX + R'_2C{=}O \rightarrow R'_2(R)COMgX \xrightarrow{H_2O} R'_2(R)COH + HOMgX$$

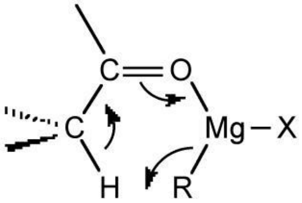


Unfortunately, for some carbonyls there is a competing side reaction of enolization, where the starting ketone is reformed upon hydrolysis.

When the Grignard reagent has a β-hydrogen another side reaction occurs in which the carbonyl group is reduced and an alkene is formed.

$$\mathrm{R_2C{=}O + (CH_3CH_2)MgX \rightarrow R_2(H)COH + H_2C{=}CH_2}$$

Both the enolization and reduction occur via similar 6-membered cyclic transition states (Figure).



Representation of the 6-membered transition state reaction for enolization of a ketone.

Grignards react with α,β-unsaturated ketones to give either the 1,2-addition product or the 1,4-addition product, or both.

$$\begin{aligned}\mathrm{Ph(H)C{=}C(H)\text{-}C(O)Me + EtMgBr} &\xrightarrow{\mathrm{H_2O}} \mathrm{Ph(H)C{=}C(H)\text{-}C(OH)EtMe}\\ &\qquad + \\ &\qquad \mathrm{Ph(H)EtC\text{-}CH_2\text{-}C(O)Me}\end{aligned}$$

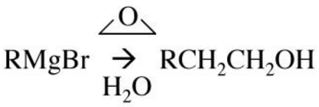
Reaction with acyl halides

Acyl halides react with Grignards to give ketones, Equation. Best results are obtained if the reaction is carried out at low temperature and in the presence of a Lewis acid catalysts (e.g., $FeCl3$).

$$\mathrm{CH_3C(O)Cl + RMgX \rightarrow CH_3C(O)R + XMgCl}$$

Reaction with epoxides

Oxirane (epoxide) rings are opened by Grignards, Equation, in a useful reaction that extends the carbon chain of the Grignard by two carbon atoms. This reaction is best performed with ethylene oxide since the magnesium halide formed is a Lewis acid catalyst for further reactions in the case ofsubstituted oxiranes.



$$RMgBr \xrightarrow[H_2O]{\text{(ethylene oxide)}} RCH_2CH_2OH$$

Reaction with salts

One of the most useful methods of preparing organometallic compounds is the exchange reaction ofone organometallic compound with a salt of a different metal, Equation. This is an equilibrium process, whose equilibrium constant is defined by the reduction potential of both metals. In general the reaction will proceed so that the more electropositive metal will form the more ionic salt (usually chloride).

$$RM + M'X \rightleftharpoons RM' + MX$$

Grignard reagents are particularly useful in this regard, and may be used to prepare a wide range oforganometallic compounds. For example:

$$2\ CH_3CH_2MgCl + CdCl_2 \rightarrow Cd(CH_2CH_3)_2 + 2\ MgCl_2$$

$$4\ CH_3MgCl + SiCl_4 \rightarrow Si(CH_3)_4 + 4\ MgCl_2$$

The reaction with a Grignard is milder than the analogous reaction with lithium reagents, and leads to a lower incident of side-products.

USES OF ORGANOMAGNESIUM COMPOUNDS

Organomagnesium compounds, most famously Grignard reagents, are workhorses in organic synthesis due to their versatility and powerful nucleophilic character. Here are some of their key uses:

1. Carbon-Carbon Bond Formation:

Addition to carbonyls: Grignard reagents react with aldehydes, ketones, and esters to form alcohols. This is a fundamental reaction for synthesizing various alcohols, including primary, secondary, and terminal alcohols.

Cross-coupling reactions: Grignard reagents can participate in various cross-coupling reactions to form carbon-carbon bonds, leading to complex organic molecules. Some examples include the Kumada-Tamao-Corriu reaction and Negishi coupling.

Epoxide ring opening: Grignard reagents can open epoxides to form alcohols with controlled stereochemistry, useful for constructing specific ring systems.

2. Functional Group Transformations:

Preparation of other organometallic reagents: Grignard reagents can be converted into other organometallic reagents like lithium or copper derivatives, expanding their synthetic applications.
Hydroboration and amination: Grignard reagents can be used in conjunction with hydroboration to introduce boron and then amine groups, creating valuable intermediates for further synthesis.

3. Other Applications:

Polymerization initiators: Grignard reagents can initiate the polymerization of certain monomers, leading to functional polymers.
Chemical sensors: The reactivity of Grignard reagents can be tailored for sensing specific chemical species.

ORGANOZINC COMPOUND

organozinc compounds are a fascinating class of chemicals that feature a direct bond between carbon and zinc. They play a vital role in organic synthesis, serving as versatile reagents for various transformations. Here's a deeper dive into their intriguing world:

Structure and Properties:

- **Carbon-Zinc Bond:** The defining characteristic of organozinc compounds is the covalent bond between a carbon atom and a zinc atom. This bond exhibits some polarity due to the difference in electronegativity between carbon and zinc, with the carbon atom being slightly more negative.
- **Types:** Organozinc compounds can be classified based on the number of carbon atoms bonded to the zinc atom. Dorganozinc compounds (R2Zn) have two carbon atoms bonded to zinc, while monorganozinc compounds (RZnX) have one carbon and one other group (X) bonded to zinc.
- **Reactivity:** Compared to other organometallic reagents like Grignard reagents, organozinc compounds are generally less reactive. This makes them more selective and easier to handle, reducing the risk of unwanted side reactions.

Applications in Organic Synthesis:

- **C-C Bond Formation:** Organozinc compounds excel in forming carbon-carbon bonds, a fundamental step in constructing complex organic molecules. They participate in various coupling reactions, including Stille, Negishi, and Suzuki-Miyaura couplings, enabling the efficient synthesis of diverse carbon chains and ring systems.

CC Bond Formation using Organozinc Compounds

- **Functionalization Reactions:** Beyond C-C bond formation, organozinc reagents can be employed for various functional group transformations. They can add alkyl groups, introduce hydroxyl groups, and participate in ring-opening reactions, expanding the synthetic possibilities.
- **Natural Product Synthesis:** Organozinc compounds find valuable applications in the synthesis of natural products, including pharmaceuticals and bioactive molecules. Their selectivity and ability to form complex carbon frameworks make them essential tools for replicating nature's intricate chemical creations.

Examples of Organozinc Compounds:

- **Diethylzinc (Et2Zn):** A colorless liquid, the most common organozinc compound used as a precursor for various reagents.
- **Diethylzinc bromide (Et2ZnBr):** A white solid, readily prepared from diethylzinc and zinc bromide, used in Stille couplings.
- **Simmons-Smith reagent (CH2IZnCl):** A valuable reagent for cyclopropanation reactions, enabling the synthesis of cyclopropane rings, a key motif in many natural products.
- **Negishi reagent (RZnCH2CH3):** A versatile reagent for Negishi couplings, allowing the formation of carbon-carbon bonds with unactivated alkyl halides.

Organozinc compounds in organic chemistry contain carbon to zinc chemical bonds. **Organozinc chemistry** is the science of organozinc compounds describing their physical properties, synthesis and reactions

Organozincs can be categorized according to the number of carbon substituents that are bound to the metal.

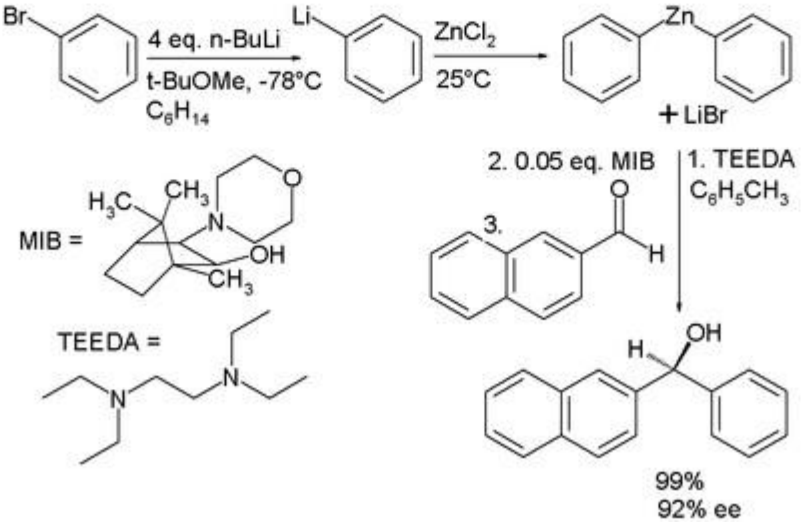
1. Diorganozinc (R_2Zn): A class of organozinc compounds in which two alkyl ligands. These may be further divided into subclasses depending on the other ligands

attached

2. Heteroleptic (RZnX): Compounds which an electronegative or monoanionic ligand (X), such as a halide, is attached to the zinc center with another alkyl or aryl substituent (R).
3. Ionic organozinc compounds: This class is divided into organozincates (R_nZn^-) and organozinc cations ($RZnL_n^+$).

Preparation:

Several methods exist for the generation of organozinc compounds. Commercially available diorganozinc compounds are dimethylzinc, diethylzinc and diphenylzinc. These reagents are expensive and difficult to handle. In one study the active organozinc compound is obtained from much cheaper organobromine precursors:

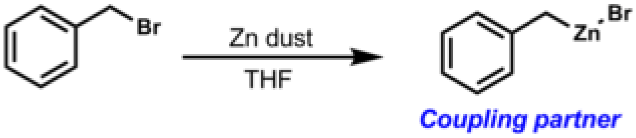


From zinc metal

Frankland's original synthesis of diethylzinc involves the reaction of ethyl iodide with zinc metal. The zinc must be activated to facilitate this redox reaction. One of such activated form of zinc employed by Frankland is zinc-copper couple.

$$2EtI + 2Zn^0 \rightarrow Et_2Zn + ZnI_2$$

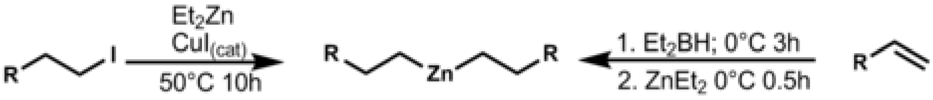
Riecke zinc, produced by in situ reduction of $ZnCl_2$ with potassium, is another



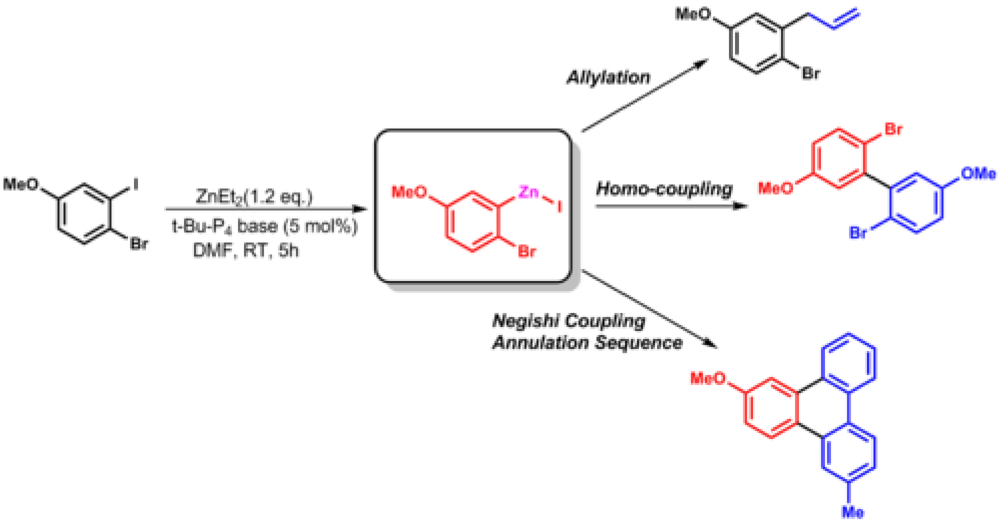
activated form of zinc. This form has proven useful for reactions such as Negishi coupling and Fukuyama coupling. Formation of organozinc reagents is facilitated for alkyl or aryl halides bearing electron- withdrawing substituents, e.g., nitriles and esters.

Functional group exchange

The two most common zinc functional group interconversion reactions are with halides and boron, which is catalyzed by copper iodide (CuI) or base. The boron intermediate is synthesized by an initial hydroboration reaction followed by treatment with diethyl zinc. This synthesis shows the utility of organozinc reagents by displaying high selectivity for the most reactive site in the molecule, as well as creating useful coupling partners.



This group transfer reaction can be used in allylation, or other coupling reactions (such as Negishi coupling).



β-Silyl diorganozinc compounds

One of the major drawbacks of diorganozinc alkylations is that only one of the two alkyl substituents is transferred. This problem can be solved by using Me3SiCH2-(TMSM), which is a non-transferable group.

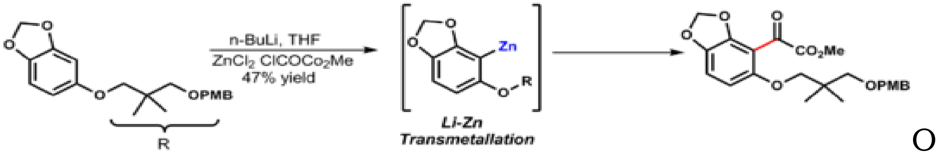
Transmetallation

Transmetallation is similar to the interconversions displayed above zinc can exchange with other metals such as mercury, lithium, copper, etc. One example of this reaction is the reaction of diphenylmercury with zinc metal to form diphenylzinc and metallic mercury:

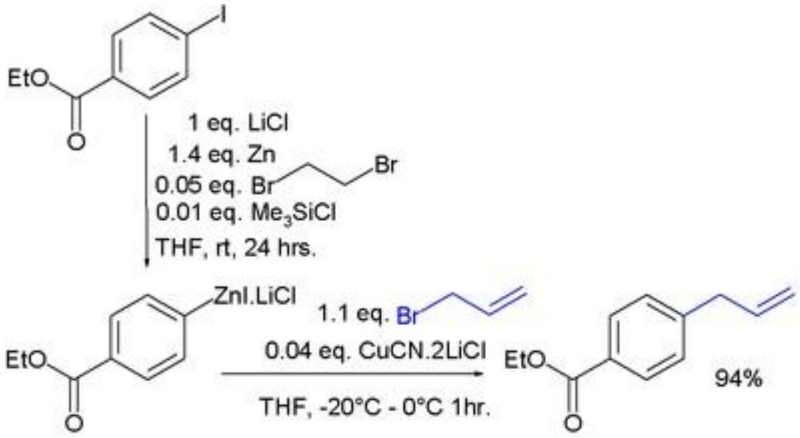
$$HgPh_2 + Zn \rightarrow ZnPh_2 + Hg$$

The benefit of transmetalling to zinc it is often more tolerant of other functional groups in the molecule due to the low reactivity which increases selectivity.

- In the synthesis of Maoecrystal V, a directed ortho metalation gives the initial aryl-lithium species, which is transmetallated to the desired arylzinc compound. The arylzinc compound is significantly less reactive than the aryl-lithium species and thus better tolerates the functionality in the subsequent coupling with methyl chlorooxaloacetate. Esters are significantly stable against organozinc reagents.



Organozinc can be obtained directly from zinc metal:



In this method zinc is activated by 1,2-dibromoethane and trimethylsilyl chloride. A key ingredient is lithium chloride which quickly forms a soluble adduct with the organozinc compound thus removing it from the metal surface.

Reactions

In many of their reactions organozincs appear as intermediates.

- In the **Frankland–Duppa reaction** (1863) an oxalate ester (ROCOCOOR) reacts with an alkyl halide R'X, zinc and hydrochloric acid to the α-hydroxycarboxylic esters RR'COHCOOR[19]

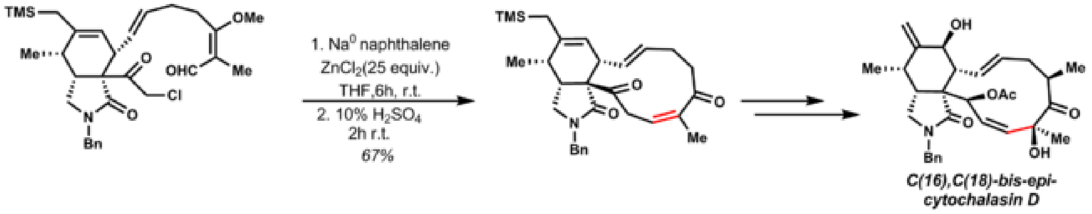
Reformatsky reaction

This organic reaction can be employed to convert α-haloester and ketone or aldehyde to a β- hydroxyester. Acid is needed to protonate the resulting alkoxide during work up. The initial step is an oxidative addition of zinc metal into the carbon-halogen bond, thus forming a carbon-zinc enolate. This C-Zn enolate can then rearrange to the Oxygen-Zinc enolate via coordination. Once this is formed the other carbonyl containing starting material will coordinate in the manner shown below and give the product after protonation. The benefits of the Reformatsky reaction over the conventional aldol reaction protocols is the following:

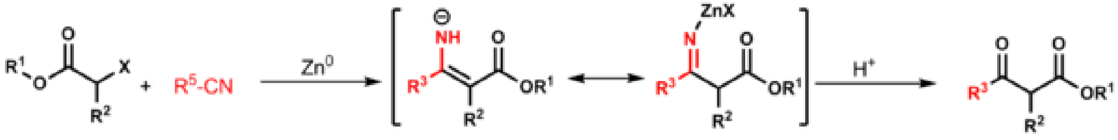
1. Allows for exceedingly derivatized ketone substrates
2. The ester enolate intermediate can be formed in the presence of enolizable moieties
3. Well suited for intramolecular reactions

Below shows the six-membered transition state of the Zimmerman–Traxler model (Chelation Control, see Aldol reaction), in which R^3 is smaller than R^4

The Reformatsky reaction has been employed in numerous total syntheses such as the synthesis of C(16),C(18)-bis-epi-cytochalasin D:

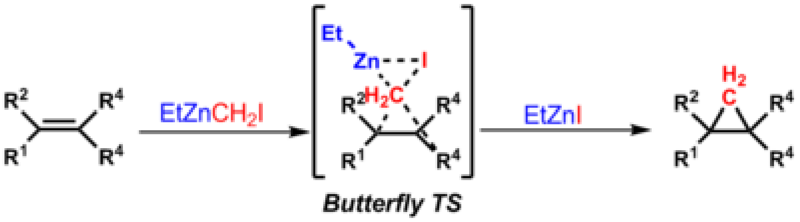


The Reformatsky reaction even allows for with zinc homo-enolates. A modification of the Reformatsky reaction is the Blaise reaction.[21]

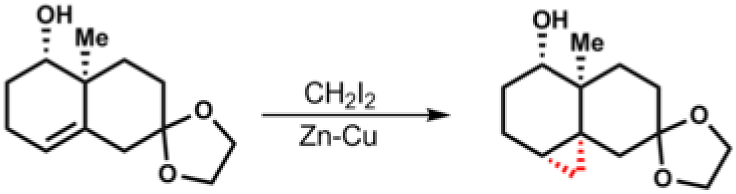


Simmons–Smith reaction

The Simmons–Smith reagent is used to prepare cyclopropanes from olefin using methylene iodide as the methylene source. The reaction is effected with zinc. The key zinc-intermediate formed is a carbenoid (iodomethyl)zinc iodide which reacts with alkenes to afford the cyclopropanated product. The rate of forming the active zinc species is increased via ultrasonication since the initial reaction occurs at the surface of the metal. (3.4)



Although the mechanism has not been fully elaborated it is hypothesized that the organozinc intermediate is a metal-carbenoid. The intermediate is believed to be a three-centered "butterfly- type". This intermediate can be directed by substituents, such as alcohols, to deliver the cyclopropane on the same side of the molecule. Zinc-copper couple is commonly used to activatezinc.



PROPERTIES OF ORGANOZINC COMPOUND

The properties of organozinc compounds are quite diverse and depend on the specific type and structure of the compound. However, here are some general properties to keep in mind:

Physical Properties:

- **Bonding:** The carbon-zinc bond in organozinc compounds is polarized towards the carbon due to the difference in electronegativity. This polarization leads to interesting properties like:

  - **Low melting and boiling points:** Many organozinc compounds are volatile and readily ignite or decompose at high temperatures.
  - **Solubility:** Generally soluble in nonpolar solvents like pentane or dimethylether, but react with protic solvents like water or alcohols, liberating hydrocarbons.
  - **Geometry:** Usually adopt a two-coordinate or three-coordinate geometry around the zinc atom, with linear configurations in dialkylzinc compounds.

Chemical Properties:

- **Reactivity:** Most organozinc compounds are highly reactive, especially towards air and moisture. They can readily undergo:
  - **Pyrophoric behavior:** Some ignite spontaneously in contact with air.
  - **Hydrolysis:** Decompose in water or protic solvents, releasing hydrocarbons and zinc hydroxide.
  - **Oxidation:** Sensitive to oxidation, readily reacting with oxygen to form zinc oxide.
- **Lewis acidity:** Diorganozinc compounds exhibit mild Lewis acidity, forming complexes with Lewis bases like amines.

Synthetic Applications:

- **Organozinc compounds are important reagents in organic synthesis, commonly used for:**
  - **Nucleophilic addition reactions:** Grignard reagents (organozinc halides) are powerful nucleophiles, adding to carbonyl groups and other electrophiles.
  - **Carbenoid formation:** Can be used to generate carbenes, reactive intermediates involved in various cyclization reactions.
  - **Cross-coupling reactions:** Useful for coupling alkyl, aryl, and alkenyl groups in various carbon-carbon bond formation reactions.

Specific Types of Organozinc Compounds:

- **Dialkylzincs (R2Zn):** Monomeric with linear geometry, widely used as Grignard reagents.
- **Organozinc halides (RZnX):** Form aggregates via halogen bridges, commonly used as precursors to other organozinc compounds.
- **Lithium zincates (R3ZnLi):** Important intermediates in some synthetic methods, possess carbanionic character.

USES OF ORGANOZINC COMPOUND

Here are the key uses of organozinc compounds, incorporating images where relevant:

1. Organic Synthesis:

- **Cross-coupling reactions:** Organozinc reagents are widely employed in various cross-coupling reactions to form carbon-carbon bonds,
- **Barbier Reactions:** Used for chain elongation of alkyl halides or carbonyl compounds.
- **Simmons-Smith Reaction:** Used to synthesize cyclopropanes.

2. Catalytic Asymmetric Synthesis:

- Due to their compatibility with chiral ligands, organozinc reagents are valuable for asymmetric synthesis of optically pure compounds, which are essential for pharmaceuticals and agrochemicals.

3. Polymerization:

- Initiators for ring-opening polymerization of cyclic esters and lactones.
- Catalysts for living radical polymerization.

4. Pharmaceuticals and Agrochemicals:

- Synthesis of bioactive compounds, including drugs and pesticides.
- Production of ephedrine derivatives, which are used as bronchodilators and decongestants.
- Synthesis of Efavirenz, an HIV-1 reverse transcriptase inhibitor.

5. Other Applications:

- Anti-wear additives in lubricating oils.
- Reductants in organic synthesis.
- Catalysts for hydrosilylation reactions.

6. Potential Future Applications:

- Organic light-emitting diodes (OLEDs).
- Solar cells.

- Drug delivery systems.

Organolithium compound:

The alkali metals (Li, Na, K etc.) and the alkaline earth metals (Mg and Ca, together with Zn) are good reducing agents, the former being stronger than the latter. These same metals reduce the carbon-halogen bonds of alkyl halides. The halogen is converted to a halide anion, and the carbon bonds to the metal which has characteristics similar to a carbanion (R:-).

Organolithium compounds are a class of chemical compounds containing a carbon-lithium (C-Li) bond. They are highly reactive organometallic reagents, crucial in organic synthesis for various purposes. Here's a breakdown of their key aspects:

Structure and Properties:

- **Carbon-lithium bond:** The defining feature is the covalent bond between carbon and lithium. This bond is highly polar due to the significant electronegativity difference between carbon and lithium.
- **Oligomerization:** Organolithium compounds typically exist as oligomers in solution, meaning they form clusters of molecules linked by lithium bridges. This structure influences their reactivity and stability.
- **Reactivity:** Their high reactivity stems from the strong polarity of the C-Li bond and the carbanion character of the carbon atom. They readily react with various electrophiles, including protons, water, and carbon dioxide.

Applications:

- **Organic synthesis:** Organolithium compounds are versatile reagents used in numerous synthetic transformations. They can act as nucleophiles for carbon-carbon bond formation, deprotonating agents for generating carbanions, and bases for various reactions.
- **Polymerization initiators:** They can initiate the polymerization of certain monomers, leading to the production of various polymers.
- **Asymmetric synthesis:** They play a crucial role in asymmetric synthesis, enabling the creation of chiral molecules with high enantiomeric purity, essential in the pharmaceutical industry.

Handling and Safety:

- **Highly reactive:** Organolithium compounds are highly air and moisture-sensitive, often pyrophoric (igniting spontaneously in contact with air). They require specialized handling techniques under inert atmospheres.
- **Corrosive and flammable:** They can be corrosive to certain materials and pose fire hazards. Proper safety precautions and protective equipment are essential when working with them.

Formation

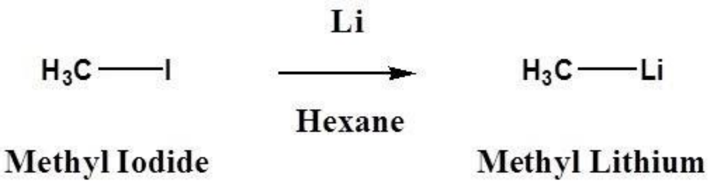
- **An Alkyl Lithium Reagent**

$R3C{-}X+2Li \rightarrow R3C{-}Li+LiX(1)$

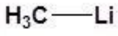
- **A Grignard Regent**

$R3C{-}X+Mg \rightarrow R3C{-}MgX(2)$

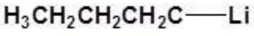
Halide reactivity in these reactions increases in the order: Cl < Br < I and Fluorides are usually not used. The alkyl magnesium halides described in the second reaction are called Grignard Reagents. Although the formulas drawn here for the alkyl lithium and Grignard reagents reflect the stoichiometry of the reactions and are widely used in the chemical literature, they do not accurately depict the structural nature of these remarkable substances. Mixtures of polymeric and other associated and complexed species are in equilibrium under the conditions normally used for their preparation.



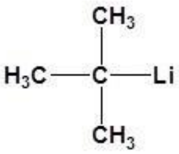
Common Organometallic Reagents



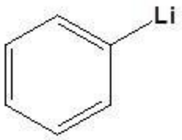
Methyl Lithium



Butyl Lithium



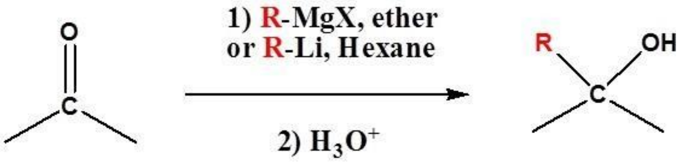
t-Butyl Lithium



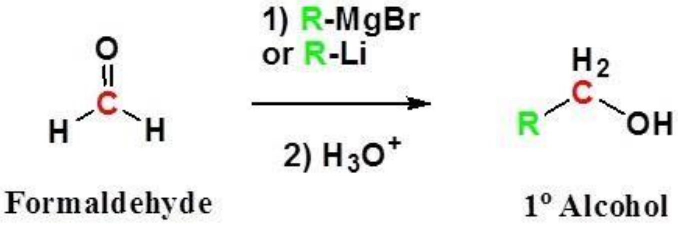
Phenyl Lithium

Reaction of Organolithium Reagents with Various Carbonyls

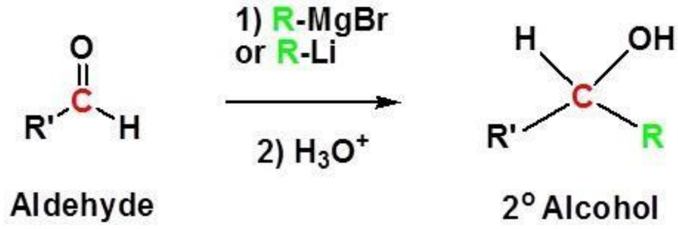
Because organometallic reagents react as their corresponding carbanion, they are excellent nucleophiles. The basic reaction involves the nucleophilic attack of the carbanionic carbon in the organometallic reagent with the electrophilic carbon in the carbonyl to form alcohols.



Both Grignard and Organolithium Reagents will perform these reactions. Addition to formaldehyde gives 1° alcohols

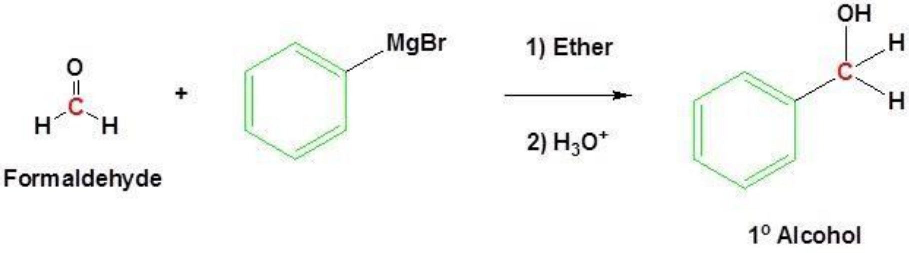


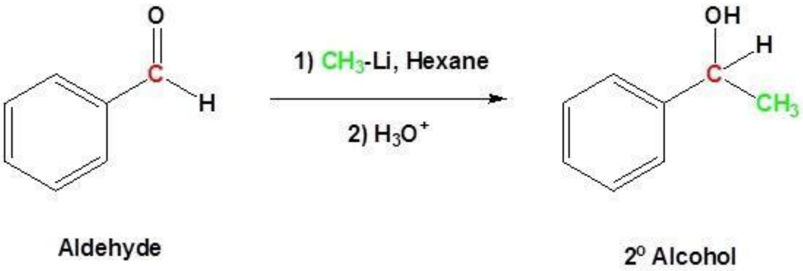
Addition to aldehydes gives 2° alcohols

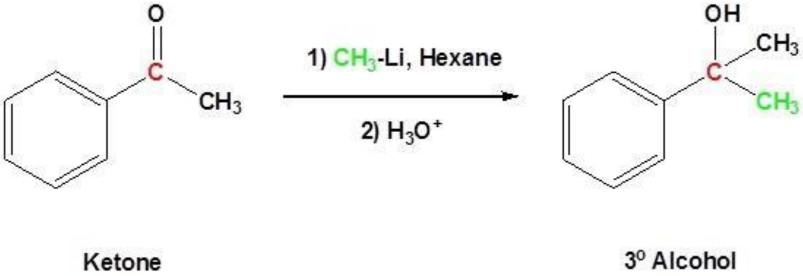


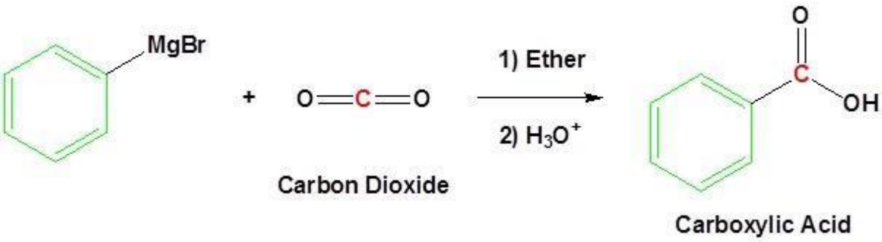
Addition to ketones gives 3° alcohols

Addition to carbon dioxide (CO2) forms a carboxylic acid

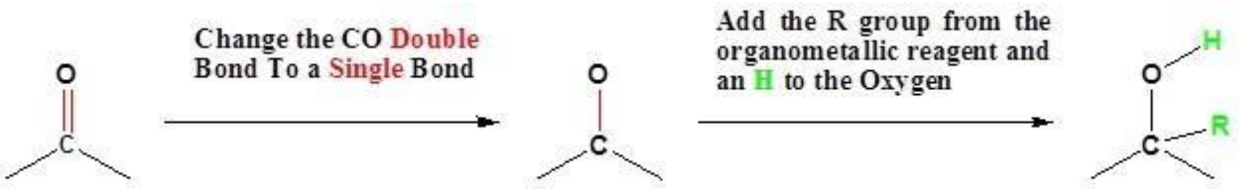






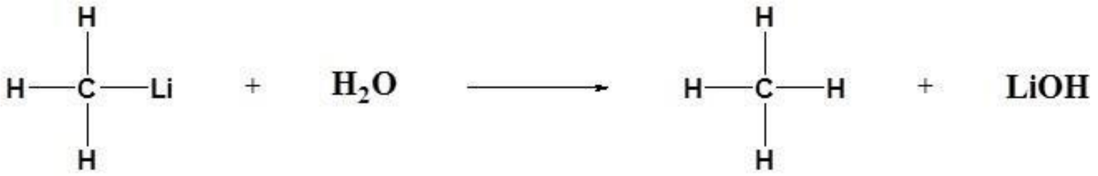


Going from Reactants to Products Simplified



Organometallic Lithium as Bases

These reagents are very strong bases (pKa's of saturated hydrocarbons range from 42 to 50). Although not usually done with Grignard reagents, organolithium reagents can be used as strong bases. Both Grignard reagents and organolithium reagents react with water to form the corresponding hydrocarbon. This is why so much care is needed to insure dry glassware and solvents when working with organometallic reagents.



In fact, the reactivity of Grignard reagents and organolithium reagents can be exploited to create a new method for the conversion of halogens to the corresponding hydrocarbon (illustrated below). The halogen is converted to an organometallic reagent and then subsequently reacted with water to from an alkane.

$$R{-}X \xrightarrow[\text{2) } H_2O]{\text{1) Mg, Ether or Li, Hexane}} R{-}H$$

$X = Cl, Br, I$

ORGANOCOPPER COMPOUND:

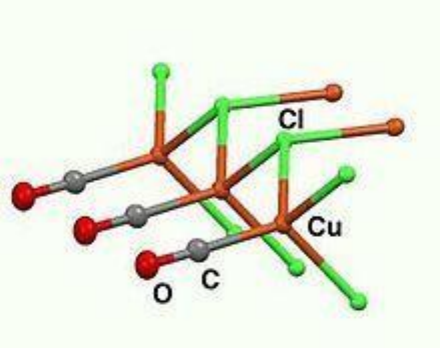
Organocopper compounds in organometallic chemistry contain carbon to copper chemical bonds. **Organocopper chemistry** is the science of organocopper compounds describing their physical properties, synthesis and reactions. They are reagents in organic chemistry.

The first organocopper compound, the explosive copper(I) acetylide Cu_2C_2 (Cu-C≡C-Cu), was synthesized by Rudolf Christian Böttger in 1859 by passing acetylene gas through copper(I) chloride solution:[4]

$$C_2H_2 + 2\ CuCl \rightarrow Cu_2C_2 + 2\ HCl$$

Simple complexes with CO, alkene, and Cp ligands:

Copper(I) salts have long been known to bind CO, albeit weakly. A representative complex is CuCl(CO), which is polymeric. In contrast to classical metal carbonyls, pi-backbonding is not strong in these compounds.



Part of the framework of CuCl(CO). In this coordination polymer, the Cu centers are tetrahedral linked by triply bridging chloride ligands.

Alkenes bind to copper(I), although again generally weakly. The binding of ethylene to Cu in proteins is of broad significance in plant biology so much so that ethylene is classified as a plant hormone. Its presence, detected by the Cu-protein, affects ripening and many other developments.

Although copper does not form a metallocene, half-sandwich complexes can be produced. One such derivative is (η-cyclopentadienyl triethylphosphine) copper.

Alkyl and aryl copper(I) compounds

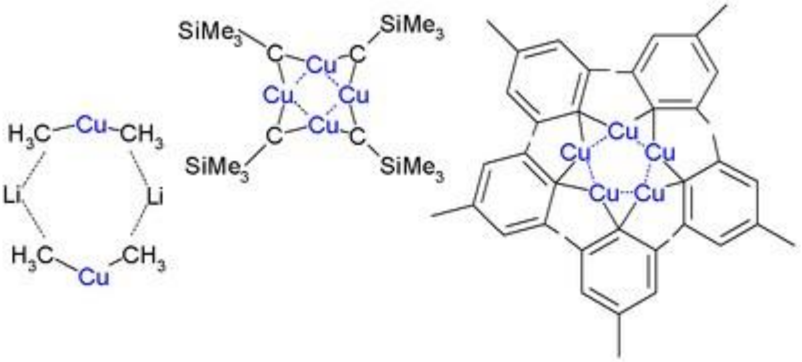
Copper halides react with organolithium reagents to give organocopper compounds. Thus, phenylcopper is prepared by reaction of phenyllithium with copper(I) bromide

in diethyl ether. Grignard reagents can be used in place of organolithium compounds. Gilman also investigated the dialkylcuprates. These are obtained by combining two equivalent of RLi with Cu(I) salts.
Alternatively, these cuprates are prepared from oligomeric neutral organocopper compounds by treatment with one equivalent of organolithium reagent.

Compounds of the type $[CuR_n]^{(n-1)-}$ are reactive towards oxygen and water, forming copper(I) oxide. They also tend to be thermally unstable, which can be useful in certain coupling reactions. Despite or because of these difficulties, organocopper reagents are frequently generated and consumed in situ with no attempt to isolate them. They are used in organic synthesis as alkylating reagents because they exhibit greater functional group tolerance than corresponding Grignard and organolithium reagents. The electronegativity of copper is much higher than its next-door neighbor in the group 12 elements, zinc, suggesting diminished nucleophilicity for its carbon ligands.

Copper salts react with terminal alkynes to form the acetylides.

Alkyl halides react with organocopper compounds with inversion of configuration. On the other hand, reactions of organocopper compound with alkenyl halides proceed with retention of subtrate's configuration.

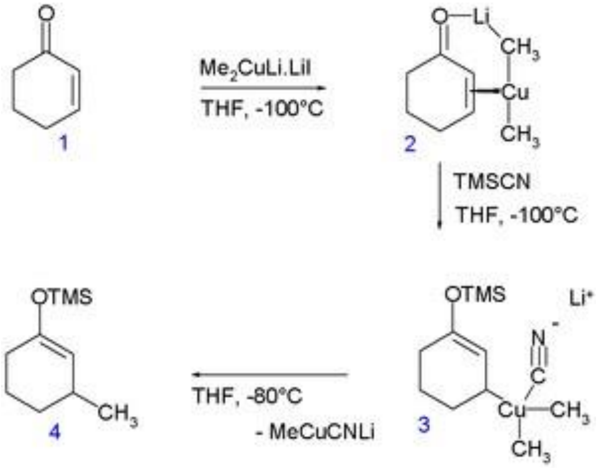


Lithium dimethylcuprate is a dimer in diethyl ether, forming an 8-membered ring with two lithium atoms linking two methyl groups. Similarly, lithium diphenylcuprate forms a dimeric etherate, [{Li(OEt2)}(CuPh2)]2, in the solid state.

Alkyl and aryl copper(III) compounds

The involvement of the otherwise rare Cu(III) oxidation state has been demonstrated in the conjugate addition of the Gilman reagent to an enone:[11] In a so-called rapidinjection NMR experiment at -100 °C, the Gilman reagent Me2CuLi (stabilized by lithium iodide) was introduced to cyclohexenone (**1**) enabling the detection of the copper — alkene pi complex **2**. On subsequent addition of trimethylsilyl cyanide the Cu(III) species **3** is formed (indefinitely stable at that temperature) and on increasing the temperature to -80 °C the conjugate addition product **4**.

According to an accompanying in silico experiments [12] the Cu(III) intermediate has



a square planar molecular geometry with the cyano group in cis orientation with respect to the cyclohexenyl methine group and anti-parallel to the methine proton. With other ligands than the cyano group this study predicts room temperature stable Cu(III) compounds.

Reactions of organocuprates:

Cross-coupling reactions

Prior to the development of palladium-catalyzed cross coupling reactions, copper was the preferred catalyst for almost a century. Palladium offers a faster, more selective reaction. However, in recent years copper has reemerged as a synthetically useful metal, because of its lower cost and because it is an eco-friendly metal.[13]

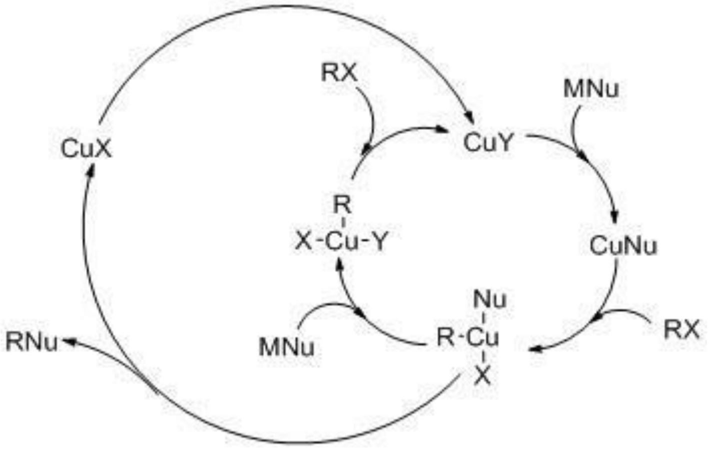
Reactions of R_2CuLi with alkyl halides R'-X give the coupling product:

$R_2CuLi + R'X \rightarrow R\text{-}R' + CuR + LiX$

The reaction mechanism involves oxidative addition (OA) of the alkyl halide to Cu(I), forming a planar Cu(III) intermediate, followed by reductive elimination (RE). The nucleophilic attack is the rate-determining step. In the substitution of iodide, a single-electron transfer mechanism is proposed.

Many electrophiles participate in this reaction. The approximate order of reactivity, beginning with the most reactive, is as follows: acid chlorides> aldehydes > tosylates ~ epoxides > iodides > bromides > chlorides > ketones > esters > nitriles >> alkenes

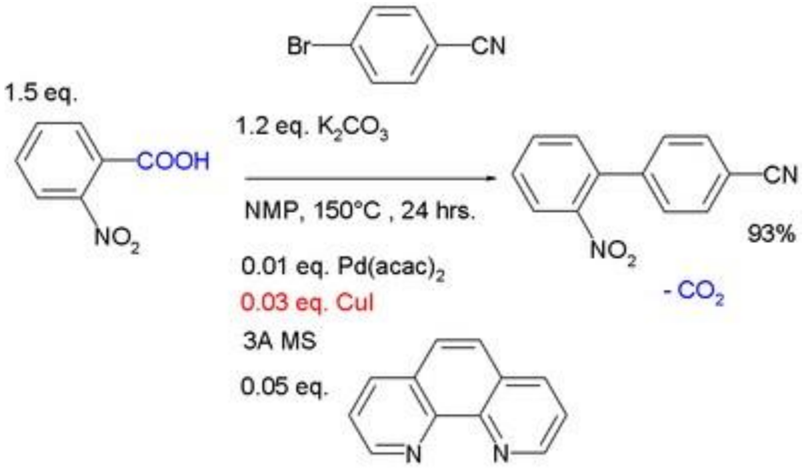
Generally the OA-RE mechanism is analogous to that of palladium-catalyzed cross coupling reactions. One difference between copper and palladium is that copper can undergo single-electron transfer processes.



Coupling reactions

Oxidative coupling is the coupling of copper acetylides to conjugated alkynes in the Glaser coupling (for example in the synthesis of cyclooctadecanonaene) or to aryl halides in the Castro-Stephens Coupling.

Reductive coupling is a coupling reaction of aryl halides with a stoichiometric equivalent of copper metal that occurs in the Ullmann reaction. In an example of a present-day cross coupling reaction called **decarboxylative coupling**, a catalytic amount of Cu(I) displaces a carboxyl group forming the arylcopper (ArCu) intermediate. Simultaneously, a palladium catalyst converts an aryl bromide to the organopalladium intermediate (Ar'PdBr), and on transmetallation the biaryl is formed from ArPdAr'.

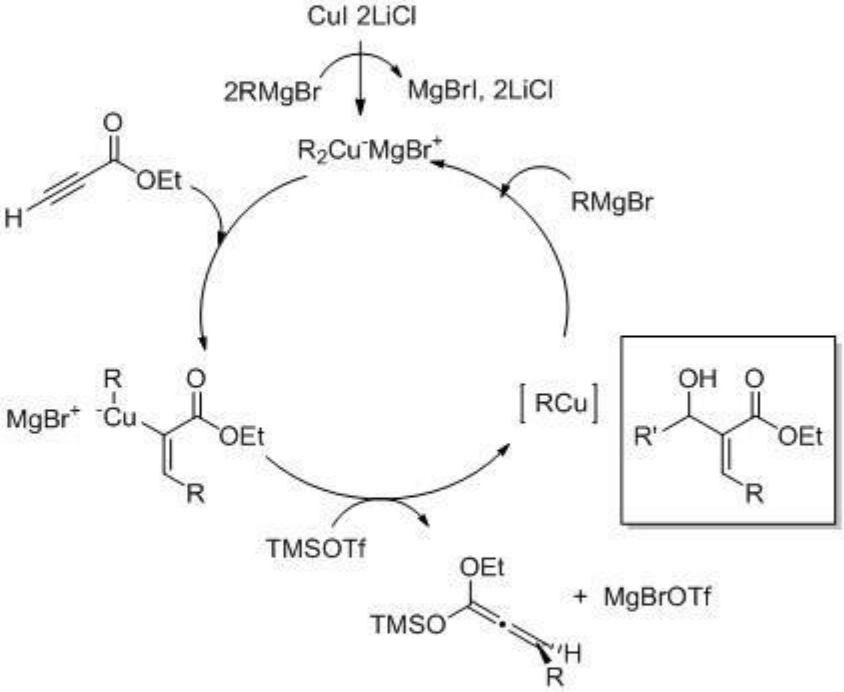


Redox neutral coupling is the coupling of terminal alkynes with halo-alkynes with a copper(I) salt in the Cadiot-Chodkiewicz coupling. Thermal coupling of two organocopper compounds is also possible.

Carbocupration

Carbocupration is a nucleophilic addition of organocopper reagents (R-Cu) to acetylene orterminal alkynes resulting in an alkenylcopper compound (RC=C-Cu). It is a special case ofcarbometalation and also called the **Normant reaction**.

Figure: Catalytic cycle for carbocupration for the Synthesis of Aldol, Baylis-Hillman



Type Products

Synthetic applications

- The Chan-Lam coupling enables the formation of aryl carbon-hetoroatom bonds. It involves coupling of boronic acids, stannanes, or siloxanes with NH- or OH-containing substrates.
- Ullmann reaction involves copper-mediated reactions of aryl halides. Two types of Ullmann reaction are recognized:
- Classic copper-promoted synthesis of symmetric biaryl compounds)
- Copper-promoted nucleophilic aromatic substitution.
- Sonogashira coupling reaction, which utilizes both copper and palladium, entails the coupling of aryl and/or vinyl halides with terminal alkynes.

ORGANOLEAD COMPOUND

Organolead compounds are chemical compounds containing a chemical bond between carbon and lead.

Organolead chemistry is the corresponding science. Sharing the same group with carbon, lead is tetravalent.

"Organolead compound" is a broad term for a class of molecules that contain both carbon and lead atoms directly bonded together. These organometallic compounds have diverse properties and applications, but also raise concerns about their environmental and health impacts.

Here's a breakdown of what you might be interested in:

General information:

- **Structure:** Organolead compounds have a lead atom central to the molecule, with organic groups (like alkyl or aryl) attached to it. The types of groups and their arrangement influence the compound's properties.
- **Examples:** Tetramethyllead ($Pb(CH3)4$) and tetraethyllead ($Pb(C2H5)4$) were once widely used as antiknock agents in gasoline, but are now banned in many countries due to their toxicity. Other organolead compounds find uses in lubricants, pesticides, and even medicine.
- **Properties:** These compounds vary in their physical and chemical characteristics. Some are liquids, while others are solids. They are generally lipophilic (fat-soluble) and can be persistent in the environment.

Environmental and health concerns:

- **Toxicity:** Lead is a toxic element, and exposure to organolead compounds can be harmful to humans and wildlife. These compounds can affect the nervous system, kidneys, and other organs.
- **Environmental persistence:** Due to their lipophilic nature, organolead compounds can bioaccumulate in food chains, posing risks to organisms higher up the chain.
- **Regulations:** Due to their harmful effects, many countries have restricted or banned the use of certain organolead compounds, particularly tetraethyllead in gasoline.

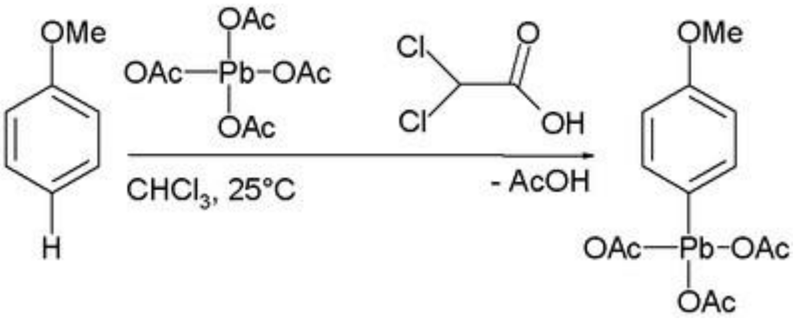
Research and development:

- **Alternatives:** Scientists are researching and developing safer alternatives to organolead compounds for various applications.
- **Remediation:** Methods are being investigated to clean up environments contaminated with organolead compounds.

Synthesis

Organolead compounds can be derived from Grignard reagents and lead chloride. For example, methylmagnesium chloride reacts with lead chloride to tetramethyllead, a water-clear liquid with boiling point 110 °C and density 1.995 g/cm^3. Reaction of a lead(II) source with sodium cyclopentadienide gives the lead metallocene, plumbocene.

Certain arene compounds react directly with lead tetraacetate to aryl lead compounds in an electrophilic aromatic substitution. For instance anisole with lead tetraacetate forms 'p- methoxyphenyllead triacetate in chloroform and dichloroacetic acid:



Other compounds of lead are organolead halides of the type $R_nPbX_{(4-n)}$, organolead sulfinates ($R_nPb(OSOR)_{(4-n)}$) and organolead hydroxides ($R_nPb(OH)_{(4-n)}$). Typical reactions are:

$R_4Pb + HCl \rightarrow R_3PbCl + RH R_4Pb + SO_2 \rightarrow R_3PbO(SO)R$
$R_3PbCl + 1/2Ag_2O \text{ (aq)} \rightarrow R_3PbOH + AgCl R_2PbCl_2 + 2\ OH^- \rightarrow R_2Pb(OH)_2 + 2\ Cl^-$

$R_2Pb(OH)_2$ compounds are amphoteric. At pH lower than 8 they form R_2Pb^{2+} ions and with pH higher than 10, $R_2Pb(OH)_3^-$ ions.

Derived from the hydroxides are the plumboxanes:

$2\ R_3PbOH + Na \rightarrow (R_3Pb)_2O + NaOH + 1/2\ H_2$

which give access to polymeric alkoxides:

$(R_3Pb)_2O + R'OH \rightarrow 1/n\ (R_3PbOR')_n - n\ H_2O$

Reactions

The C–Pb bond is weak and for this reason homolytic cleavage of organolead compounds to free radicals is easy. In its anti-knocking capacity, its purpose is that of a radical initiator. General reaction types of aryl and vinyl organoleads are transmetalation for instance with boronic acids and acid-catalyzed heterocyclic cleavage. Organoleads find use in coupling reactions between arene compounds. They are more reactive than the likewise organotins and can therefore be used to synthesise sterically crowded biaryls.

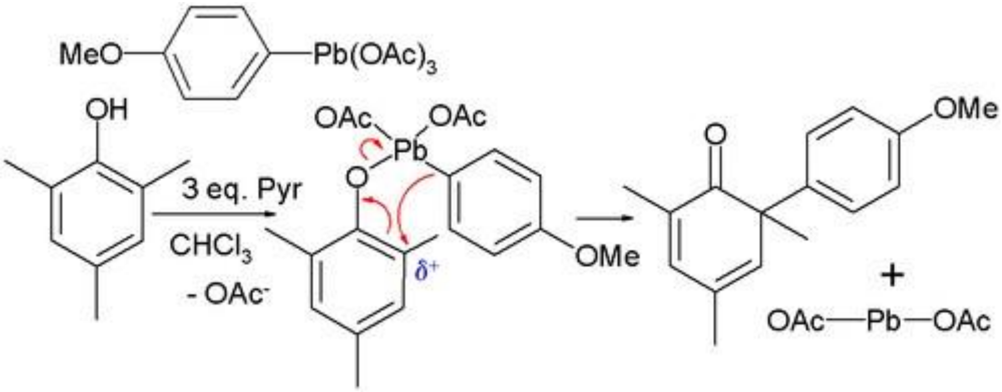
In **oxyplumbation**, organolead alkoxides are added to polar alkenes:

$H_2C{=}CH\text{-}CN + (Et_3PbOMe)_n \rightarrow MeO\text{-}CH_2\text{-}HC(PbEt_3)\text{-}CN \rightarrow MeO\text{-}CH_2\text{-}CH_2\text{-}CN$

The alkoxide is regenerated in the subsequent methanolysis and, therefore, acts as a catalyst.

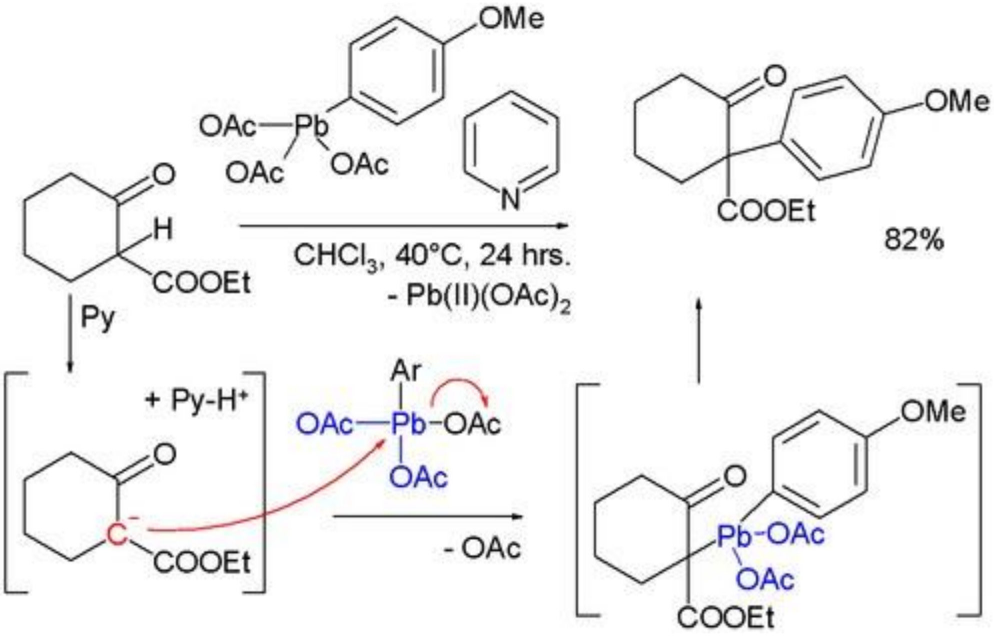
Aryllead triacetates

The lead substituent in *p*-methoxyphenyllead triacetate is displaced by carbon nucleophiles, such as the phenol mesitol, exclusively at the aromatic ortho position:[5]



The reaction requires the presence of a large excess of a coordinating amine such as pyridine which presumably binds to lead in the course of the reaction. The reaction is insensitive to radical scavengers and therefore a free radical mechanism can be ruled out. The reaction mechanism is likely to involve nucleophilic displacement of an acetate group by the phenolic group to a diorganolead intermediate which in some related reactions can be isolated. The second step is then akin to a Claisen rearrangement except that the reaction depends on the electrophilicity (hence the ortho preference) of the phenol.

The nucleophile can also be the carbanion of a β-dicarbonyl compound:



The carbanion forms by proton abstraction of the acidic α-proton by pyridine (now serving a double role) akin to the Knoevenagel condensation. This intermediate displaces an acetate ligand to a diorganolead compound and again these intermediates can be isolated with suitable reactants as unstable intermediates. The second step is reductive elimination with formation of a new C–C bond and lead(II) acetate.

Organophosphorus compound

organophosphorus compounds are a diverse group of organic chemicals that contain phosphorus-carbon bonds. They have a wide range of applications, including:

- **Insecticides:** Organophosphorus compounds are some of the most effective insecticides available. They work by inhibiting the enzyme acetylcholinesterase, which is essential for nerve function in insects. Common examples of organophosphorus insecticides include malathion, parathion, and diazinon.

Nerve agents: Some organophosphorus compounds are highly toxic and can be used as nerve agents. These compounds work in the same way as insecticides, but they are much more potent and can be fatal to humans. Examples of nerve agents include sarin, VX, and tabun.

- **Flame retardants:** Organophosphorus compounds are also used as flame retardants in plastics, textiles, and other materials. They work by breaking down the chains of polymers in the material, which prevents the spread of fire.
- **Plasticizers:** Organophosphorus compounds can also be used as plasticizers, which are additives that make plastics more flexible and durable.
- **Lubricants:** Some organophosphorus compounds are used as lubricants in engines and other machinery.
- **Medicines:** A few organophosphorus compounds are used as medicines. For example, echothiophate is used to treat glaucoma.

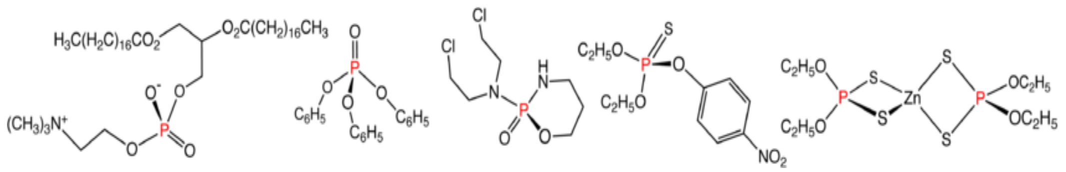
The use of organophosphorus compounds is controversial because they can be toxic to humans and the environment. However, they are also very effective in many applications, and there is no easy replacement for them in some cases.

Organophosphorus compounds are organic compounds containing phosphorus. They are used primarily in pest control as an alternative to chlorinated hydrocarbons that persist in the environment. Some organophosphorus compounds are highly effective insecticides, although some are extremely toxic to humans, including sarin and VX nerve agents.

Organophosphorus(V) compounds, main categories

Phosphate esters and amides

Phosphate esters have the general structure P(=O)(OR)3 feature P(V). Such species are of technological importance as flame retardant agents, and plasticizers. Lacking a P−C bond, these compounds are in the technical sense not organophosphorus compounds but esters of phosphoric acid. Many derivatives are found in nature, such as phosphatidylcholine. Phosphate ester are synthesized by alcoholysis of phosphorus oxychloride. A variety of mixed amido-alkoxo derivatives are known, one medically significant example being the anti-cancer drug cyclophosphamide. Also derivatives containing the thiophosphoryl group (P=S) include the pesticide malathion. The organophosphates prepared on the largest scale are the zinc dithiophosphates, as additives for motor oil. Several million kilograms of this coordination complex are produced annually by the reaction of phosphorus pentasulfide with alcohols.[6]



Illustrative organophosphates and related compounds: phosphatidylcholine, triphenylphosphate, cyclophosphamide, parathion, and zinc dithiophosphate.

Phosphine oxides, imides, and chalcogenides

Phosphine oxides (designation $\sigma^4\lambda^5$) have the general structure R3P=O with formal oxidation state
V. Phosphine oxides form hydrogen bonds and some are therefore soluble in water. The P=O bond is very polar with a dipole moment of 4.51 D for triphenylphosphine oxide.
Compounds related to phosphine oxides include phosphine imides (R3PNR') and related chalcogenides (R3PE, where E = S, Se, Te). These compounds are some of the most thermally stable organophosphorus compounds.

Phosphonium salts and phosphoranes

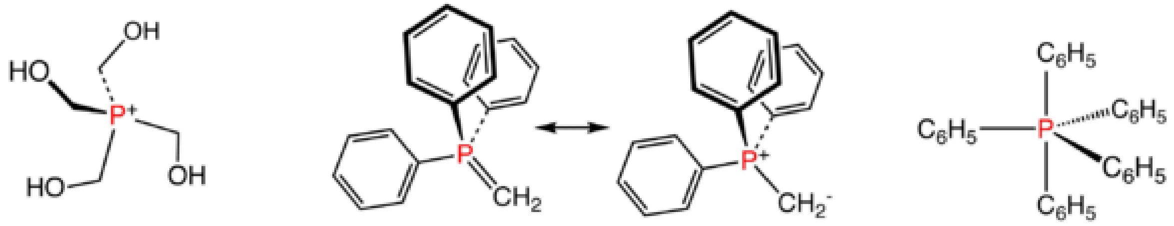
Compounds with the formula $[PR4^{+}]X^{-}$ comprise the phosphonium salts. These species are tetrahedral phosphorus(V) compounds. From the commercial perspective, the most important member is tetrakis(hydroxymethyl)phosphonium chloride, $[P(CH_2OH)_4]Cl$, which is used as a fire retardant in textiles. Approximately 2M kg are produced annually of the chloride and the related sulfate.[6] They are generated by the reaction of phosphine with formaldehyde in the presence of the mineral acid:

$$PH_3 + HX + 4\ CH_2O \rightarrow [P(CH_2OH)\ ^{+}]X^{-}$$

A variety of phosphonium salts can be prepared by alkylation and arylation of organophosphines:

$$PR_3 + R'X \rightarrow [PR_3R'^{+}]X^{-}$$

The methylation of triphenylphosphine is the first step in the preparation of the Wittig reagent.



Illustrative phosphorus(V) compounds: the phosphonium ion $P(CH_2OH)_4^{+}$, two resonance structures for the Wittig reagent Ph_3PCH_2, and pentaphenylphosphorane, a rare pentaorganophophorus compound.

The parent phosphorane ($\sigma^5\lambda^5$) is PH_5, which is unknown. Related compounds containing both halide and organic substituents on phosphorus are fairly common. Those with five organic substituents are rare, although $P(C_6H_5)_5$ is known, being derived from $P(C_6H_5)_4^{+}$ by reaction with phenyllithium.

Phosphorus ylides are unsaturated phosphoranes, known as Wittig reagents, e.g. $CH_2P(C_6H_5)_3$. These compounds feature tetrahedral phosphorus(V) and are considered relatives of phosphine oxides. They also are derived from phosphonium salts, but by deprotonation not alkylation.

Organophosphorus(III) compounds, main categories

Phosphites, phosphonites, and phosphinites

Phosphites, sometimes called phosphite esters, have the general structure $P(OR)_3$ with oxidation state +3. Such species arise from the alcoholysis of phosphorus trichloride:

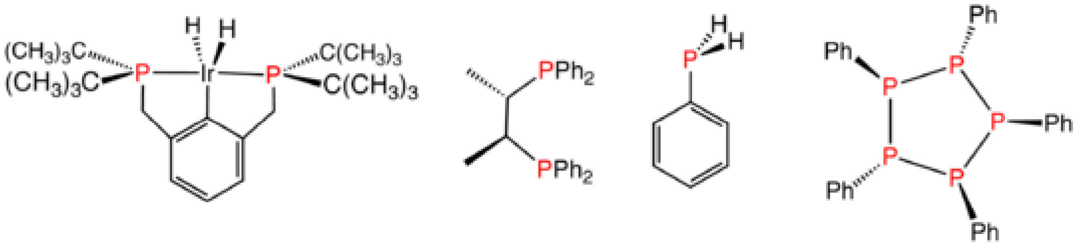
$$PCl_3 + 3\,ROH \rightarrow P(OR)_3 + 3\,HCl$$

The reaction is general, thus a vast number of such species are known. Phosphites are employed in the Perkow reaction and the Michaelis–Arbuzov reaction. They also serve as ligands in organometallic chemistry.

Intermediate between phosphites and phosphines are phosphonites ($P(OR)_2R'$) and phosphinite ($P(OR)R'_2$). Such species arise via alcoholysis reactions of the corresponding phosphinous and phosphonous chlorides (($PClR'_2$) and PCl_2R', respectively).

Phosphines

The parent compound of the phosphines is PH_3, called phosphine in the US and British Commonwealth, but phosphane elsewhere. Replacement of one or more hydrogen centers by an organic substituents (alkyl, aryl), gives $PH_{3-x}R_x$, an organophosphine, generally referred to as phosphines.



Various reduced organophosphorus compounds: a complex of an organophosphine pincer ligand, the chiral diphosphine used in homogeneous catalysis, the primary phosphine $PhPH_2$, and the phosphorus(I) compound $(PPh)_5$. Reactions

Organophosphines are nucleophiles and ligands. Two major applications are as reagents in the Wittig reaction and as supporting phosphine ligands in homogeneous catalysis.

Their nucleophilicity is evidenced by their reactions with alkyl halides to give phosphonium salts. Phosphines are nucleophilic catalysts in organic synthesis, e.g. the Rauhut–Currier reaction and Baylis-Hillman reaction.

Phosphines are reducing agents, as illustrated in the Staudinger reduction for the conversion of organic azides to amines and in the Mitsunobu reaction for converting alcohols into esters. In these processes, the phosphine is oxidized to phosphorus(V). Phosphines have also been found to reduce activated carbonyl groups, for instance the reduction of an α-keto ester to an α-hydroxy ester in *scheme 2*. In the proposed reaction mechanism, the first proton is on loan from the methyl group in trimethylphosphine (triphenylphosphine does not react).

Primary and secondary phosphines

In addition to the other reactions associated with phosphines, those bearing P-H groups exhibit additional reactivity associated with the P-H bonds. They are readily deprotonated using strong bases to give phosphide anions. Primary and secondary phosphines are generally prepared by reduction of related phosphorus halides or esters.

Phosphaalkenes and phosphaalkynes

Compounds with carbon phosphorus(III) multiple bonds are called phosphaalkenes ($R_2C=PR$) and phosphaalkynes ($RC\equiv P$). They are similar in structure, but not in reactivity, to imines ($R_2C=NR$) and nitriles ($RC\equiv N$), respectively. In the compound phosphorine, one carbon atom in benzene is replaced by phosphorus. Species of this type are relatively rare but for that reason are of interest to researchers. A general method for the synthesis of phosphaalkenes is by 1,2-elimination of suitable precursors, initiated thermally or by base such as DBU, DABCO, or triethylamine.

Organophosphorus(0), (I), and (II) compounds

Compounds where phosphorus exists in a formal oxidation state of less than III are uncommon, but examples are known for each class. Organophosphorus(0) species are debatably illustrated by the carbene adducts, $[P(NHC)]_2$, where NHC is an N-heterocyclic carbene. With the formulae $(RP)_n$ and $(R_2P)_2$, respectively, compounds of phosphorus(I) and (II) are generated by reduction of the related organophosphorus(III) chlorides:

$$5\ PhPCl_2 + 5\ Mg \rightarrow (PhP)_5 + 5\ MgCl_2$$

$$2\ Ph_2PCl + Mg \rightarrow Ph_2P\text{-}PPh_2 + MgCl_2$$

Diphosphenes, with the formula R_2P_2, formally contain phosphorus-phosphorus double bonds. These phosphorus(I) species are rare but are stable provided that the organic substituents are large enough to prevent catenation. Many mixed-valence compounds are known, e.g. the cage $P_7(CH_3)_3$.

ORGANOBORON COMPOUND

Organoborane or **organoboron** compounds are chemical compounds of boron and carbon that are organic derivatives of BH_3, for example trialkyl boranes. **Organoboron chemistry** or **organoborane chemistry** is the chemistry of these compounds. Organoboron compounds are important reagents in organic chemistry enabling many chemical transformations, the most important one called hydroboration.

preparation

From Grignard reagents

Simple organoboranes such as triethylborane or tris(pentafluorophenyl)boron can be prepared from trifluoroborane (as the ether complex) and the ethyl or pentafluorophenyl Grignard reagent. The borates (R_4B^- are generated via addition of R^--equivalents (RMgX, RLi, etc.) to R_3B).

From alkenes

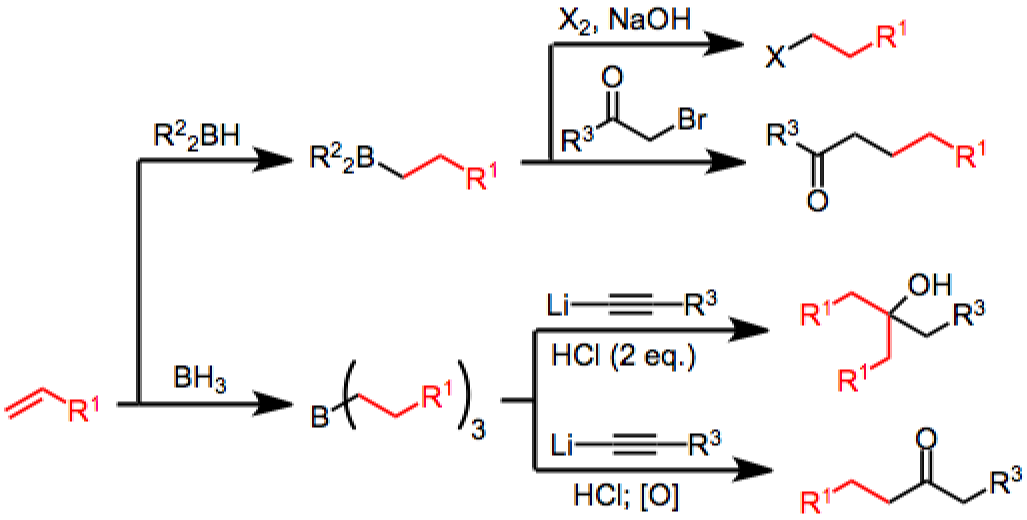
Alkenes insert into B-H bonds of boranes in a process called hydroboration. The process involves anti-Markovnikov addition. Hydroboration of alkenes or alkynes with borane (BH_3) or borane equivalents leads to the conversion of only 33% of the starting olefin to product after oxidation or protonolysis—the remaining olefin is incorporated into boron-containing byproducts. One organoboron reagent that is often employed in synthesis is 9-BBN. Hydroborations take place stereospecifically in a *syn* mode, that is on the same face of the alkene. In this concerted reaction the transition state is represented as a square with the corners occupied by carbon, carbon, hydrogen and boron with maximum overlap between the two olefin p-orbitals and the empty boron orbital.

By borylation

Metal-catalyzed C-H Borylation reactions are transition metal catalyzed organic reactions that produce an organoboron compound through functionalization of aliphatic and aromatic C-H bonds. A common reagent in this type of reaction is bis(pinacolato)diboron.

Reactions

Boron–carbon bonds are polarized toward carbon. Thus, the carbon attached to boron is nucleophilic. This property is harnessed to transfer one of the R groups to an electrophilic center either inter- or (more often) intramolecularly. In the latter case, the nucleophilic R group is able to undergo 1,2-migration towards an electrophilic carbon attached to boron. The resulting reorganized borane can then be oxidized or subjected to protonolysis to afford organic products:

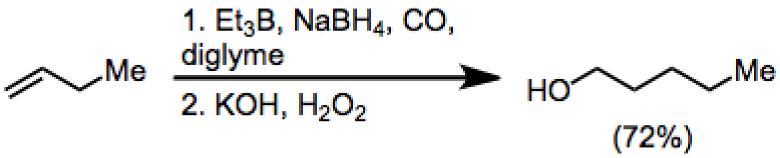


Hydroboration-oxidation

In organic synthesis the hydroboration reaction is taken further to generate other functional groups in the place of the boron group. The hydroboration-oxidation reaction offers a route to alcohols by oxidation of the borane with hydrogen peroxide or to the carbonyl group with the stronger oxidizing agent chromium oxide.

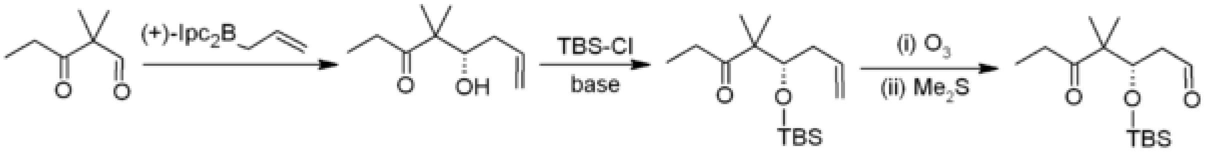
Rearrangements

Carbon monoxide is found to react with trialkylboranes. What follows is a 1,2-rearrangement whereby an alkyl substituent migrates from boron to the carbon of the carbonyl group. Homologated primary alcohols result from the treatment of organoboranes with carbon monoxide and a hydride.



Allylboration

Asymmetric allylboration demonstrates another useful application of organoboranes in carbon– carbon bond formation. In this example from Nicolaou's synthesis of the epothilones, asymmetricallylboration (using an allylborane derived from chiral alpha-pinene) is used in conjunction with TBS protection and ozonolysis. Overall, this provides a two-carbon homologation sequence that delivers the required acetogenin sequence.



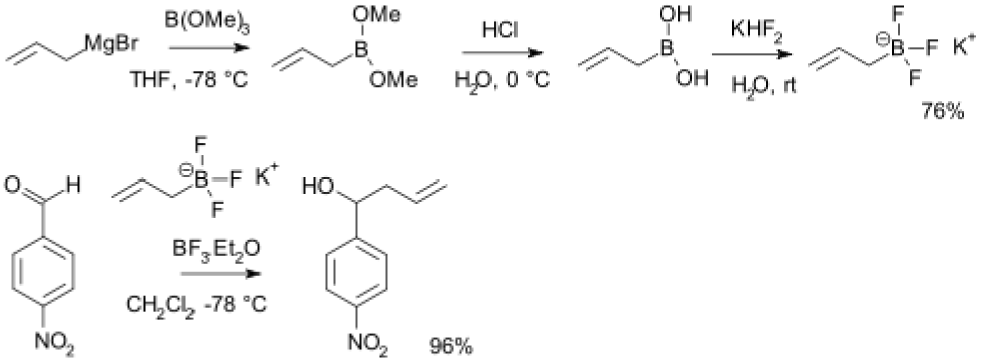
As reducing agent

Borane hydrides such as 9-BBN and L-selectride (lithium tri-sec-butylborohydride) are reducing agents. An example of an asymmetric catalyst for carbonyl reductions is the CBS catalyst. This catalyst is also based on boron, the purpose of which is coordination to the carbonyl oxygen atom.

Borates

Trialkylboranes, BR3, can be oxidized to the corresponding borates, B(OR)3. One method for the determination of the amount of C-B bonds in a compound is by oxidation of R3B with trimethylamine oxide (Me3NO) to B(OR)3. The trimethylamine (Me3N) formed can then be titrated.

Boronic acids RB(OH)2 react with potassium bifluoride K[HF2] to form trifluoroborate salts K[RBF3] which are precursors to nucleophilic alkyl and aryl boron difluorides, ArBF2. The salts are more stable than the boronic acids themselves and used for instance in alkylation of certain aldehydes:

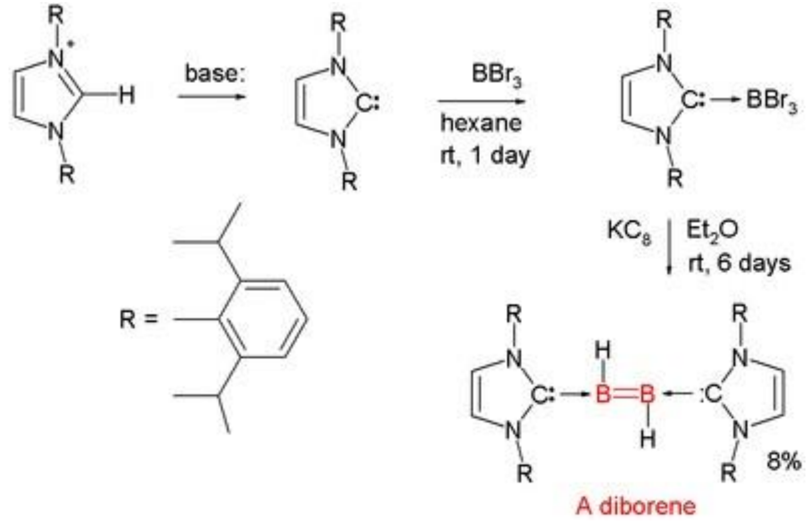


Suzuki reaction and related reactions

Organoboron compounds also lend themselves to transmetalation reactions, especially with organopalladium compounds. This reaction type is exemplified in the Suzuki reaction, which involves coupling of aryl- or vinyl-boronic acid with an aryl- or vinyl-halide catalyzed by a palladium(0) complex.

Diborenes

Chemical compounds with boron to boron double bonds are rare.. Each boron atom has a proton attached to it and each boron atom is coordinated to a NHC carbene. The parent structure with the additional carbene ligands is diborane(2).



A reported diboryne is based on similar chemistry.

Uses:

Organic Synthesis:

- **Hydroboration-Oxidation:** A versatile reaction that adds a boron atom and a hydrogen atom across an alkene double bond, followed by oxidation to produce alcohols. It's highly regioselective and anti-Markovnikov, meaning the hydrogen atom attaches to the more substituted carbon atom.
- **Suzuki Coupling:** A widely used cross-coupling reaction that forms carbon-carbon bonds between an aryl or vinyl boronic acid and an aryl or vinyl halide. It's valuable for creating complex organic molecules.

- **Petasis Reaction:** Forms carbon-carbon bonds between a boronic acid and an amine, often used to construct amine-containing heterocycles.
- **Boronic Esters as Protecting Groups:** Boronic esters can reversibly protect diols or 1,2-diols in carbohydrate chemistry under mild conditions.

Polymer Science:

- **Initiator Systems for Adhesives:** Organoboron compounds can initiate polymerization in acrylic adhesives, allowing them to bond challenging substrates like low-energy plastics.
- **Functional Polymers:** Boron-containing polymers can have unique properties like luminescence, self-healing, and stimuli-responsiveness.

Medicine:

- **Antibacterial and Antiparasitic Agents:** Some organoboron compounds exhibit antibacterial, antifungal, antimalarial, and antiparasitic activity, making them potential drug candidates.
- **Boron Neutron Capture Therapy (BNCT):** This cancer treatment involves using boron-10-containing compounds that selectively accumulate in tumor cells. When irradiated with neutrons, boron-10 undergoes fission, releasing alpha particles that destroy the tumor cells.
- **Carbohydrate Recognition:** Boronic acids can reversibly bind to diol-containing molecules like carbohydrates, making them useful for various applications, including:
  - Blood glucose monitoring
  - Affinity chromatography
  - Drug delivery

Other Uses:

- **Organic Light-Emitting Diodes (OLEDs):** Boron-containing compounds can be used as efficient emitters in OLEDs.
- **Catalysts for Organic Reactions:** Organoboron compounds can act as catalysts in various organic reactions, such as oxidations, reductions, and cross-couplings.
- **Supramolecular Chemistry:** Boronic acids can form reversible bonds with diols, enabling the construction of self-assembled structures and materials.

UNIT III

CHEMISTRY OF ALCOHOLS, PHENOLS AND ETHERS

Nomenclature:

Alcohols are organic compounds in which a hydrogen atom of an aliphatic carbon is replaced with a hydroxyl group. Thus an alcohol molecule consists of two parts; one containing the alkyl group and the other containing functional group hydroxyl group.

Individual sources of different types of alcohols:

- **Ethanol:** This is the alcohol found in alcoholic beverages and is mainly produced through the fermentation of sugars by yeasts. Common sources include grains like barley, corn, wheat, and rice, as well as fruits like grapes and berries.
- **Methanol:** This is a toxic alcohol often used in industrial applications. It can be found naturally in some fruits and vegetables, but its main source is the production of wood pulp and biodiesel.
- **Isopropyl alcohol:** This is a common rubbing alcohol with antiseptic properties. It is primarily produced synthetically from petroleum.
- **Other alcohols:** A vast array of other alcohols exist, each with its unique properties and uses. These can be derived from various sources, including:
  - **Natural:** Fruits, vegetables, plants, and even animal tissues can contain different types of alcohols, often in small amounts.
  - **Synthetic:** Many alcohols are produced in chemical labs through various processes like fermentation, oxidation, and reduction.

2. Individual person as a source of alcohol:

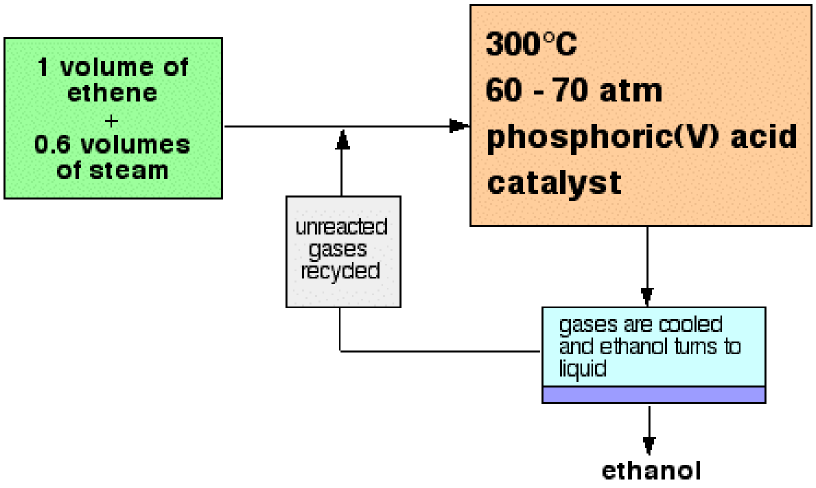
- **Alcoholic beverages:** Individuals can obtain alcohol through consuming alcoholic beverages, such as beer, wine, liquor, and cocktails.
- **Overripe fruits:** Some overripe fruits can naturally ferment and produce small amounts of alcohol.
- **Medications:** Certain medications may contain alcohol as an inactive ingredient.

Source of Alcohols:

Ethanol is manufactured by reacting ethene with steam. The catalyst used is solid silicon dioxide coated with phosphoric(V) acid. The reaction is reversible.

$$H_2C{=}CH_2(g) + H_2O(g) \xrightleftharpoons{H_3PO_4} CH_3CH_2OH(g)$$

Only 5% of the ethene is converted into ethanol at each pass through the reactor. By removing the ethanol from the equilibrium mixture and recycling the ethene, it is possible to achieve an overall 95% conversion. A flow scheme for the reaction looks like this:



PREPARATION OF ALCOHOLS

Hydration of Alkenes: Hydration of alkenes refers to the process of adding water (H_2O) to a carbon-carbon double bond in an alkene molecule. This reaction results in the formation of an alcohol. It's a fundamental reaction in organic chemistry with various applications in producing different types of alcohols.

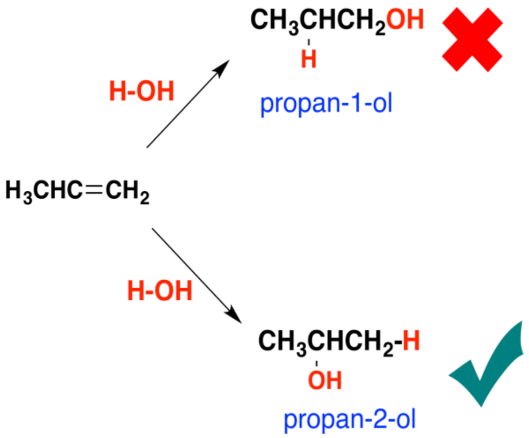
To understand hydration of alkenes better, I need more information about what you'd like to know specifically. Here are some options:

1. **The mechanism of hydration:** I can explain the stepwise process of how water adds to the alkene, including the role of acid catalysts and the formation of a carbocation intermediate.

2. **Regioselectivity in hydration:** Markovnikov's rule predicts which carbon atom in the alkene will bond with the hydroxyl group (OH) from water. I can explain this rule and its limitations.
3. **Factors affecting the rate of hydration:** Temperature, concentration of acid catalyst, and the type of alkene all influence the reaction rate. I can discuss these factors and their effects.
4. **Applications of alkene hydration:** This reaction is used to produce various alcohols, including ethanol, propanol, and butanol. I can provide examples of these applications and their importance.

The manufacture of other alcohols from alkenes

Some - but not all - other alcohols can be made by similar reactions. The catalyst used and the reaction conditions will vary from alcohol to alcohol. The reason that there is a problem with some alcohols is well illustrated with trying to make an alcohol from propene, CH3CH=CH2. In principle, there are two different alcohols which might be formed:



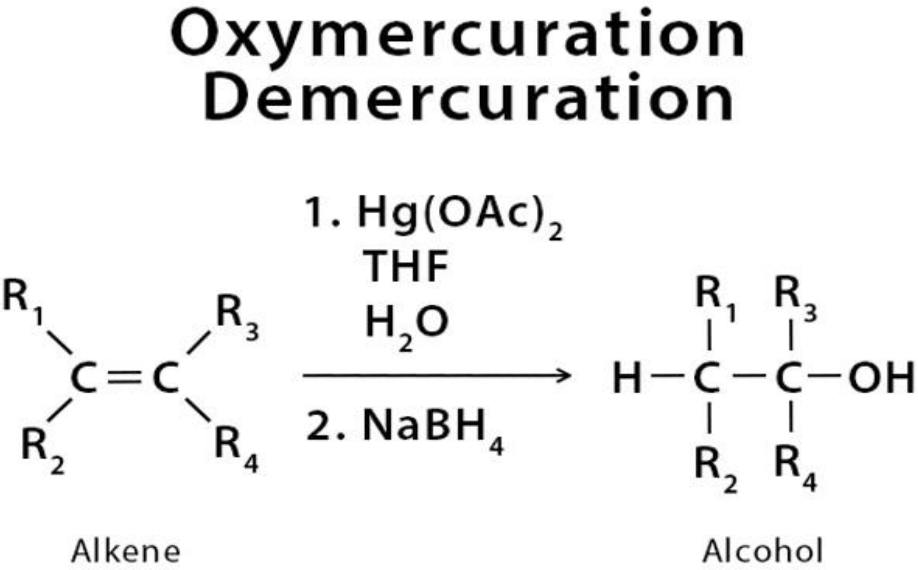
OXYMERCURATION:

Oxymercuration: Adding water to alkenes with a twist

Oxymercuration is a nifty organic chemistry reaction that converts alkenes (molecules with a double bond between carbon atoms) into alcohols (molecules with a hydroxyl group, -OH). It's unique because it offers distinct advantages over direct hydration and other methods. Here's the lowdown:

The Basic Process:

1. **Addition:** We start with an alkene and mix it with mercury(II) acetate (Hg(OAc)2) in a watery solution. This step involves mercury "grabbing" onto the alkene, forming a three-membered ring called a mercurinium ion.
2. **Water Attack:** Next, water comes to the party and attacks the mercurinium ion. It prefers the carbon with more substituents (following Markovnikov's rule), placing the hydroxyl group there and leaving the mercury on the other carbon.
3. **Demercuration:** Finally, we kick mercury out of the picture using a reducing agent like sodium borohydride (NaBH4). This leaves us with the final product: an alcohol with the hydroxyl group and hydrogen positioned trans to each other (anti-addition).



- **Markovnikov Regioselectivity:** Oxymercuration always delivers the alcohol regioisomer predicted by Markovnikov's rule. No carbocation rearrangements, like in direct hydration, mess with the outcome.
- **Anti-Stereoselectivity:** The hydroxyl and hydrogen groups end up on opposite sides of the molecule (anti-addition), offering control over the molecule's spatial arrangement.
- **Mild Conditions:** The reaction happens at room temperature and doesn't require harsh reagents, making it gentle on sensitive molecules.

Applications:

- **Synthesis of Alcohols:** Oxymercuration provides a reliable route to various alcohols, especially when other methods might be troublesome due to competing reactions or unwanted rearrangements.
- **Synthesis of Ethers:** By substituting water with alcohols in the second step, you can introduce different groups on the carbon instead of a hydroxyl, leading to ethers.
- **Control of Stereochemistry:** The anti-selectivity can be valuable in synthesizing molecules with specific spatial arrangements.

Limitations:

- **Mercury Toxicity:** Mercury compounds are hazardous and require careful handling and disposal. This raises environmental concerns and limits the widespread use of oxymercuration.
- **Alternatives Exist:** Other reactions like hydroboration-oxidation offer similar benefits without the mercury burden.

Overall, oxymercuration remains a valuable tool in the organic chemist's toolbox, especially for situations where controlled hydration and stereochemistry are crucial. However, its mercury dependence necessitates consideration of safer alternatives whenever possible.

Carbocation rearrangement is a process in which the carbocation intermediate can form a more stable ion. With carbocation rearrangement, the reaction would not be able to hydrate quickly under mild conditions and be produced in high yields. This reaction is very fast and proceeds with 90% yield.

This reaction involves a mercury acting as a reagent attacking the alkene double bond to form a *Mercurinium Ion Bridge*. A water molecule will then attack the most substituted carbon to open the mercurium ion bridge, followed by proton transfer to solvent water molecule.

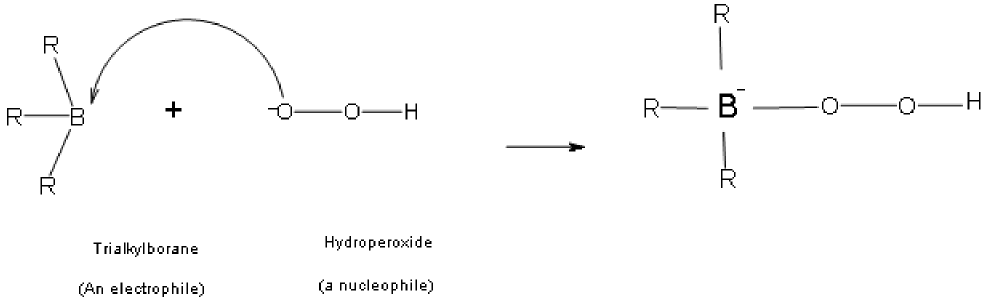
The organomercury intermediate is then reduced by sodium borohydride - the mechanism for this final step is beyond the scope of our discussion here. Notice that overall, the oxymercuration - demercuration mechanism follows Markovnikov's Regioselectivity with the OH group is attached to the most substituted carbon and the H is attach to the least substituted carbon. The reaction is useful, however, because strong acids are not required, and carbocation rearrangements are avoided because no discreet carbocation intermediate forms.

Hydroboration:

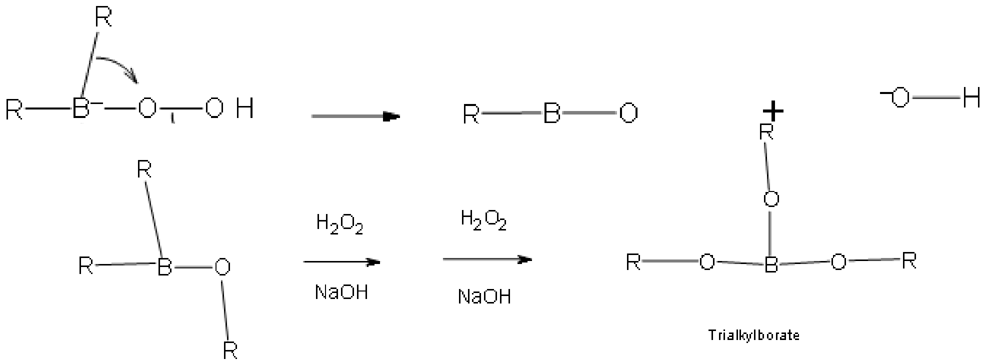
- Part 1: the first part of this mechanism deals with the donation of a pair of electrons from the hydrogen peroxide ion. the hydrogen peroxide is the nucleophile in this reaction because it is the electron donor to the newly formed trialkylborane that resulted from hydroboration.

$$\underset{\text{Hydrogen Peroxide}}{HOOH} + OH^- \longrightarrow \underset{\text{Hydrogen Peroxide ion}}{HOO^-} + HOH$$

Epoxidation



- Part 2: In this second part of the mechanism, a rearrangement of an R group with its pair of bonding electrons to an adjacent oxygen results in the removal of a hydroxide ion.



Two more of these reactions with hydroperoxide will occur in order give a trialkylborate

Part 3: This is the final part of the Oxidation process. In this part the trialkylborate reacts with aqueous NaOH to give the alcohol and sodium borate.

$$\underset{\text{Trialkylborate}}{(RO)_3B} + 3\,NaOH \longrightarrow 3\,ROH + \underset{\text{Sodium Borate}}{Na_3BO_3}$$

If you need additional visuals to aid you in understanding the mechanism, click on the outside links provided here that will take you to other pages and media that are very helpful as well.

Hydroboration-oxidation: A powerful route to alcohols

Hydroboration, followed by oxidation, is a versatile and widely used method for converting alkenes (containing a carbon-carbon double bond) into alcohols. It's a two-step process:

Step 1: Hydroboration:

- The alkene reacts with a borane (BH3) or a substituted borane (e.g., diborane, 9-BBN).
- The boron atom adds to the less substituted carbon of the double bond, while the hydrogen atom adds to the more substituted carbon. This is called anti-Markovnikov addition, as it goes against the usual Markovnikov rule.
- The result is an organoborane intermediate.

Step 2: Oxidation:

- The organoborane intermediate is treated with an oxidizing agent (e.g., hydrogen peroxide, alkaline sodium peroxide) to convert the boron-carbon bond into a hydroxyl group (-OH).
- This final step forms the desired alcohol product.

Key advantages of hydroboration-oxidation:

- **Regioselectivity:** The anti-Markovnikov addition ensures that the hydroxyl group ends up on the less substituted carbon, which can be valuable for controlling the properties of the alcohol product.
- **Stereospecificity:** The reaction is stereospecific, meaning that the starting material's stereochemistry is preserved in the final product. This can be crucial for synthesizing chiral alcohols.

- **Mild reaction conditions:** The reaction proceeds under mild conditions, making it suitable for sensitive functional groups.
- **Wide range of alkenes:** Various alkenes, including terminal, internal, and cyclic, can be readily converted to alcohols using this method.

Examples:

- Converting propene (CH3CH=CH2) to 1-propanol (CH3CH2CH2OH).
- Synthesizing cis-2-butanol from cis-2-butene.
- Preparing cyclohexanol from cyclohexene.

Limitations:

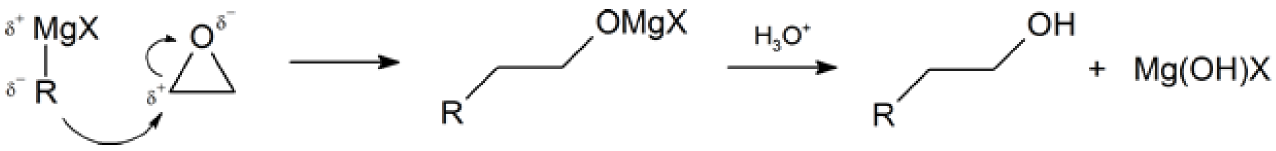
- Handling borane can be challenging due to its toxicity and flammability.
- Strong oxidants can lead to side reactions and overoxidation.
- Bulky substituents on the borane reagent may affect the reaction rate and selectivity.

GRIGNARD ADDITION:

Grignard reagents are among the most frequently used reagents in organic synthesis. They react with a wide variety of substrates; however, in this section, we are concerned only with those reactions that produce alcohols. Notice that in a reaction involving a Grignard reagent, not only does the functional group get changed, but the number of carbon atoms present also changes. This fact provides us with a useful method for ascending a homologous series. For example:

$$CH_3OH \xrightarrow{SOCl_2} CH_3Cl \xrightarrow[\text{ether}]{Mg} CH_3MgCl \xrightarrow[2.\ H_3O^+]{1.\ HCHO} CH_3CH_2OH$$

One important route for producing an alcohol from a Grignard reagent has been omitted from the discussion in the reading. It involves the reaction of the Grignard reagent with ethylene oxide to produce a primary alcohol containing two more carbon atoms than the original Grignard reagent.

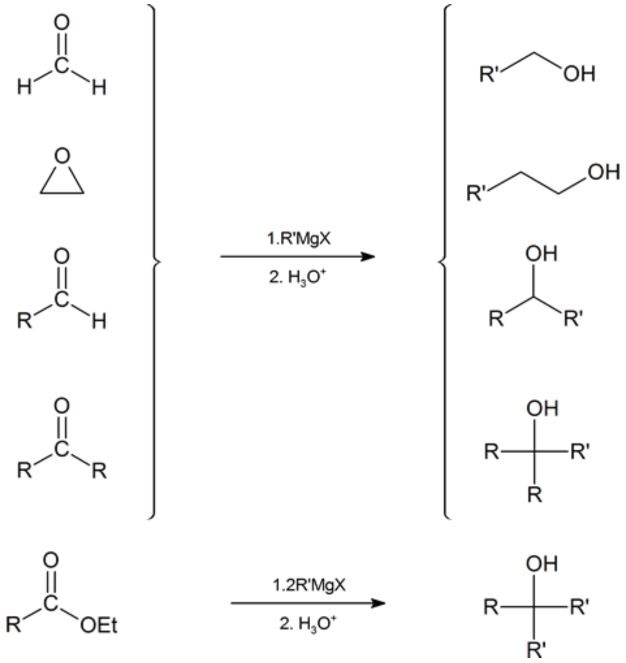


As mentioned in the reading, both organolithium and Grignard reagents are good nucleophiles.

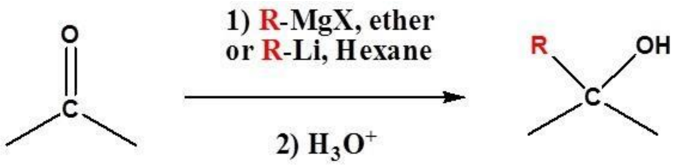
They also act as strong bases in the presence of acidic protons such as −CO2H, −OH, −SH, −NH and terminal alkyne groups. Not only do acidic protons interfere with the nucleophilic attack on the carbonyl of these organometallic reagents, if the starting materials possess any acidic protons, reagents cannot be generated in the first place. They are also the reason these reactions must be carried out in a water-free environment.

Another limitation of preparing Grignard and organolithium reagents is that they cannot already contain a carbonyl group (or other electrophilic multiple bonds like C=N C≡N, N=O S=O) because it would simply react with itself.

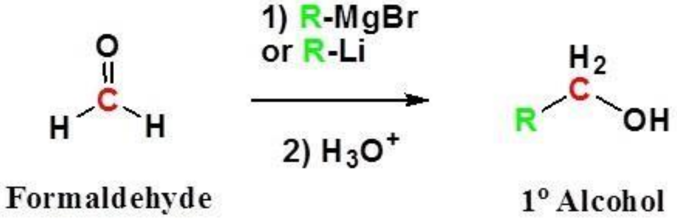
A summary of the methods used to prepare alcohols from Grignard reagents is provided below.



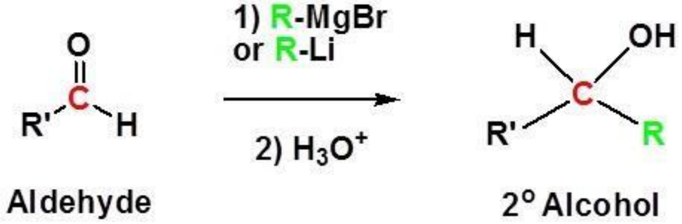
Because organometallic reagents react as their corresponding carbanion, they are excellent nucleophiles. The basic reaction involves the nucleophilic attack of the carbanionic carbon in the organometallic reagent with the electrophilic carbon in the carbonyl to form alcohols.



Both Grignard and Organolithium Reagents will perform these reactions. Addition to formaldehyde gives 1o alcohols



Addition to aldehydes gives 2° alcohols



Addition to ketones gives 3o alcohols

REDUCTION:

While Grignard reagents are not primarily known for their reducing ability, they can indeed participate in certain reduction reactions under specific circumstances. Here's a breakdown of their behavior:

Main Role:

- Grignard reagents are more renowned for their **nucleophilic additions to carbonyl compounds**, such as ketones and aldehydes, resulting in the formation of various alcohols.
- They also excel in **carbon-carbon bond formation reactions** via coupling with other organometallic species or electrophilic carbon centers.

Reduction Capabilities:

- Grignard reagents possess a weak hydride (H-) character due to the carbon-magnesium bond polarity. This hydride can transfer under specific conditions, leading to reduction.
- However, reduction is not their dominant pathway and often competes with other, more favored reactions like nucleophilic addition.

Types of Reduction with Grignard Reagents:

- **Reduction of certain carbonyl compounds:** Under specific conditions, like using bulky or hindered Grignard reagents and protic solvents, reduction of ketones to secondary alcohols can occur.
- **Pinakol coupling:** In the presence of catalytic Cu(I) salts, Grignard reagents can undergo self-coupling, leading to pinacol products (diols) with a new carbon-carbon bond formed. This can be seen as a reductive coupling process.
- **Reduction of metal ions:** Grignard reagents can act as reducing agents for certain metal ions like Cr(VI) to Cr(III) or Fe(III) to Fe(II).

Factors Affecting Reduction:

- **Grignard reagent structure:** Bulkier Grignard reagents favor reduction due to steric hindrance hindering other pathways.
- **Solvent:** Protic solvents like water or alcohols promote hydride transfer and reduction.
- **Temperature:** Lower temperatures tend to favor reduction over competing reactions.
- **Presence of catalysts:** Certain catalysts like Cu(I) salts can promote specific reduction pathways like pinakol coupling.

Conclusion:

While not their primary function, Grignard reagents can participate in reduction reactions under specific conditions. Understanding these scenarios and the influencing factors is crucial for effective synthetic planning involving these versatile reagents.

Feel free to ask if you have any further questions about specific reduction reactions or require additional details on the mechanisms involved.

The most common sources of the hydride Nucleophile are lithium aluminum hydride (LiAlH4) and sodium borohydride (NaBH4). Note! The hydride anion is not present during this reaction; rather, these reagents serve as a source of hydride due to the presence of a polar metal-hydrogen bond.
Because aluminum is less electronegative than boron, the Al-H bond in LiAlH4 is more polar, thereby, making LiAlH4 a stronger reducing agent.

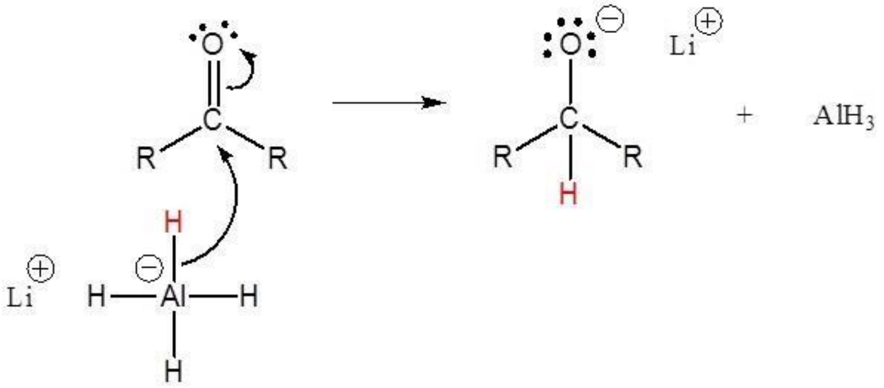
Addition of a hydride anion ($H:^-$) to an aldehyde or ketone gives an alkoxide anion, which on protonation yields the corresponding alcohol. Aldehydes produce 1°-alcohols and ketones produce 2°-alcohols.

In metal hydrides reductions the resulting alkoxide salts are insoluble and need to be hydrolyzed (with care) before the alcohol product can be isolated. In the sodium borohydride reduction the methanol solvent system achieves this hydrolysis automatically. In the lithium aluminum hydride reduction water is usually added in a second step. The lithium, sodium, boron and aluminum end up as soluble inorganic salts at the end of either reaction. Note! LiAlH4 and NaBH4 are both capable of reducing aldehydes and ketones to the corresponding alcohol.

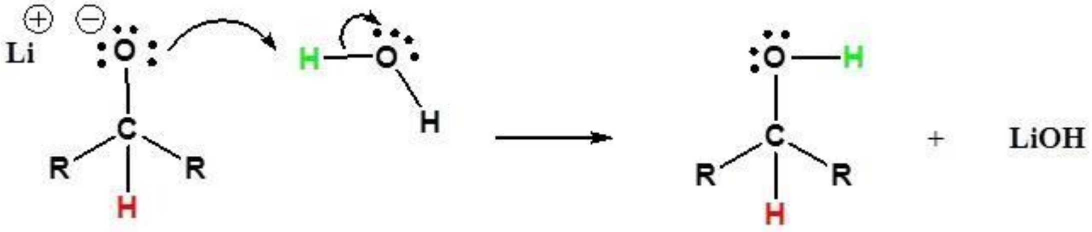
Mechanism

This mechanism is for a LiAlH4 reduction. The mechanism for a NaBH4 reduction is the same except methanol is the proton source used in the second step.

1) Nucleopilic attack by the hydride anion



2) The alkoxide is protonated



Physical Properties:

1. **The Boiling Point of Alcohols**
   Alcohols generally have higher boiling points in comparison to other hydrocarbons having equal molecular masses. This is due to the presence of intermolecular hydrogen bonding between hydroxyl groups of alcohol molecules. In general, the boiling point of alcohols increases with an increase in the number of carbon atoms in the aliphatic carbon chain. On the other hand, the boiling point decreases with an increase in branching in aliphatic carbon chains the Van der Waals forces decreases with a decrease in surface area. Thus primary alcohols have a higher boiling point.
2. **Solubility of Alcohols**
   The solubility of alcohol in water is governed by the hydroxyl group present. The hydroxyl group in alcohol is involved in the formation of intermolecular hydrogen bonding. Thus, hydrogen bonds are formed between water and alcohol molecules which make alcohol soluble in water. However, the alkyl group attached to the hydroxyl group is hydrophobic in nature. Thus, the solubility of alcohol decreases with the increase in the size of the alkyl group.

3.The Acidity of Alcohols

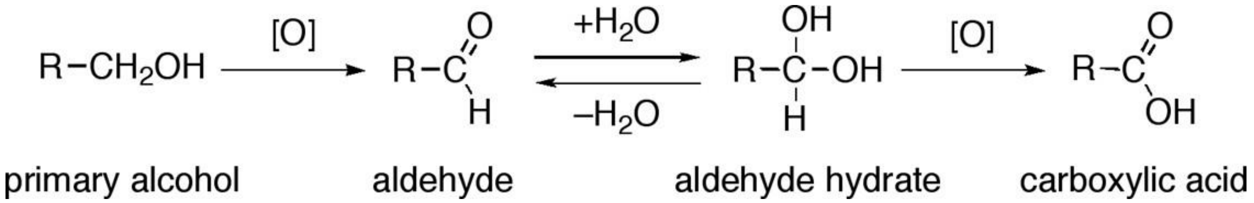
Alcohols react with active metals such as sodium, potassium etc. to form the corresponding alkoxide. These reactions of alcohols indicate their acidic nature. The acidic nature of alcohol is due to the polarity of –OH bond. The acidity of alcohols decreases when an electron-donating group is attached to the hydroxyl group as it increases the electron density on the oxygen atom. Thus, primary alcohols are generally more acidic than secondary and tertiary alcohols. Due to the presence of unshared electrons on the oxygen atom, alcohols act as Bronsted bases too.

Chemical Properties:

Alcohols exhibit a wide range of spontaneous chemical reactions due to the cleavage of the C-O bond and O-H bond. Some prominent chemical reactions of alcohols are:

1. Oxidation of Alcohol

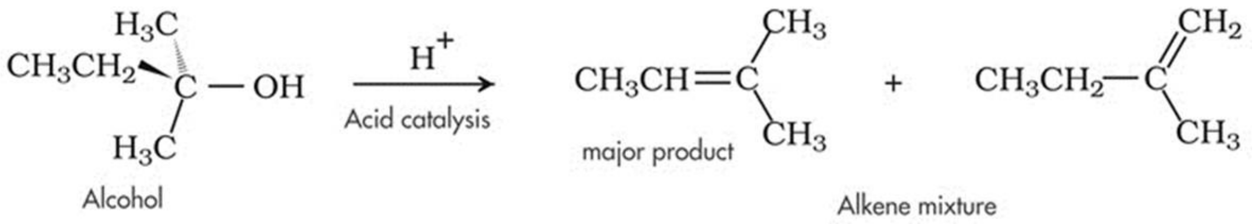
- Alcohols undergo oxidation in the presence of an oxidizing agent to produce aldehydes and ketones which upon further oxidation give carboxylic acids.



Alcohols: Physical and Chemical Properties

2. Dehydration of Alcohol

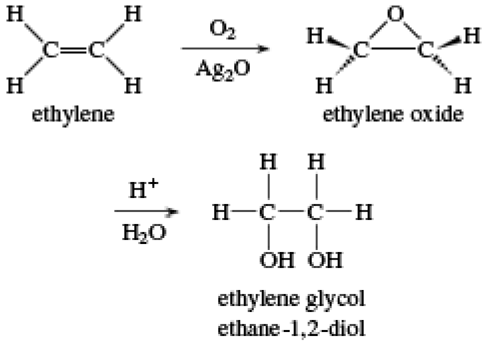
- Upon treatment with protic acids, alcohols undergo dehydration (removal of a molecule of water) to form alkenes. Dehydration of alcohol



Uses :

Glycols From Dihydroxylation:

Glycol, also called **ethane-1,2-diol**, the simplest member of the glycol family of organic compounds. A glycol is an alcohol with two hydroxyl groups on adjacent carbon atoms (a 1,2-diol). The common name *ethylene glycol* literally means “the glycol derived from ethylene.”



Ethylene glycol is a clear, sweet, slightly viscous liquid that boils at 198 °C (388.4 °F). Its most common use is as an automotive antifreeze. A 1:1 solution of ethylene glycol and water boils at 129 °C (264.2 °F) and freezes at −37 °C (−34.6 °F), serving as an excellent coolant in automotive radiators. Ethylene glycol is highly poisonous; animals or humans that drink the solution becomevery ill and may die.

Uses:

Grignard reagents, with their powerful carbon-magnesium bond, are like versatile workhorses in the world of organic chemistry. They excel in crafting intricate molecules, especially by forming new carbon-carbon bonds – the backbone of countless organic compounds. Here's a peek into their impressive repertoire:

1. Building Carbon Chains:

- Grignard reagents can add their carbon chains to carbonyl groups (found in aldehydes, ketones, and esters) like Legos, giving rise to alcohols. Imagine taking a simple ketone and attaching a Grignard reagent's carbon tail – presto, you've got a longer alcohol molecule! This reaction, called the Grignard reaction, is a cornerstone of organic synthesis.

2. Ring Formation:

Grignard reagents can also participate in intramolecular cyclizations, where the carbon chain wraps around and joins with itself, forming fascinating ring structures. This opens doors to synthesizing complex natural products and pharmaceuticals.

3. Functional Group Transformations:

Grignard reagents are adept at swapping functional groups. They can replace halogens with hydroxyl groups (making alcohols from halides), introduce amino groups, or even convert esters to ketones. It's like chemical switcheroo, giving chemists precise control over molecular structures.

4. Beyond Carbon:

Grignard reagents aren't limited to just carbon. They can react with elements like boron, silicon, and tin, paving the way for the synthesis of organometallic compounds with unique properties and applications in materials science and catalysis.

5. Industrial Applications:

Grignard reagents aren't just lab bench stars; they play a crucial role in some industrial processes. For example, they're used in the production of Tamoxifen, a drug for treating breast cancer.

Safety First:

It's important to remember that Grignard reagents are powerful and require careful handling due to their air and moisture sensitivity. But in the right hands, they are invaluable tools for unlocking the wonders of the molecular world.

- In addition to its use in antifreeze
- Ethylene glycol is used as an ingredient in hydraulic fluids, Printing inks, and paint solvents.
- It is also used as a reagent in making polyesters Explosives,
- Alkyd resins

GLYCEROLS FORM DIHYDROXYLATION:

The dihydroxylation of glycerols is a chemical reaction that introduces two hydroxyl groups (-OH) into a glycerol molecule. Glycerol, also known as propane-1,2,3-triol, is a naturally occurring sugar alcohol with the formula $CH_2OHCHOHCH_2OH$.

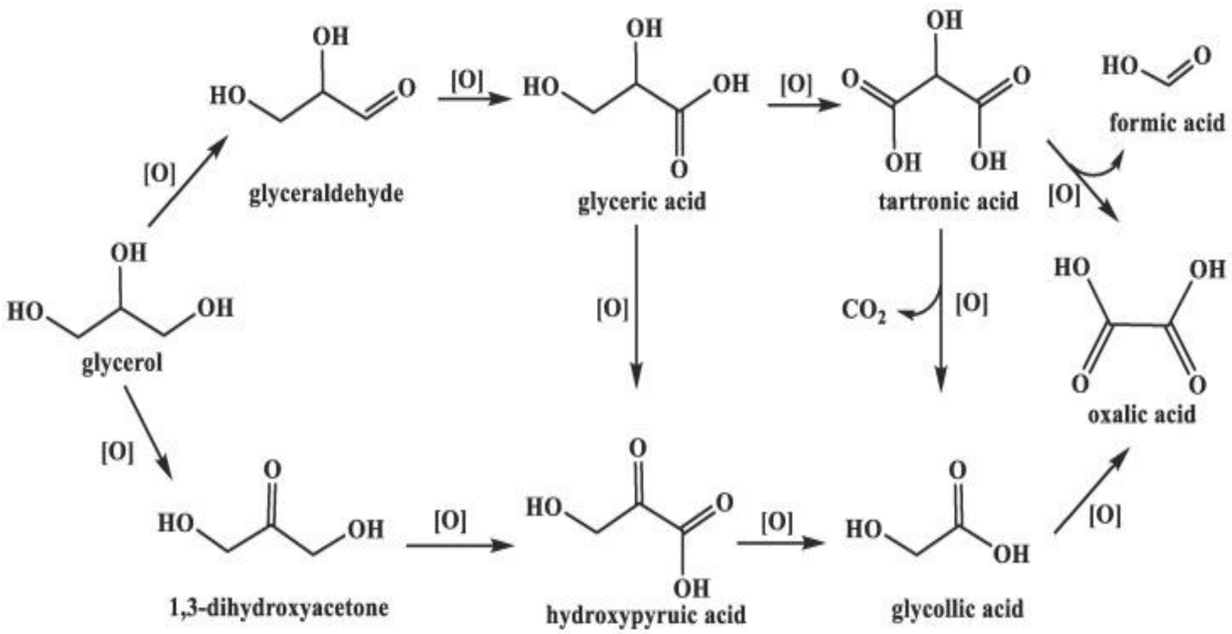
There are several ways to achieve dihydroxylation of glycerols, each with its own advantages and disadvantages. Some common methods include:

- **Osmium tetroxide (OsO_4) oxidation:** This is a powerful and versatile method that can selectively introduce hydroxyl groups at specific positions on the glycerol molecule. However, OsO_4 is toxic and expensive, and its use requires careful handling and safety precautions.
- **Potassium permanganate ($KMnO_4$) oxidation:** This is a less expensive and more readily available alternative to OsO_4, but it is less selective and can lead to overoxidation of the glycerol molecule.
- **Hydrogen peroxide (H_2O_2) oxidation:** This is a relatively mild and environmentally friendly method, but it often requires the use of transition metal catalysts to achieve good yields.
- **Enzymatic dihydroxylation:** This method uses enzymes to catalyze the dihydroxylation reaction. Enzymes are highly selective and can be tailored to target specific positions on the glycerol molecule. However, enzymatic dihydroxylation can be slow and expensive.

The specific method used for dihydroxylation of glycerols will depend on the desired product, the reaction conditions, and the cost and availability of reagents.

Here are some additional details about the dihydroxylation of glycerols:

- The dihydroxylation reaction can be regiospecific, meaning that the hydroxyl groups can be introduced at specific positions on the glycerol molecule. This can be achieved by using specific reagents or catalysts, or by controlling the reaction conditions.
- The dihydroxylation reaction can also be stereospecific, meaning that the hydroxyl groups can be introduced with a specific spatial arrangement. This can be achieved by using chiral reagents or catalysts.
- Dihydroxylated glycerols are important intermediates in the synthesis of a variety of pharmaceuticals, cosmetics, and other products.



Properties:

Glycerols, also known as 1,2,3-propanetriols, are organic compounds with three hydroxyl (-OH) groups attached to a central carbon atom. The dihydroxylation of glycerols refers to the process of adding two hydroxyl groups to a molecule that originally lacked them.

In the context of properties, the dihydroxylation of glycerols significantly impacts their physical and chemical characteristics. Here's a breakdown of the key changes:

Physical properties:

- **Viscosity:** Glycerols are viscous liquids at room temperature. The addition of hydroxyl groups further increases hydrogen bonding, leading to even higher viscosity. This makes dihydroxylated glycerols thicker and more syrupy compared to their non-hydroxylated counterparts.
- **Solubility:** The presence of multiple hydroxyl groups makes dihydroxylated glycerols highly polar and water-soluble. They readily form hydrogen bonds with water molecules, making them excellent humectants (substances that attract and retain moisture).
- **Melting and boiling points:** The increased intermolecular hydrogen bonding due to dihydroxylation also raises the melting and boiling points of glycerols. This is because more energy is required to overcome the attractive forces between molecules in the solid and liquid states.

Chemical properties:

- **Reactivity:** The hydroxyl groups in dihydroxylated glycerols are reactive and can participate in various chemical reactions, including esterification, etherification, and oxidation. These reactions are crucial for the synthesis of numerous important derivatives like glycerol esters, which are used in pharmaceuticals and cosmetics.
- **Acidity:** Dihydroxylated glycerols exhibit weak acidic properties due to the ability of the hydroxyl groups to lose protons (H+). This acidity can be further influenced by the specific substituents attached to the carbon chain.

It's important to note that the specific properties of dihydroxylated glycerols can vary depending on the nature and position of the additional hydroxyl groups. For example, 1,2-ethanediol and 1,3-propanediol, both dihydroxylated derivatives of alkanes, have distinct properties due to the different arrangements of their hydroxyl groups.

Uses:

Glycerols, also known as glycerol or glycerin, are trihydroxy alcohols, meaning they have three hydroxyl (-OH) groups attached to a central carbon chain. The dihydroxylation of glycerol refers to the process of adding two additional hydroxyl groups to the molecule, resulting in a six-carbon sugar alcohol known as sorbitol.

Sorbitol has a wide range of uses, including:

Sweetener: Sorbitol is a sugar alcohol with about 60% of the sweetness of sucrose (table sugar) but contains significantly fewer calories. This makes it a popular sweetener for people with diabetes, as it does not cause significant spikes in blood sugar levels. Sorbitol is also used in sugar-free chewing gum, candies, and baked goods.

Humectant: Sorbitol has excellent moisture-retention properties, making it a valuable ingredient in cosmetics, toiletries, and pharmaceuticals. It helps to prevent products from drying out and becoming cracked or brittle.

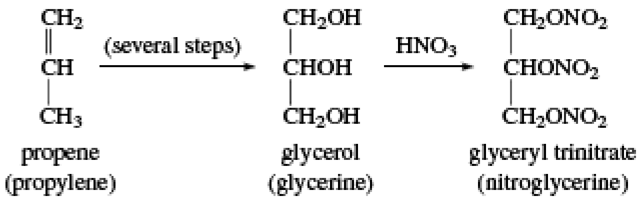
Food additive: Sorbitol is used as a thickener, texturizer, and bulking agent in various food products such as ice cream, yogurt, salad dressings, and sauces. It also helps to prevent crystallization of sugars in frozen desserts.

Laxative: Sorbitol has a laxative effect due to its osmotic properties. When ingested, it draws water into the intestines, stimulating bowel movements and relieving constipation. Sorbitol is available as an over-the-counter laxative in various forms, including tablets, liquid syrups, and chewable gums.

Other uses: Sorbitol is also used in various industrial applications, such as the production of resins, plasticizers, and lubricants. It is also a component of some antifreeze solutions.

It's important to note that while sorbitol is generally safe for most people, excessive consumption can lead to digestive side effects such as bloating, gas, and diarrhea. Additionally, individuals with fructose intolerance should avoid sorbitol, as it can be converted to fructose in the body and worsen symptoms.

Glycerol has numerous uses. It is a basic ingredient in the gums and resins used to make many modern protective coatings such as automotive enamels and exterior house paints. Glycerin reacted with nitric and sulfuric acid forms the explosive nitroglycerin (or nitroglycerine).



Glycerol is also a component of mono- and diglyceride emulsifiers, which are used as softening agents in baked goods, plasticizers in shortening, and stabilizers in ice cream. Its varied uses in the pharmaceutical and toilet goods fields include skin lotions, mouthwashes, cough medicines, drug solvents, serums, vaccines, and suppositories. Another significant use is as a protective medium for freezing red blood cells, sperm cells, eye corneas, and other living tissues. At one time, its largest single use was as automotive antifreeze; methanol and ethylene glycol have replaced it for this purpose.

Fats and oils are valued chiefly as sources of the carboxylic acids that are present, combined in the form of esters with glycerol. When the acids are set free from these compounds, glycerol remains as a solution in water and is purified by coagulating and settling extraneous matter, evaporating the water, and distilling.

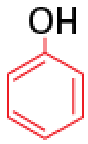
PREPARATION OF PHENOLS :

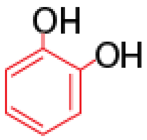
Phenol:

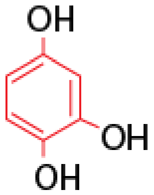
Classification of Phenol

Depending on the number of hydroxyl groups attached, phenols can be classified into three types.

- **Monohydric phenols**: They contain one -OH group.
- **Dihydric phenols**: They contain two -OH groups. They may be ortho-, meta- or para- derivative.
- **Trihydric phenols**: They contain three -OH groups.


Monohydric


Dihydric


Trihydric

Phenols are organic compounds characterized by a hydroxyl group (-OH) directly attached to an aromatic ring, most commonly a benzene ring. They are important in various industries and applications, from disinfectants and resins to pharmaceuticals and dyes.

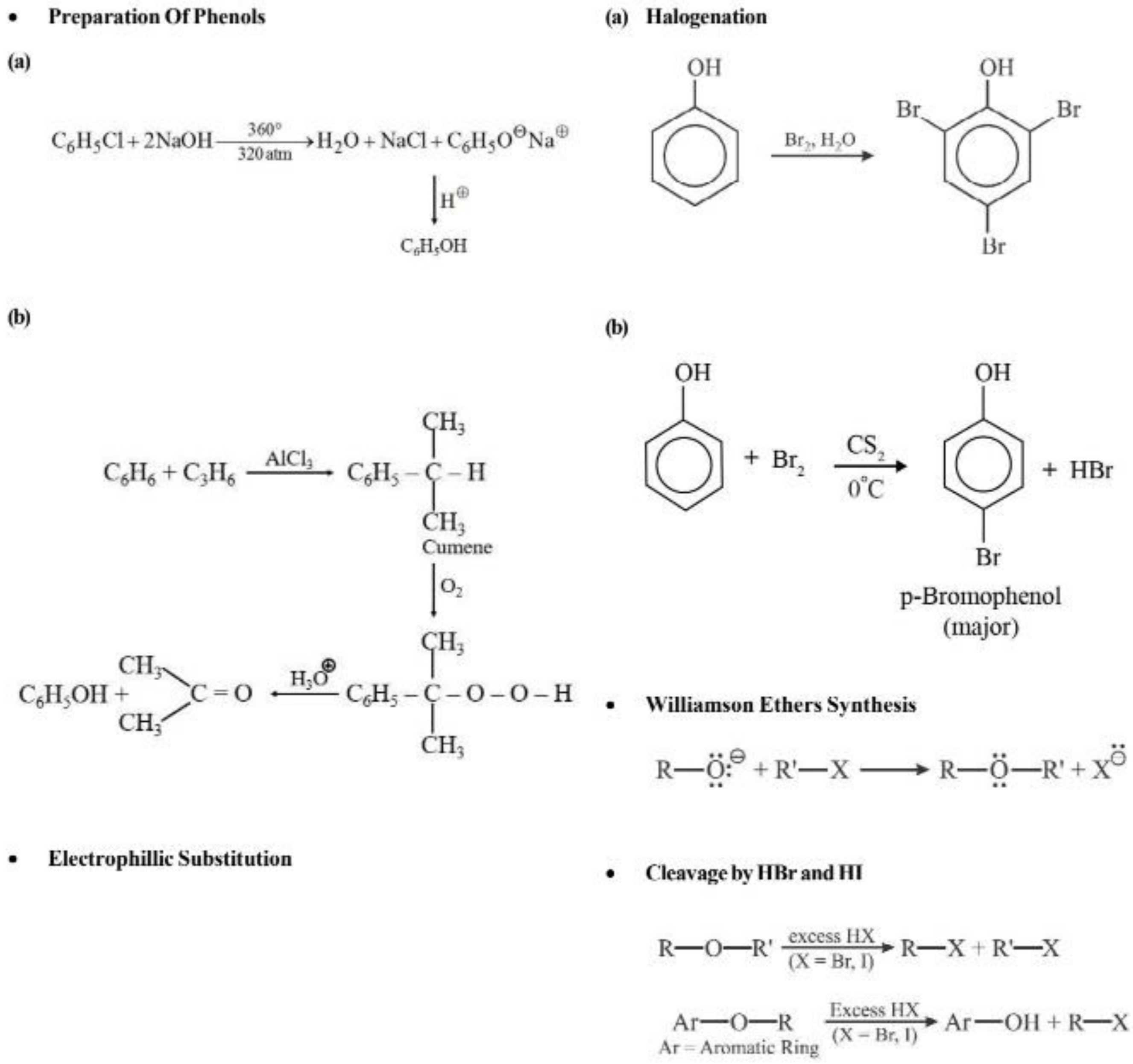
There are several methods for preparing phenols, each with its own advantages and limitations. Here are some key approaches:

1. From Haloarenes:

Dow process: This industrial method involves reacting chlorobenzene with sodium hydroxide at high temperature and pressure to obtain sodium phenoxide, which is then acidified to liberate phenol.

2. From Benzene Sulphonic Acid:

This method involves sulfonating benzene with oleum (concentrated sulfuric acid) followed by fusion with sodium hydroxide to generate sodium phenoxide. Similar the Dow process, acidification yields phenol to.



- **Preparation Of Phenols**

(a)

$$C_6H_5Cl + 2NaOH \xrightarrow[320\,atm]{360^{\circ}} H_2O + NaCl + C_6H_5O^{\ominus}Na^{\oplus}$$

$$\downarrow H^{\oplus}$$

$$C_6H_5OH$$

(b)

$$C_6H_6 + C_3H_6 \xrightarrow{AlCl_3} C_6H_5-\overset{CH_3}{\underset{CH_3}{C}}-H$$

Cumene

$$\downarrow O_2$$

$$C_6H_5OH + \begin{matrix} CH_3 \\ CH_3 \end{matrix} \!\!> C=O \xleftarrow{H_3O^{\oplus}} C_6H_5-\overset{CH_3}{\underset{CH_3}{C}}-O-O-H$$

- **Electrophillic Substitution**

(a) Halogenation

(b)

p-Bromophenol
(major)

- **Williamson Ethers Synthesis**

$$R—\ddot{\underset{\cdot\cdot}{O}}:^{\ominus} + R'—X \longrightarrow R—\ddot{\underset{\cdot\cdot}{O}}—R' + X^{\ddot{\ominus}}$$

- **Cleavage by HBr and HI**

$$R—O—R' \xrightarrow[(X = Br,\, I)]{\text{excess HX}} R—X + R'—X$$

$$Ar—O—R \xrightarrow[(X - Br,\, I)]{\text{Excess HX}} Ar—OH + R—X$$

Ar = Aromatic Ring

3. From Diazonium Salts:

When an aromatic primary amine is treated with nitrous acid, it converts to a diazonium salt. Heating this salt in the presence of water results in the release of nitrogen gas and formation of the corresponding phenol.

4. From Cumene:

Oxidation of cumene (isopropylbenzene) in the presence of air produces cumene hydroperoxide. Subsequent treatment with dilute acid cleaves the hydroperoxide to generate phenol and acetone.

5. Other Methods:

- **Kolbe-Schmitt reaction:** This reaction involves the conversion of salicylic acid (a hydroxybenzoic acid) to phenol through thermal decarboxylation.
- **Raschig process:** This method, now largely obsolete, was based on the fusion of benzene with sodium hydroxide at high temperature.
- The choice of method for preparing phenols depends on factors such as:
- **Availability of starting materials:** Haloarenes and benzene are readily available, while cumene and diazonium salts may require additional synthesis steps.
- **Cost and efficiency:** The Dow process is widely used due to its efficiency and relatively low cost.
- **Purity requirements:** Some methods, like the Raschig process, generate significant impurities and require further purification.
- **Environmental considerations:** Certain methods, like the Kolbe-Schmitt reaction, involve harsh conditions and may generate hazardous byproducts.

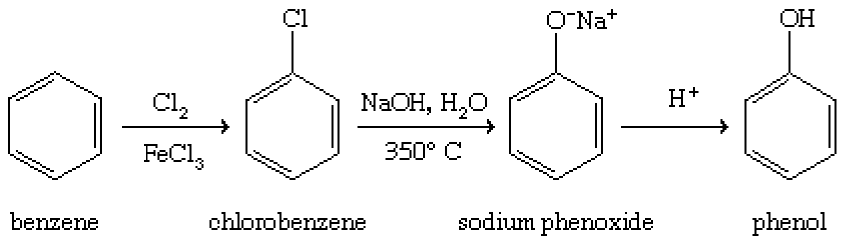
Phenol, any of a family of organic compounds characterized by a hydroxyl (—OH) group attached to a carbon atom that is part of an aromatic ring. Besides serving as the generic name for the entire family, the term *phenol* is also the specific name for its simplest member, monohydroxybenzene (C6H5OH), also known as benzenol, or carbolic acid.

Phenols are similar to alcohols but form stronger hydrogen bonds. Thus, they are more soluble in water than are alcohols and have higher boiling points. Phenols occur either as colourless liquids or white solids at room temperature and may be highly toxic and caustic.
Most of the phenol used today is produced from benzene, through either hydrolysis of chlorobenzene or oxidation of isopropylbenzene (cumene).

Synthesis:

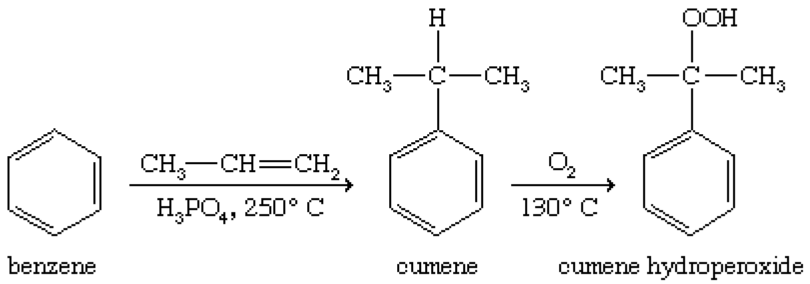
Hydrolysis of chlorobenzene (the Dow process)

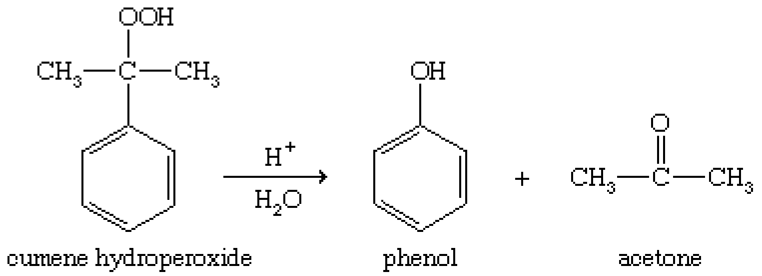
Benzene is easily converted to chlorobenzene by a variety of methods, one of which is the Dow process. Chlorobenzene is hydrolyzed by a strong base at high temperatures to give a phenoxide salt, which is acidified to phenol.



Oxidation of isopropylbenzene

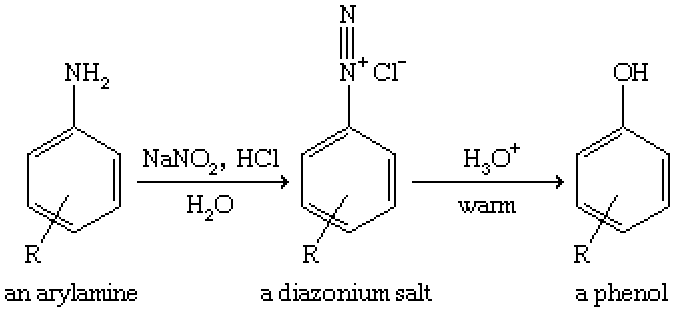
Benzene is converted to isopropylbenzene (cumene) by treatment with propylene and an acidic catalyst. Oxidation yields a hydroperoxide (cumene hydroperoxide), which undergoes acid- catalyzed rearrangement to phenol and acetone. Although this process seems more complicated than the Dow process, it is advantageous because it produces two valuable industrial products: phenol and acetone.





General synthesis of phenols

To make more-complicated phenolic compounds, a more general synthesis is needed. The cumene hydroperoxide reaction is fairly specific to phenol itself. The Dow process is somewhat more general, but the stringent conditions required often lead to low yields, and they may destroy any other functional groups on the molecule. A milder, more general reaction is the diazotization of an arylamine (a derivative of aniline, $C_6H_5NH_2$) to give a diazonium salt, which hydrolyzes to a phenol. Most functional groups can survive this technique, as long as they are stable in the presence of dilute acid.



R = alkyl group or functional group at any position

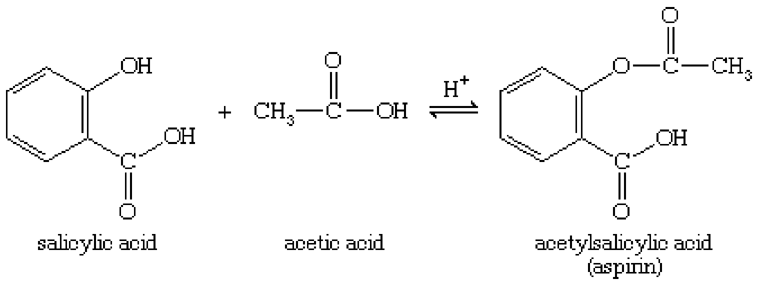
Physical properties:

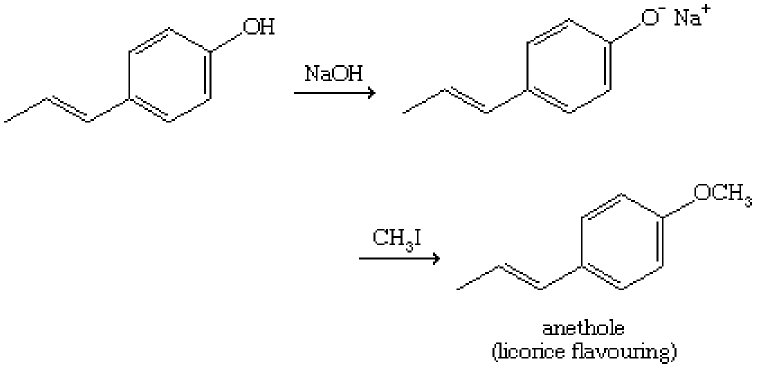
Similar to alcohols, phenols have hydroxyl groups that can participate in intermolecular hydrogen bonding; in fact, phenols tend to form stronger hydrogen bonds than alcohols. (*See* chemical bonding: Intermolecular forces for more information about hydrogen bonding.) Hydrogen bonding results in higher melting points and much higher boiling points for phenols than for hydrocarbons

with similar molecular weights. For example, phenol (molecular weight [MW] 94, boiling point [bp] 182 °C [359.6 °F]) has a boiling point more than 70 degrees higher than that of toluene ($C_6H_5CH_3$; MW 92, bp 111 °C [231.8 °F]).

Chemical Properties:

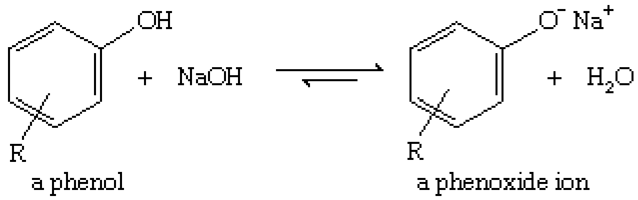
Much of the chemistry of phenols is like that of alcohols. For example, phenols react with acids to give esters, and phenoxide ions (ArO^-) can be good nucleophiles in Williamson ether synthesis.





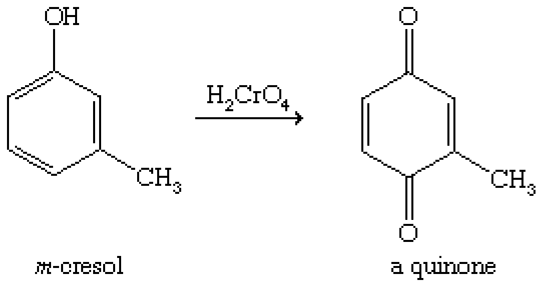
Acidity of phenols

Although phenols are often considered simply as aromatic alcohols, they do have somewhat different properties. The most obvious difference is the enhanced acidity of phenols. Phenols are not as acidic as carboxylic acids, but they are much more acidic than aliphatic alcohols, and they are more acidic than water. Unlike simple alcohols, most phenols are completely deprotonated by sodium hydroxide (NaOH).



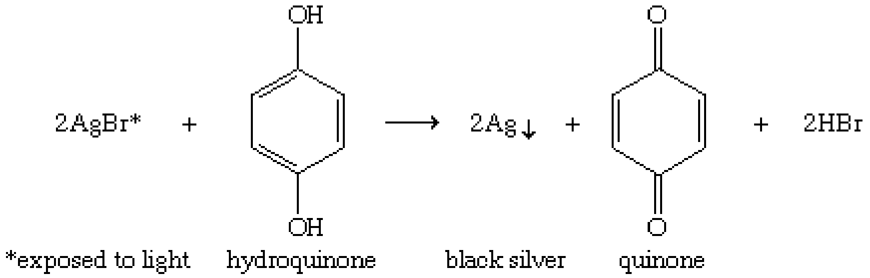
Oxidation

Like other alcohols, phenols undergo oxidation, but they give different types of products from those seen with aliphatic alcohols. For example, chromic acid oxidizes most phenols to conjugated 1,4- diketones called quinones. In the presence of oxygen in the air, many phenols slowly oxidize to give dark mixtures containing quinones.



Hydroquinone (1,4-benzenediol) is a particularly easy compound to oxidize, because it has two hydroxyl groups in the proper relationship to give up hydrogen atoms to form a quinone.

Hydroquinone is used in developing photographic film by reducing activated (exposed to light) silver bromide (AgBr) to black metallic silver (Ag↓). Unexposed grains of silver bromide react more slowly than the exposed grains.



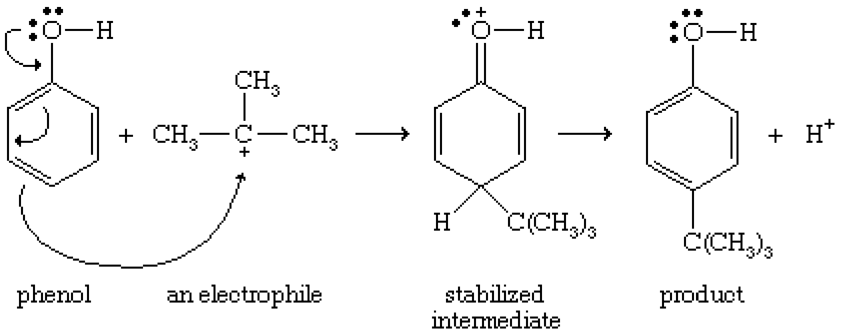
Uses:

Phenols are similar to alcohols but form stronger hydrogen bonds. Thus, they are more soluble in water than are alcohols and have higher boiling points. Phenols occur either as colourless liquids or white solids at room temperature and may be highly toxic and caustic.

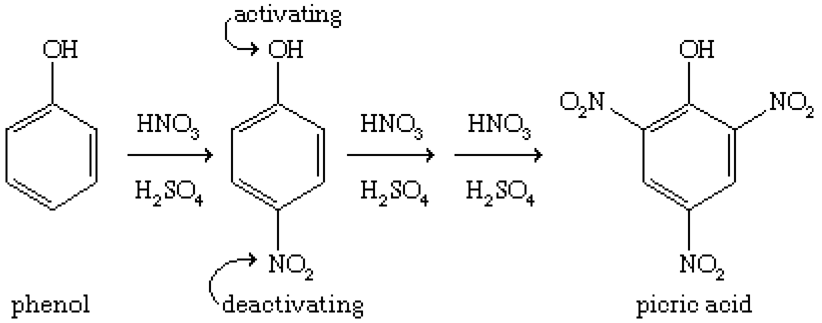
Phenol, the cresols (methylphenols), and other simple alkylated phenols can be obtained from the distillation of coal tar or crude petroleum

Aromatic Electrophilic Substitution Mechanism:

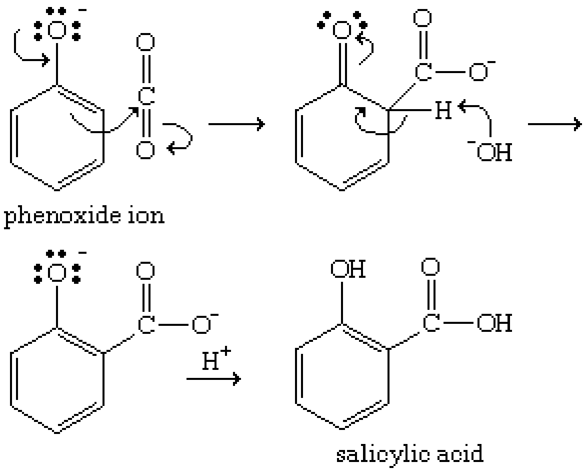
Phenols are highly reactive toward electrophilic aromatic substitution, because the nonbonding electrons on oxygen stabilize the intermediate cation. This stabilization is most effective for attack at the *ortho* or *para* position of the ring; therefore, the hydroxyl group of a phenol is considered to be activating (i.e., its presence causes the aromatic ring to be more reactive than benzene) and *ortho*- or *para*-directing.



Picric acid (2,4,6-trinitrophenol) is an important explosive that was used in World War I. An effective explosive needs a high proportion of oxidizing groups such as nitro groups. Nitro groups are strongly deactivating (i.e., make the aromatic ring less reactive), however, and it is often difficult to add a second or third nitro group to an aromatic compound. Three nitro groups are more easily substituted onto phenol, because the strong activation of the hydroxyl group helps to counteract the deactivation of the first and second nitro groups.



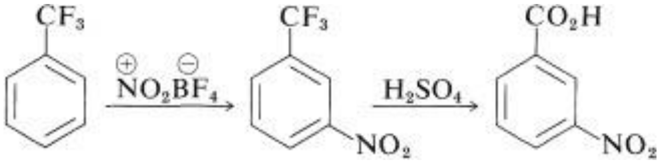
Phenoxide ions, generated by treating a phenol with sodium hydroxide, are so strongly activated that they undergo electrophilic aromatic substitution even with very weak electrophiles such as carbon dioxide (CO2). This reaction is used commercially to make salicylic acid for conversion to aspirin and methyl salicylate.



Theory of Orientation And Reactivity:

Basically, three experimental problems are involved in the substitution reactions of aromatic compounds: (1) proof of structure of the isomers that are formed; (2) determination of the percentage of each isomer formed, if the product is a mixture; and (3) measurement of the reactivity of the compound being substituted relative to some standard substance, usually benzene.

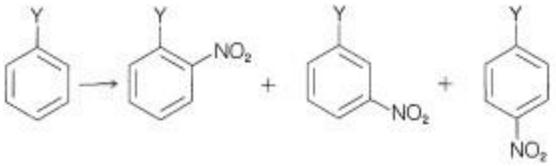
For benzenoid compounds, structures can be established by the historically important substitution method or with the aid of correlations between spectroscopic properties and positions of substitution. Also, it is often possible to identify the isomers by converting them to compounds of known structure. For example, trifluoromethylbenzene on nitration gives only one product, which has been shown to be the 3-nitro derivative by conversion to the known 3-nitrobenzoic acid by concentrated sulfuric acid:

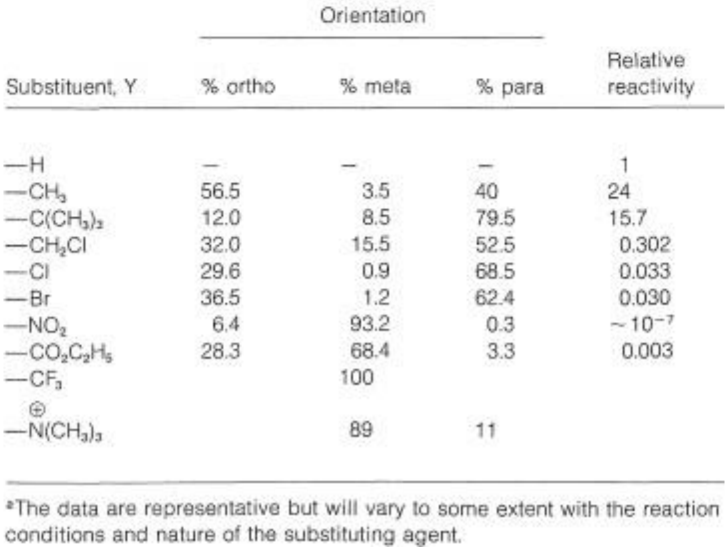


The ratios of isomers formed in substitution reactions can be determined by spectroscopic means or by the analytical separation methods.

The reaction most studied in connection with the orientation problem is nitration, but the principles established also apply for the most part to the related reactions of halogenation, sulfonation, alkylation, and acylation. Some illustrative data for the nitration of a number of mono-substituted benzene derivatives are given in

Table. The table includes the percentage of ortho, meta, and para isomers formed, along with their reactivities relative to benzene. We see that there is a wide range of reactivity according to the nature of the substituent, and that the ortho, meta, and para positions are *not* equally reactive. Although these substituent effects may appear complex.



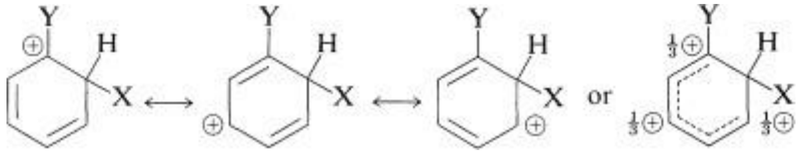


Substituent, Y	% ortho	% meta	% para	Relative reactivity
	Orientation			
—H	–	–	–	1
—CH_3	56.5	3.5	40	24
—$C(CH_3)_3$	12.0	8.5	79.5	15.7
—CH_2Cl	32.0	15.5	52.5	0.302
—Cl	29.6	0.9	68.5	0.033
—Br	36.5	1.2	62.4	0.030
—NO_2	6.4	93.2	0.3	~10^{-7}
—$CO_2C_2H_5$	28.3	68.4	3.3	0.003
—CF_3		100		
—$\overset{\oplus}{N}(CH_3)_3$		89	11	

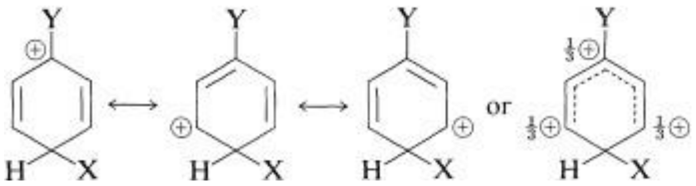
[a] The data are representative but will vary to some extent with the reaction conditions and nature of the substituting agent.

The positive charge in the ring is dispersed mainly on alternate carbons, as shown below.

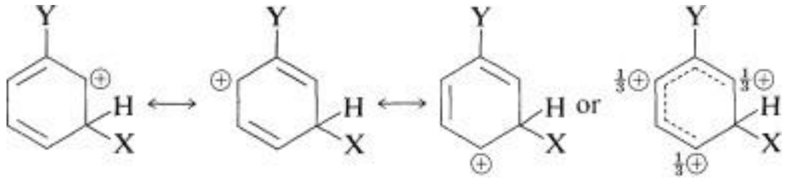
ortho substitution



para substitution

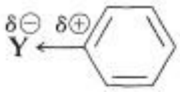


meta substitution



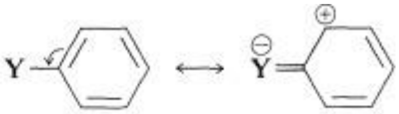
The substituent Y

should (and does) exert its electronic influence more strongly from the ortho and para positions than from the meta position because Y in the ortho and the para positions is close to a positively charged ring carbon. This electronic influence will be stabilizing if Y has a net electron-donating effect, and destabilizing if Y is electron withdrawing. A group can withdraw electrons relative to hydrogen if it is more electronegative than hydrogen and this is called the electron-withdrawing inductive effect. A group also can withdraw electrons by the **resonance effect**:



electron-withdrawing inductive effect

$Y = —CF_3, —\overset{\oplus}{N}R_3$



electron-withdrawing resonance effect

$Y = —NO_2, —CO_2R$

Phenols, a fascinating group of organic compounds, find their way into a surprising array of applications! Here's a peek into their diverse world:

Disinfectants & Antiseptics:

- Remember the sting of mouthwash? Phenols in low concentrations are present in disinfectants, mouthwashes, and even household cleaners. They were even early pioneers in surgical antiseptics, though their high toxicity led to safer alternatives.

Chemicals & Plastics:

- Phenol itself serves as a starting material for many industrial giants. Think plastics like Bakelite, found in circuit boards and insulation, or polycarbonates used in CDs and DVDs. Even explosives like picric acid have phenol at their core.

Pharmaceuticals & Medicine:

- Aspirin, that trusty pain reliever, is a close cousin of phenol. Several other drugs also draw inspiration from its structure. Phenol derivatives like BHT act as antioxidants in food, protecting it from spoilage.

Research & Science:

- Phenol's ability to dissolve certain molecules makes it a hero in extracting DNA and RNA from cells, aiding in genetic research.

Cosmetics & Personal Care:

- Sunscreens, skin-lightening creams, and hair dyes might surprise you with their hidden phenolic ingredient. These derivatives add specific properties like sun protection or color enhancement.

Other Applications:

- Phenol even finds its way into adhesives, rubber production, and textile dyes.

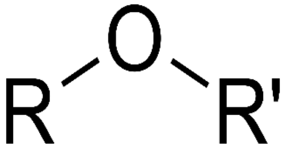
ETHER COMPOUNDS:

Common names of ethers simply give the names of the two alkyl groups bonded to oxygen and add the word *ether*. The current practice is to list the alkyl groups in alphabetical order (*t*-butyl methyl ether), but older names often list the alkyl groups in increasing order of size (methyl *t*-butyl ether). If just one alkyl group is described in the name, it implies two identical groups, as in ethyl ether for diethyl ether.

Ethers are a diverse class of organic compounds that feature an oxygen atom bonded to two carbon atoms. These carbon atoms can be part of alkyl groups (straight or branched chains) or aryl groups (aromatic rings). The general formula for ethers is R-O-R', where R and R' represent the two carbon atoms.

Here are some key points about ethers:

- **Structure:** Ethers have a tetrahedral geometry around the oxygen atom, with bond angles of approximately 109.5°. This is similar to the structure of alcohols and water, but with both hydrogen atoms replaced by carbon atoms.



Ether structure

- **Properties:** Ethers are typically colorless liquids with pleasant smells. They are generally less polar than alcohols and have lower boiling points due to the absence of hydrogen bonding. However, ethers can form weak hydrogen bonds with water molecules, which makes some of them moderately soluble in water.
- **Nomenclature:** Ethers can be named using two different systems: common names and IUPAC names. Common names are based on the two alkyl or aryl groups attached to the oxygen atom, listed in alphabetical order followed by the word "ether". For example, CH3CH2OCH2CH3 is called diethyl ether. IUPAC names are more systematic and use the alkoxy group (-OR) as a substituent on the larger alkyl or aryl group. For example, CH3CH2OCH2CH3 is named ethoxyethane.
- **Classification:** Ethers can be classified into different types based on the structure of the carbon atoms attached to the oxygen atom. Aliphatic ethers have only alkyl groups attached to the oxygen atom. Aromatic ethers have at least one aryl group attached to the oxygen atom. Cyclic ethers have the oxygen atom incorporated into a ring.

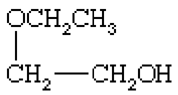
Ethers have a wide range of applications in various industries. Some of the most common uses include:

- **Solvents:** Ethers are widely used as solvents in paints, coatings, and adhesives. They are also used to extract oils and fats from foods and to clean electronic components.
- **Anesthetics:** Diethyl ether was once a commonly used anesthetic, but it has largely been replaced by safer and more effective drugs.
- **Pharmaceuticals:** Some ethers have pharmaceutical properties and are used as drugs. For example, methoxyflurane is an inhaled anesthetic, and phenytoin is an anticonvulsant medication.

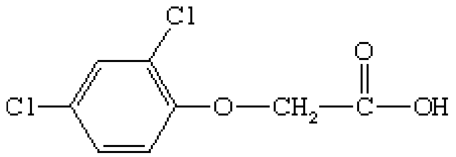
- **Fragrances:** Many ethers have pleasant smells and are used in perfumes and other fragrances.

Overall, ethers are a versatile class of organic compounds with a wide range of properties and applications. Understanding their structure, properties, and nomenclature is essential for anyone working in the fields of chemistry, biology, or medicine.

Systematic (IUPAC) names for ethers use the more complex group as the root name, with the oxygen atom and the smaller group named as an alkoxy substituent. Examples given above are ethoxyethane (diethyl ether), methoxyethane (methyl ethyl ether), 2-methoxy-2-methylpropane (MTBE), and phenoxybenzene (diphenyl ether). The IUPAC nomenclature works well for compounds with additional functional groups, because the other functional groups can be described in the root name.



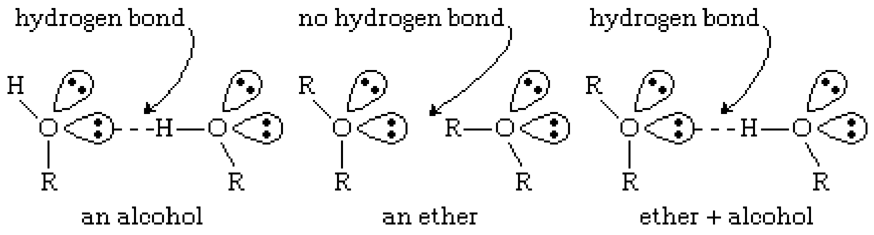
2-ethoxyethanol
(ethyl cellosolve)

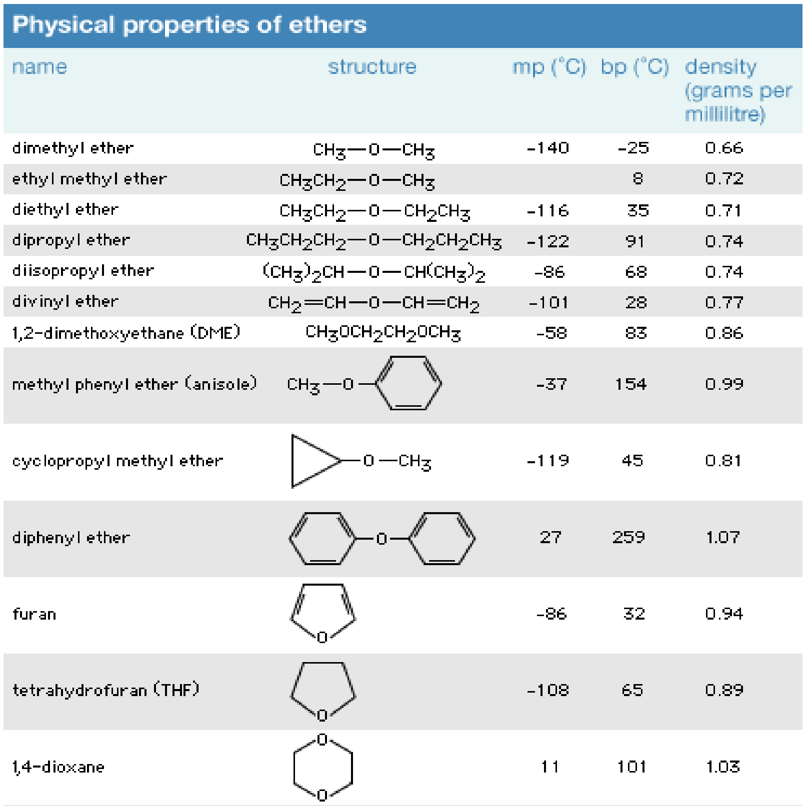


2,4-dichlorophenoxyacetic acid
(2,4-D herbicide)

Preparation of Ethers:

Ethers lack the hydroxyl groups of alcohols. Without the strongly polarized O—H bond, ether molecules cannot engage in hydrogen bonding with each other. Ethers do have nonbonding electron pairs on their oxygen atoms, however, and they can form hydrogen bonds with other molecules (alcohols, amines, etc.) that have O—H or N—H bonds. The ability to form hydrogen bonds with other compounds makes ethers particularly good solvents for a wide variety of organic compounds and a surprisingly large number of inorganic compounds. (For more information about hydrogen bonding, *see* chemical bonding: Intermolecular forces.)





Physical properties of ethers

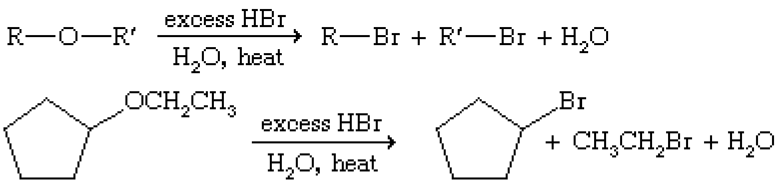
name	structure	mp (°C)	bp (°C)	density (grams per millilitre)
dimethyl ether	CH_3—O—CH_3	-140	-25	0.66
ethyl methyl ether	CH_3CH_2—O—CH_3		8	0.72
diethyl ether	CH_3CH_2—O—CH_2CH_3	-116	35	0.71
dipropyl ether	$CH_3CH_2CH_2$—O—$CH_2CH_2CH_3$	-122	91	0.74
diisopropyl ether	$(CH_3)_2CH$—O—$CH(CH_3)_2$	-86	68	0.74
divinyl ether	CH_2=CH—O—CH=CH_2	-101	28	0.77
1,2-dimethoxyethane (DME)	$CH_3OCH_2CH_2OCH_3$	-58	83	0.86
methyl phenyl ether (anisole)	CH_3—O—	-37	154	0.99
cyclopropyl methyl ether	—O—CH_3	-119	45	0.81
diphenyl ether	—O—	27	259	1.07
furan	O	-86	32	0.94
tetrahydrofuran (THF)	O	-108	65	0.89
1,4-dioxane	O O	11	101	1.03

Because ether molecules cannot engage in hydrogen bonding with each other, they have much lowerboiling points than do alcohols with similar molecular weights. For example, the boiling point of diethyl ether ($C_4H_{10}O$, molecular weight [MW] 74) is 35 °C (95 °F), but the boiling point of 1- butanol (or *n*-butyl alcohol; $C_4H_{10}O$, MW 74) is 118 °C (244 °F). In fact, the boiling points of ethers are much closer to those of alkanes with similar molecular weights; the boiling point of pentane(C_5H_{12}, MW 72) is 36 °C (97 °F), close to the boiling point of diethyl ether.

REACTIONS OF ETHERS

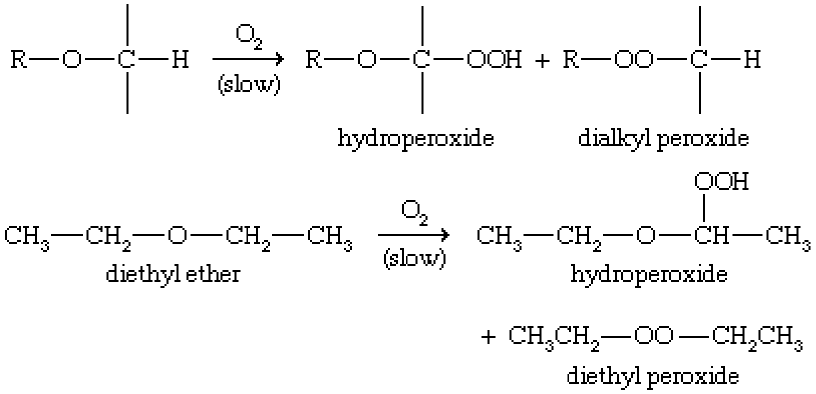
Cleavage

Ethers are good solvents partly because they are not very reactive. Most ethers can be cleaved, however, by hydrobromic acid (HBr) to give alkyl bromides or by hydroiodic acid (HI) to give alkyliodides.



Autoxidation

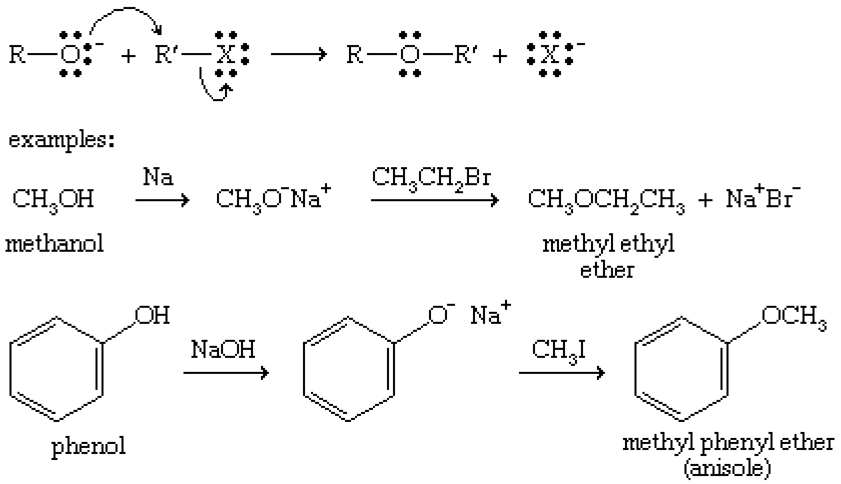
Autoxidation is the spontaneous oxidation of a compound in air. In the presence of oxygen, ethers slowly autoxidize to form hydroperoxides and dialkyl peroxides. If concentrated or heated, these peroxides may explode. To prevent such explosions, ethers should be obtained in small quantities, kept in tightly sealed containers, and used promptly.



Dehydration of Alcohols

Williamson's Synthesis:

The most versatile method for making ethers is the Williamson ether synthesis, named for English chemist Alexander Williamson, who devised the method in the 19th century. It uses an alkoxide ion to attack an alkyl halide, substituting the alkoxy (—O—R) group for the halide. The alkyl halide must be unhindered (usually primary), or elimination will compete with the desired substitution.



Silyl Ether:

- A silyl ether is the compound obtained when one or both carbon atoms bonded to the ethergroup in an ether molecule is replaced by silicon atoms.

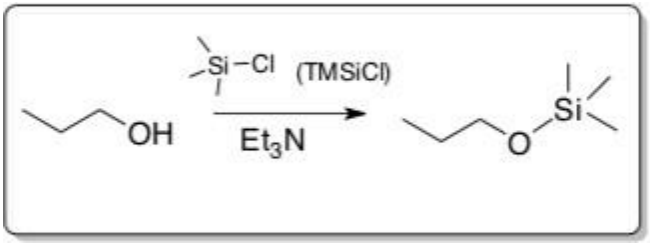
eg:

$$(CH_3)_3Si-O-CH_2CH_3$$

- The oxygen atom in a silyl ether molecule is called the silyl ether group.

$$(CH_3)_3Si-\boxed{O}-CH_2CH_3$$

silyl ether group



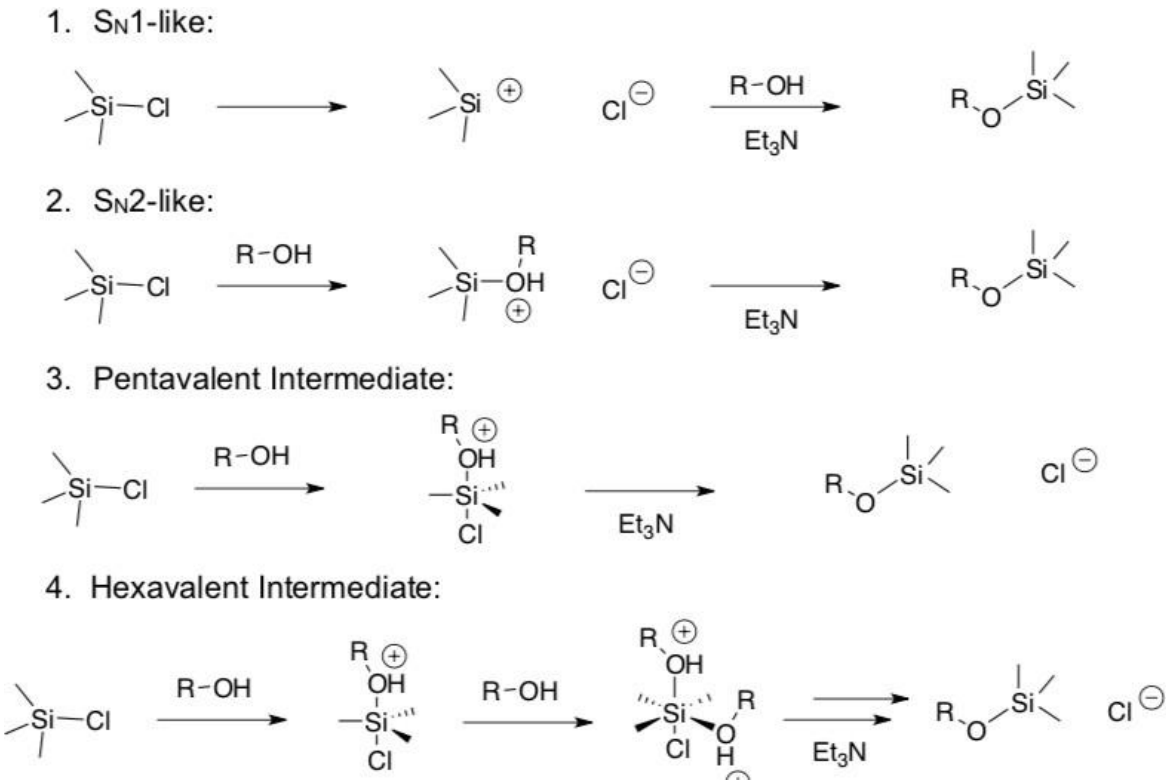
Formation of Silyl Ethers

Silyl ethers are functional groups with Si covalently bonded to an alkoxy group. Silyl ethers are inert to many reagents that react with alcohols, so they serve as protecting groups in organic synthesis.

Silicon is capable of making pentavalent and hexavalent complexes.

- Propose a reason. There are several hotly contested theories so there is no “right” answer.

Because of the ability to make 5 or 6 bonds, the mechanism for the formation of silyl ethers could proceed in four ways:

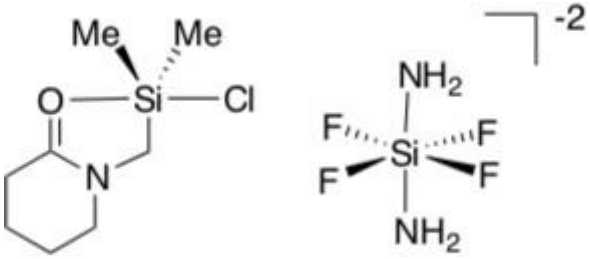


For each *of the mechanisms proposed above,*

- Draw the arrows showing electron flow.
- Circle the rds.
- Determine the molecularity of the reaction.

Mechanistic Studies

A number of complexes of the following type have been isolated and characterized by x-raycrystallography.



These complexes lend support to the existence of silicon complexes making 5 and 6 bonds.

- Which mechanisms have five and six coordinate reactive intermediates. The ability to make these stable structures supports the possibility of which reaction mechanisms? (circle one ortwo)

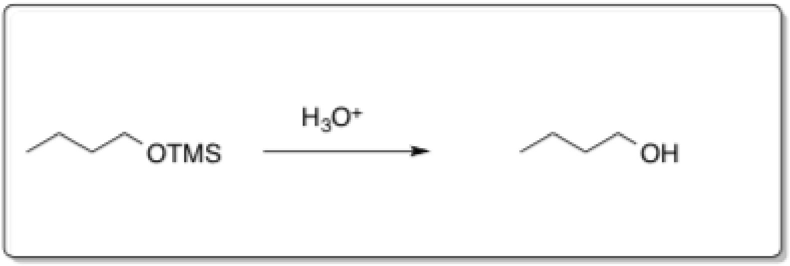
SN1-like SN2-like Pentavalent Intermediate Hexavalent Intermediate

The kinetic data suggests that the reaction is **second order** in the nucleophilic alcohol.

- Which reaction mechanism does this data support? (circle one)

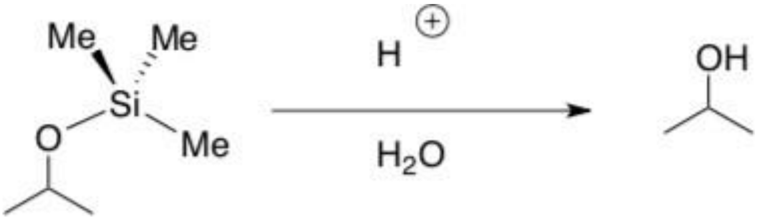
SN1-like SN2-like Pentavalent Intermediate Hexavalent Intermediate

Removal of a Silyl Ether

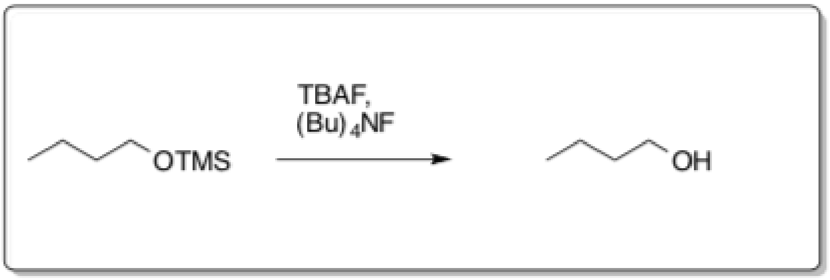


The silyl reaction is reversible. Often under acidic aqueous conditions.

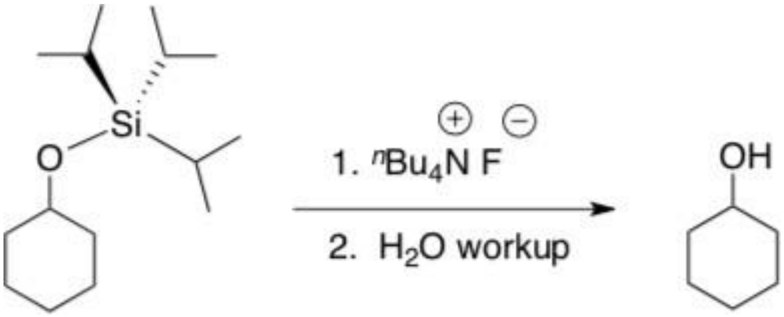
- Provide a likely mechanism with a hexavalent intermediate.



Bulkier silyl ethers are frequently cleaved via addition of fluoride salts using a similar mechanism. (Bu4NF is frequently abbreviated TBAF)



- Provide a likely mechanism for the reaction below. Include a hexavalent intermediate.



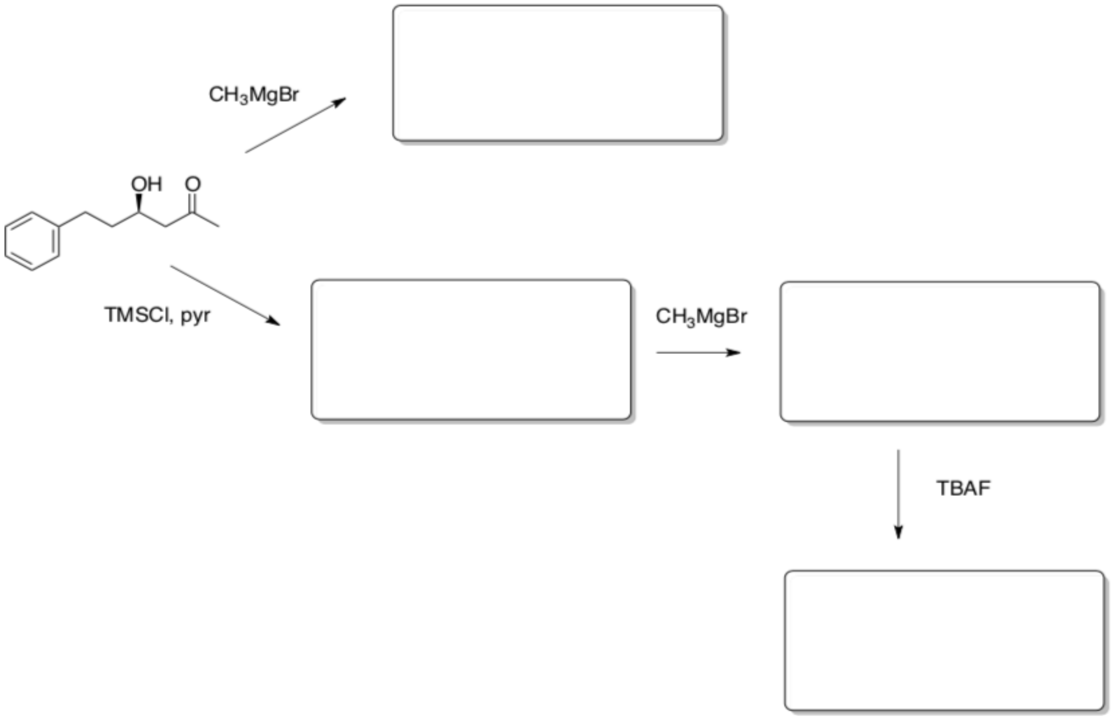
- Explain why this bulky silyl group can be reversed under with fluoride but not $H3O^+$. Consider size of H2O vs F^- as well as bond strengths (Si-O 108 kcal/mol; Si-F 135 kcal/mol).

Use of Silyl Ethers as Protecting Groups

Typically, silyl groups are added to alcohols when they might react with the reagent instead of the intended reaction.

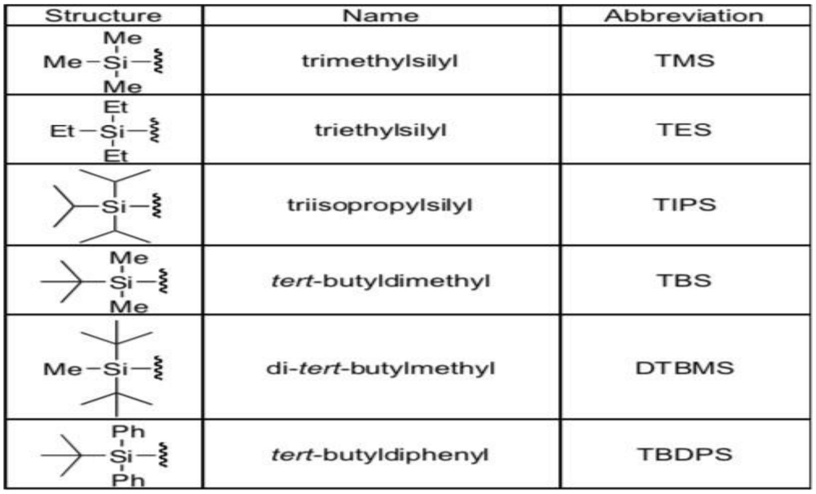
For example, Grignard reagents are strong bases and they tend to deprotonate alcohols rather than react with the carbonyl functional groups in the molecule.

- Complete the diagram below that shows this problem and how silyl groups can protect the alcohol functionality.



Common Silyl Ethers

Common silyl ethers are: trimethylsilyl (**TMS**), *tert*-butyldiphenylsilyl (**TBDPS**), *tert*-butyldimethylsilyl (**TBS/TBDMS**) and triisopropylsilyl (**TIPS**). They are particularly useful because they can be installed and removed very selectively under mild conditions.



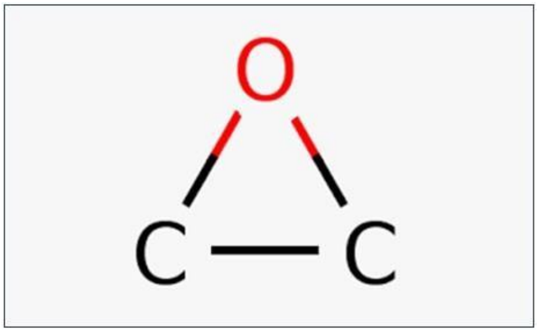
Structure	Name	Abbreviation
Me Me−Si− Me	trimethylsilyl	TMS
Et Et−Si− Et	triethylsilyl	TES
Si	triisopropylsilyl	TIPS
Me Si− Me	*tert*-butyldimethyl	TBS
Me−Si−	di-*tert*-butylmethyl	DTBMS
Ph Si− Ph	*tert*-butyldiphenyl	TBDPS

Small silyl ethers can be removed under acidic conditions.

Bulky ethers must be removed using TBAF (tetra-butyl ammonium fluoride).

Epoxide:

An epoxide is a cyclic ether which contains a three atom ring that approximates an equilateral triangle. These are highly reactive when compared to other ethers. The fundamental structure of it contains two carbon atoms of a hydrocarbon attached to an oxygen atom. The structure can be chemically shown as



Epoxide structure

Economically Ethylene oxide is the most important epoxide and is created by oxidation of ethylene over a silver catalyst. It is used as a fumigant and to make ethylene glycol, antifreeze and other useful compounds.

Epoxide synthesis:

Epoxide can be synthesized in many ways. Propylene oxide and Ethylene oxide are the two epoxides that are produced in a large scale, approximately 3 and 15 tonnes/year respectively.

- **Heterogeneously Catalyzed oxidation of alkenes**

When ethylene reacts with oxygen under a silver catalyst, epoxide is formed. According to stoichiometry, it can be chemically expressed as

$$7\ H_2C{=}CH_2 + 6\ O_2 \rightarrow 6\ C_2H_4O + 2\ CO_2 + 2\ H_2O$$

- **Homogeneously catalysed asymmetric epoxidation**

Chiral epoxides can be made from prochiral alkenes. Lot of metal complexes act as active catalysts and the most important among them are vanadium, molybdenum and titanium.

- **Nucleophilic epoxidation**

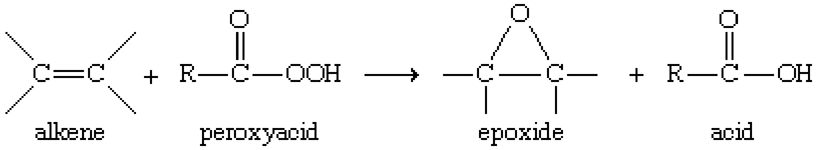
Electron deficient olefins can be epoxidized using compounds such as peroxides. This reaction has two steps: firstly, nucleophilic conjugate is added to an oxygen atom to give a stabilized carbanion.

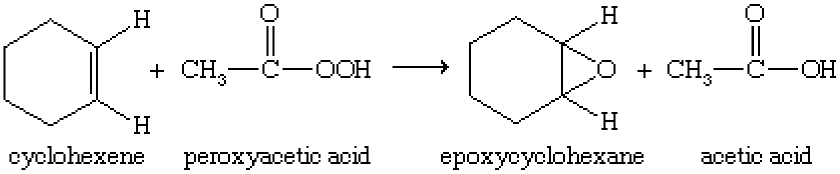
- **Biosynthesis**

Epoxides are not common in nature. They are produced generally by oxygenation of alkenes

Epoxides From Peracids:

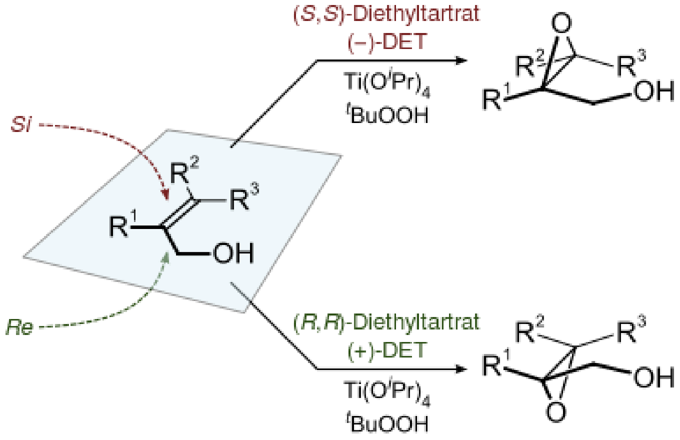
More-complex epoxides are commonly made by the epoxidation of alkenes, often using a peroxyacid (RCO_3H) to transfer an oxygen atom.





Sharpless Asymmetric Epoxidation:

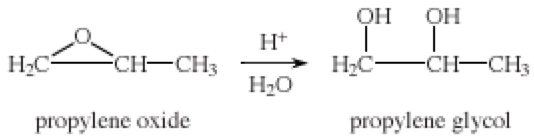
The **Sharpless epoxidation** reaction is an enantioselective chemical reaction to prepare 2,3-epoxyalcohols from primary and secondary allylic alcohols.



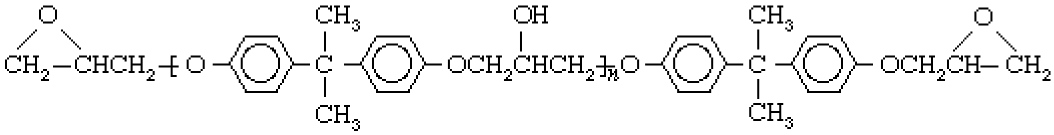
The stereochemistry of the resulting epoxide is determined by the enantiomer of the chiral tartrate diester (usually diethyl tartrate or diisopropyl tartrate) employed in the reaction. The oxidizing agent is *tert*-butyl hydroperoxide. Enantioselectivity is achieved by a catalyst formed from titanium tetra(isopropoxide) and diethyl tartrate. Only 5–10 mol% of the catalyst in the presence of 3Å molecular sieves (3Å MS) is necessary.

Reactions of Epoxides:

Epoxides are easily opened, under acidic or basic conditions, to give a variety of products with useful functional groups. For example, the acid- or base-catalyzed hydrolysis of propylene oxide gives propylene glycol.

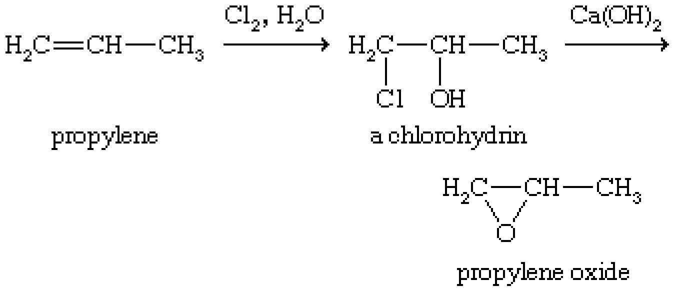


Epoxides can be used to assemble polymers known as epoxies, which are excellent adhesives and useful surface coatings. The most common epoxy resin is formed from the reaction of epichlorohydrin with bisphenol A.



Uses:

Another important industrial route to epoxides requires a two-step process. First, an alkene is converted to a chlorohydrin, and second, the chlorohydrin is treated with a base to eliminate hydrochloric acid, giving the epoxide; this is the method used to make propylene oxide.



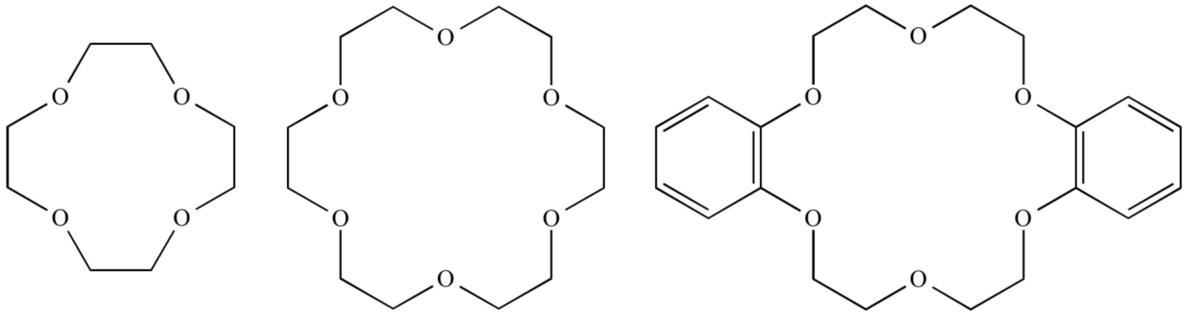
- Ethylene epoxide has many uses including generation of surfactants and detergents.
- Epoxy glues and structural materials are a result of epoxides reaction with amines.
- It is used as a stabilizer in materials like PVC. They are also used in manufacture of Epoxy resists that have low viscosity and without compromising strength and physical properties.

Epoxides are also used in things like insecticides, aerosols, resins and chemical intermediates.

Crown Ethers:

A series of cyclic ethers, featuring several oxygen atoms each separated by two carbon atoms. Called 'crown' ethers because their three-dimensional shape resembles a crown. Named as X-crown-Y, where X is the total number of atoms in the ring and Y is the total number of oxygen atoms. Crown ethers are notable because the exhibit selective cation binding (i.e., molecular recognition). For example, 12-crown-4 binds Li$^+$ more strongly than K$^+$, whereas 18-crown-6 binds K$^+$ more strongly than Li$^+$.

Structures



12-Crown-4 18-Crown-6 Dibenzo-18-crown-6

Some crown ethers.

APPLICATIONS OF CROWN ETHERS:

Phase Transfer Catalysts (PTCs):

- **Organic Synthesis:** Crown ethers are widely used as PTCs in organic synthesis to facilitate reactions between reagents in immiscible phases (e.g., aqueous and organic). They do this by encapsulating inorganic salts, making them soluble in organic solvents and increasing the reactivity of anions.
- **Examples:** Alkylations, oxidations, reductions, saponifications, esterifications, and nucleophilic substitutions.

Ion Transport and Separation:

- **Analytical Chemistry:** Crown ethers are used in ion-selective electrodes to selectively detect specific ions in solutions.
- **Environmental Remediation:** They are employed to extract heavy metal ions from wastewater and soil, purifying water and remediating contaminated sites.

- **Biochemical and Medical Applications:** Crown ethers are being explored for drug delivery, ion transport across cell membranes, and the development of artificial enzymes.

Host-Guest Chemistry:

- **Molecular Recognition and Sensing:** Crown ethers can selectively bind and recognize various molecules, including ions, amino acids, and drugs. This property is used in sensors and detection devices.
- **Catalysis:** Crown ethers can act as catalysts by binding and activating substrates within their cavities.

Other Applications:

- **Polymer Synthesis:** Crown ethers can be incorporated into polymers to create functional materials with ion transport or recognition capabilities.
- **Electrochemistry:** They are used in batteries and solar cells to improve ion transport and efficiency.
- **Nuclear Waste Treatment:** Crown ethers are being investigated for the separation of radioactive isotopes.

UNIT IV

THERMODYNAMICS-I

Definitions:

A primary goal of the study of thermochemistry is to determine the quantity of heat exchanged between a system and its surroundings. The **system** is the part of the universe being studied, while the **surroundings** are the rest of the universe that interacts with the system. A system and its surroundings can be as large as the rain forests in South America or as small as the contents of a beaker in a chemistry laboratory. The type of system one is dealing with can have very important implications in chemistry because the type of system dictates certain conditions and laws of thermodynamics associated with that system

Thermodynamics I, often referred to as Classical Thermodynamics, is a branch of physics concerned with the relationships between:

- **Heat:** The transfer of thermal energy between objects due to a temperature difference.
- **Work:** The transfer of energy that results in a force causing a displacement.
- **Temperature:** A measure of the average kinetic energy of the particles in a system.
- **Energy:** The capacity to do work.

In essence, Thermodynamics I focuses on **how energy is transferred and transformed within a system** and the limitations of these processes. It establishes fundamental principles governing energy exchanges and sets the stage for further exploration in higher-level thermodynamics courses.

Here are some key aspects of Thermodynamics I:

- **Systems and Surroundings:** It defines systems as specific parts of the universe under study and differentiates them from their surroundings. Understanding system boundaries is crucial for analyzing energy transfers.
- **Laws of Thermodynamics:** Four fundamental laws govern energy behavior in Thermodynamics I:
  - **Zeroth Law:** Defines thermal equilibrium and allows us to identify systems at the same temperature.
  - **First Law:** States that energy is conserved, and heat entering a system is either stored or used to perform work or both.

  - **Second Law:** Introduces the concept of entropy, a measure of disorder, and states that the total entropy of the universe always increases. This places fundamental limitations on the efficiency of energy conversions.
  - **Third Law:** Defines absolute zero, where entropy reaches a minimum for a perfect crystalline structure.
- **Thermodynamic State:** It emphasizes the concept of a thermodynamic state, defined by a set of measurable properties that uniquely describe the system. Changes in state relate to energy transfers.
- **Efficiency:** Thermodynamics I focuses on quantifying the efficiency of energy conversions, particularly the conversion of heat into work.

Thermodynamics I provides a powerful framework for understanding energy transformations in various fields, including:

- **Engineering:** Design of engines, power plants, and refrigeration systems.
- **Chemistry:** Understanding chemical reactions and their energy exchange.
- **Biology:** Analyzing energy flow in living organisms.
- **Material Science:** Predicting the behavior of materials under different temperature and pressure conditions.

SYSTEM:

ISOLATED SYSTEM

Now let's examine the type of system you have if you substituted a thermos for the saucepan. A thermos is used to keep things either cold or hot. Thus, a thermos does not allow for energy transfer. Additionally, the thermos, like any other closed container, does not allow matter transfer because it has a lid that does not allow anything to enter or leave the container. As a result, the thermos is what we call an isolated system. An **isolated system does not exchange energy or matter** with its surroundings. For example, if soup is poured into an insulated container (as seen below) and closed, there is no exchange of heat or matter. The fact that, in reality, a thermos is not perfect in keeping things warm/cold illustrates the difficulty in creating an truly isolated system. In fact, there are a few, if any, systems that exist in this world that are completely isolated systems.

Definition:

- An isolated system is a thermodynamic system that has **no interaction with its surroundings**. It cannot exchange matter or energy in any form, including heat, work, or radiation.
- It's a theoretical construct, as perfectly isolated systems don't exist in reality. However, many systems can be approximated as isolated for practical purposes.

Key Characteristics:

- **Total energy remains constant:** The internal energy (U) of an isolated system is conserved, as there's no energy transfer across its boundaries.
- **Entropy can increase or remain constant:** The entropy (S) of an isolated system can either increase or remain constant, depending on whether it's in equilibrium or not.
- **No external influences:** The behavior of an isolated system is solely determined by its internal properties and processes.

Applications:

- **Adiabatic processes:** Processes that occur without heat transfer, like rapid expansion or compression of gases, are often approximated as isolated systems.
- **Thermodynamic equilibrium:** Isolated systems eventually reach a state of thermodynamic equilibrium, where their properties become constant and no further change occurs.
- **Theoretical models:** Isolated systems serve as idealized models to study fundamental thermodynamic principles and concepts.

Examples of Approximate Isolated Systems:

- **Thermos flask:** Hot coffee in a thermos flask is approximately isolated, as heat transfer is minimized.
- **Insulated reaction vessel:** A well-insulated reaction vessel can be considered isolated for short-term reactions.
- **The universe:** The entire universe is sometimes considered an isolated system, although this is debated.

Importance in Thermodynamics:

- Isolated systems play a crucial role in understanding fundamental thermodynamic laws, such as:

- The First Law of Thermodynamics (energy conservation)
- The Second Law of Thermodynamics (entropy increase)
- The Third Law of Thermodynamics (unattainability of absolute zero)

Additional Points:

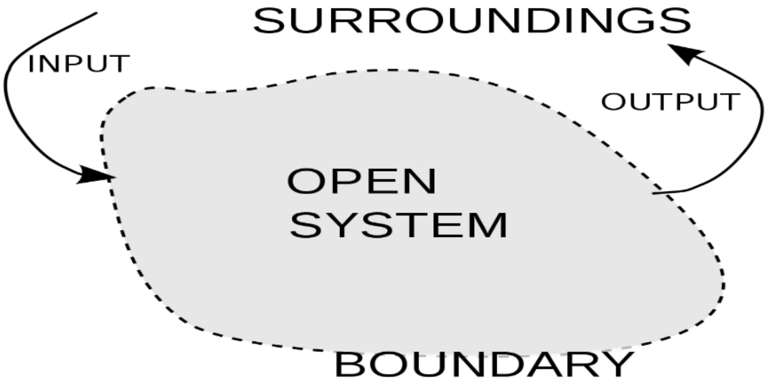
- **Contrast with other systems:** Isolated systems differ from closed systems (which can exchange energy but not matter) and open systems (which can exchange both).
- **Idealization:** While perfectly isolated systems don't exist, the concept is valuable for theoretical and practical applications.

OPEN SYSTEM

An **open system** is a system that freely exchanges *energy* and *matter* with its surroundings. For instance, when you are boiling soup in an open saucepan on a stove, energy and matter are being transferred to the surroundings through steam. The saucepan is an open system because it allows for the transfer of matter (for example adding spices in the saucepan) and for the transfer of energy (for example heating the saucepan and allowing steam to leave the saucepan).

Open Systems in Thermodynamics

- **Definition:** An open system is a thermodynamic system that can exchange both matter and energy with its surroundings. This contrasts with closed systems, which can only exchange energy, and isolated systems, which cannot exchange either matter or energy.



Open system in thermodynamics

Key Features:

- Matter can flow in and out of the system.
- Energy can be transferred in the form of heat and work.
- The system's boundaries are permeable to matter.
- The mass of the system can vary with time.

Examples:

- **Biological Systems:** All living organisms, including humans, plants, and animals, are open systems. They exchange matter (food, water, oxygen, waste products) and energy (heat, work) with their environment to maintain life processes.
- **Engines:** Internal combustion engines, steam turbines, and jet engines are open systems. They take in fuel and air, and release exhaust gases.
- **Chemical Reactors:** Chemical reactors are open systems where reactants are fed in and products are removed.
- **Refrigerators:** Refrigerators are open systems that transfer heat from the inside to the outside.
- **Earth's Atmosphere:** The atmosphere is an open system that exchanges matter and energy with the oceans, land, and space.
- **Mathematical Representation:**
- The general mass balance equation for an open system is: Accumulation = Inflow - Outflow + Generation - Consumption
- The energy balance equation is: Change in internal energy = Heat added - Work done + Energy inflow - Energy outflow

Applications:

- Understanding open systems is crucial in many fields, including:
  - Chemical engineering
  - Mechanical engineering
  - Environmental engineering
  - Biology
  - Earth science

CLOSED SYSTEM

Putting a lid on the saucepan makes the saucepan a closed system. A **closed system** is a system that exchanges **only energy** with its surroundings, not matter. By putting a lid on the saucepan, matter can no longer transfer because the lid prevents matter from entering the saucepan and leaving the saucepan. Still, the saucepan allows energy transfer. Imagine putting the saucepan on a stove and heating it. The saucepan allows energy transfer as the saucepan heats up and heats the contents inside it. For example, when a lid is put a beaker, it becomes a closed system. This fog and mist is the steam which covers the sides of the container because it cannot escape the beaker due to the lid. The fact that the beaker is able to produce this steam means that the beaker allows for energy transfer. Thus, even though a closed system cannot allow matter transfer, it can still allow energy transfer.

The methods of energy transfer in a closed system are the same as those described for an open system above.

CLOSED SYSTEMS IN THERMODYNAMICS:

Key Concepts:

- **Closed System:** A thermodynamic system that can exchange energy (as heat or work) with its surroundings, but not matter. The mass within the system remains constant.
- **Boundary:** A real or imaginary surface that separates the system from its surroundings.
- **Surroundings:** Everything outside of the system's boundary.

Energy Interactions:

- **Heat Transfer (Q):** The transfer of energy due to a temperature difference between the system and its surroundings.
  - Positive Q: Heat flows into the system.
  - Negative Q: Heat flows out of the system.
- **Work Transfer (W):** The transfer of energy due to a force acting through a distance.
  - Positive W: Work done on the system.
  - Negative W: Work done by the system.

First Law of Thermodynamics:

- **Conservation of Energy:** The total energy of a closed system remains constant, although it can change form.
- **Mathematical Expression:** $\Delta U = Q - W$
  - ΔU: Change in internal energy of the system

Internal Energy (U):

- The total energy stored within the system, including:
  - Kinetic energy of molecules
  - Potential energy of molecules
  - Chemical energy
  - Nuclear energy

Examples of Closed Systems:

- **A sealed, rigid container filled with gas**
- **A closed refrigerator**
- **A chemical reaction in a sealed flask**
- **A piston-cylinder device with valves closed**

Contrast with Other Systems:

- **Open System:** Can exchange both energy and matter with its surroundings.
- **Isolated System:** Cannot exchange energy or matter with its surroundings.

SURROUNDING:

STATE OF THE SYSTEM:

State of a function (system) is a condition of existence which is described by some measurable properties. For e.g.: water exists in three different states i.e. solid, liquid & gas depending upon the temperature at 1atm pressure.

The measurable properties of gaseous system are pressure, temperature, volume, mass or composition of substances. Any change in these properties will change the state of a system and these properties are called state variables.

Some state variables depend only on the initial and final state but not the path or process how it is carried out, and they are called state function.

If water is heated from 0°C to 50°C, then we say that the change in temperature is 50°C regardless the process how water is heated.

Intensive and Extensive Variables:

Intensive Variables:

- **Independent of the system's size or amount of matter.**
- **Remain constant if the system is divided into smaller parts.**
- **Common examples:**
    - Temperature (T)
    - Pressure (P)
    - Density (ρ)
    - Viscosity (μ)
    - Refractive index (n)
    - Specific heat capacity (c)
    - Boiling point (at a given pressure)
    - Melting point (at a given pressure)

Extensive Variables:

- **Scale with the system's size or amount of matter.**
- **Add up when two systems are combined.**
- **Common examples:**
    - Volume (V)
    - Mass (m)
    - Energy (E)
    - Enthalpy (H)
    - Entropy (S)
    - Gibbs free energy (G)
    - Number of moles (n)

Key Points:

- **Ratios of extensive variables are intensive variables.** For example, density ($\rho = m/V$) and specific heat capacity ($c = C/m$) are intensive.
- **Extensive variables can be converted to intensive variables through specific quantities.** For example, volume per unit mass (specific volume, $v = V/m$) and energy per unit mass (specific energy, $e = E/m$) are intensive.
- **Intensive variables are often used to describe the equilibrium state of a system:**

  - Systems in equilibrium have the same values of intensive variables throughout.
  - Temperature and pressure are crucial for determining phase equilibrium.
- **Extensive variables are essential for analyzing energy transfer and thermodynamic processes:**
  - Internal energy changes, heat transfer, and work done in processes depend on extensive variables.

Importance in Thermodynamics:

- **Classifying thermodynamic properties:** This distinction aids in understanding their behavior and relationships.
- **Defining thermodynamic state:** The state of a simple compressible system is fully specified by two independent intensive properties and one extensive property (e.g., mass).
- **Analyzing thermodynamic processes:** Understanding these variables is crucial for analyzing energy transfers and system changes.
- **Applying to real-world systems:** These concepts are used in various fields, including engineering, chemistry, and physics.

EXTENSIVE VARIABLE

Those state variables that depend upon the quality of matter are called extensive variables. For e.g.: mass, moles, volume, internal energy, enthalpy, entropy and free energy.

Intensive variable

Those state variables that depend upon the property of matter are called intensive variables. For e.g.: temperature, density, refractive index, etc.

THERMODYNAMIC PROCESSES:

Thermodynamic processes are the heartbeat of energy transfer, governing how systems change from one state to another. They underpin the workings of engines, refrigerators, and even natural phenomena like weather systems.

To delve deeper, let's explore some key points:

What is a thermodynamic system?

It's a defined region within the universe where we study energy transfer and transformations. Think of a piston cylinder in an engine or a closed bottle containing gas.

What are the main types of thermodynamic processes?

- **Isothermal:** Temperature remains constant (think ice melting in a warm room).
- **Adiabatic:** No heat transfer occurs (imagine compressing a gas in a perfectly insulated container).
- **Isobaric:** Pressure remains constant (like a pressure cooker releasing steam).
- **Isochoric:** Volume remains constant (e.g., heating a sealed container of water).

Why are these processes important?

They simplify complex energy exchanges, allowing us to analyze and predict system behavior. Understanding these processes helps us:

- Design efficient engines and power plants.
- Develop new chemical technologies.
- Model and understand climate change.

Beyond the basics:

There are many other fascinating aspects of thermodynamic processes, such as:

- **Cyclic processes:** Systems return to their initial state, allowing for work to be done (e.g., the Carnot cycle in heat engines).
- **Reversible processes:** Theoretically perfect processes with no energy dissipation (impossible in reality).
- **Entropy:** A measure of disorder, always increasing in isolated systems.

Isothermal process

Any physical or chemical process in which the temperature remains constant during the state changeis called isothermal process.

Here, $\Delta T=0$

Adbiatic process

Any physical or chemical process which takes place without flow of heat in or out of system duringthe state change is called adbiatic process.

Here, $\Delta Q=0$

Isobaric process

Any physical or chemical process in which the pressure of the system remains constant during the state change is called isobaric process.

Here, $\Delta P=0$

Isochoric process

Any physical or chemical process in which the volume remains constant during the state change is called isochoric process.

Here, $\Delta V=0$

Reversible and Irreversible:

Reversible process	**Irreversible process**
The process goes through infinite change so, it takes infinite time to complete.	The process goes through finite change so, it takes finite time to complete.
The process proceeds infinitesimally slowly maintaining the equation state.	This process is faster; the equilibrium state is maintained only at initial and final position of system.
During the state change it is in equilibrium state at all stages	Its is not equilibrium state during the stage change,driving force is always greaterthen opposing force.
This procsee only assumption impracticable	This procees is real and practicable

STATE AND PATH FUNCTIONS:

Thermodynamics: State and Path Functions

In thermodynamics, we deal with various properties of systems that describe their state and behavior. These properties can be broadly categorized into two types: state functions and path functions.

State functions are properties that depend only on the current state of the system, not on the path taken to reach that state. They are essentially snapshots of the system's condition at a particular moment. Examples of state functions include:

- **Temperature:** A measure of the hotness or coldness of a system.
- **Pressure:** The force exerted per unit area on the boundaries of a system.
- **Volume:** The amount of space occupied by a system.
- **Internal energy:** The total energy contained within a system.
- **Enthalpy:** A combination of a system's internal energy and the product of its pressure and volume.
- **Entropy:** A measure of the disorder or randomness of a system.

State functions can be conveniently represented by points on a state diagram, such as a pressure-volume (P-V) diagram or a temperature-entropy (T-S) diagram. These diagrams allow us to visualize the changes in state of a system without worrying about the specific path taken.

Path functions, on the other hand, depend on the specific path taken by the system between two states. They represent the process of change itself, not just the end points. Examples of path functions include:

- **Heat:** The transfer of thermal energy between a system and its surroundings.
- **Work:** The transfer of energy between a system and its surroundings that is due to a force acting through a distance.
- **Heat engine efficiency:** The ratio of the work done by a heat engine to the heat it absorbs.

Path functions cannot be represented by single points on a state diagram. They require us to specify the entire path taken by the system.

Here's an analogy to help understand the difference between state and path functions: Imagine you are driving from point A to point B in a city. The distance between A and B is a state function – it only depends on the starting and ending points, regardless of the specific route you take. However, the time it takes to complete the journey is a path function – it depends on the traffic conditions, the roads you choose, and even your driving speed.

Understanding the difference between state and path functions is crucial in various thermodynamic calculations and analyses. It allows us to accurately predict the behavior of systems and optimize processes for efficiency.

WORK OF EXPANSION AT CONSTANT PRESSURE AND AT CONSTANT VOLUME:

The work done by a system during expansion or compression can be analyzed in two specific scenarios: constant pressure and constant volume. Understanding these different situations is crucial in thermodynamics when dealing with energy transfer and changes in system properties.

Work at Constant Pressure:

- **Process:** This occurs when the pressure remains constant throughout the expansion or compression. Imagine a gas confined in a cylinder with a movable piston, where the external pressure on the piston stays fixed.
- **Formula:** The work done (W) can be calculated using the formula: $W = P * \Delta V$, where:
  - P is the constant pressure
  - ΔV is the change in volume of the system (final volume - initial volume)
- **Interpretation:** The work done is directly proportional to the pressure and the change in volume. Positive work signifies expansion (system doing work on the surroundings), while negative work represents compression (work done on the system by the surroundings).
- **Example:** If a gas expands from 2 liters to 4 liters at a constant pressure of 1 atm, the work done would be W = 1 atm * (4 liters - 2 liters) = 2 atm*L.

Work at Constant Volume:

- **Process:** This occurs when the volume of the system remains constant throughout the change in temperature or pressure. Imagine the same gas cylinder with a fixed volume, like a sealed container.
- **Formula:** In this case, the work done is zero because the system undergoes no displacement, even though the pressure or temperature may change. ΔV is zero, thus $W = P * \Delta V = 0$.

- **Interpretation:** Since there is no change in volume, the system exerts no force against the surroundings, and hence, no work is done.
- **Example:** If the gas in the sealed container is heated at constant volume, its temperature and pressure will increase, but the work done remains zero (W = 1 atm * 0 L = 0).

First Law of Thermodynamics:

Energy cannot be created or destroyed, only transformed from one form to another.

This means that the total amount of energy in a closed system remains constant, even though it may change form. For example, when you burn wood, the chemical energy stored in the wood is converted into heat and light energy. The total amount of energy remains the same, but it's just been transformed into different forms.

Here are some key points about the First Law:

- **Heat and work are the two main forms of energy transfer.** Heat is transferred through thermal contact, while work is done by a system against an external force.
- **Internal energy (U) is the total energy of a system.** It includes all forms of energy within the system, such as kinetic, potential, and chemical energy.
- **The change in internal energy (ΔU) of a system is equal to the difference between the heat (Q) added to the system and the work (W) done by the system:** $\Delta U = Q - W$.
- **The First Law applies to both closed and isolated systems.** A closed system is one that exchanges energy with the surroundings (e.g., a car engine), while an isolated system does not exchange energy with the surroundings (e.g., a thermos bottle).

The First Law of Thermodynamics has numerous applications in various fields, including:

- **Engineering:** Designing efficient engines and power plants.
- **Chemistry:** Understanding chemical reactions and predicting their energy changes.
- **Biology:** Studying the energy flow in living organisms.
- **Cosmology:** Understanding the evolution of the universe.

- Total energy in the universe remains constant.
  Energy can neither be created nor be destroyed but can be transferred from one form to another.

  When Q amount of heat is supplied to the system, some part of it is used up to increase in its internal energy and remaining some part of it is used up for work done.

  i.e. $Q=\Delta E+W$……………….(1)

  If work is done by the system. $Q=\Delta E-W$ (2)
  If work is done on the system. Where, Q= heat supplied
  W=work done

  ΔE=change in internal energy.

  ΔE at constant volume
  We have, from first law of thermodynamics; $Q=\Delta E+W$
  $Q=\Delta E+P\Delta V$

  At constant volume, $\Delta V=0$ So, $Q=\Delta E$
  It means, at constant volume condition, the total amount of heat supplied is equal to change Internal energy of system.

  ΔE at adbiatic condition
  We have, from first law of thermodynamics; $Q=\Delta E+W$
  At adbiatic condition, $Q=0$ So, $-W=\Delta E$
  It means, at adbiatic condition, the work is done by utilizing the Internal energy of system.

Advantages of first law of thermodynamics

a. Total energy of the universe remains constant.

b. Different forms of energy are inter-convertible.

c. When one form of energy disappears, an equivalent amount of energy in another form appears.

Disadvantages of first law of thermodynamics

a. It doesn't tell the extent and direction of the convertibility of one form of energy to another.

b. It doesn't tell why chemical reactions do not proceed to completion.

c. It doesn't tell why natural processes are unidirectional.

d. It doesn't explain the feasibility and spontaneity of a process.

e. It says the equivalency of work and heat. But it has been observed that the work can be completely transformed into heat but heat cannot be transformed into work without permanent change in the system or surrounding which is not explained by the law.

Statement- Definition of Internal Energy (E):

A compound itself has a definite amount of energy which includes kinetic energy, potential energy, energy of atom, constituting molecules and chemical bond energy. The sum of these different forms of energy (molecules) is called internal energy denoted by E. Internal energy is the state function so, it depends upon initial and final state and also its absolute value cannot be determined however change can be measured.

Now, change in internal energy is given by:

$\Delta E = E_p - E_r$

Where, ΔE= change in Internal energy.

E_p= Internal energy of product. E_r= Internal energy of reactant.

Sign convention of heat and work

1. **Heat (q)**

   Case I:

   When heat is absorbed by the system, q = +ve.

   Case II:

   When heat is released by the system, q = -ve.

2. Work (w)

   Case I: (Work of Expansion)

   When work is done by the system, w = +ve.

   Case II: (Work of Compression)

When work is done on the system, w = -ve.

Enthalpy (H):

It is the sum of internal energy and product of pressure and volume.

i.e. $H=E+PV$.....(1)

Here, E, P & V all are state function so H is also the state function.

Being a state function it depends upon initial and final state and also its absolute value cannot be determined however change can be measured.

Now,........................$\Delta H=H_p-H_r$ (2)

Where, H_p= enthalpy of product

H_r= Enthalpy of reactant

ΔH at constant pressure

We have, from first law of thermodynamics; $Q=\Delta E+W$

$Q=\Delta E+P\Delta V$....(1) Also, $H=E+PV$... (2)

At constant pressure, $Q=Q_p$ So, equation (1) becomes,

$Q_p=E_p-E_r+P(V_p-V_r)$

$Q_p=E_p+PV_p-(E_r+PV_r)$

$Q_p=H_p-H_r$

It means, heat of reaction at constant pressure is equal to change in enthalpy of reaction.

Heat Capacity:

When heat is absorbed by a body, the temperature of the body increases. And when heat is lost, the temperature decreases. The temperature of an object is the measure of the total kinetic energy of the particles that make up that object. So when heat is absorbed by an object this heat gets translated into the kinetic energy of the particles and as a result the temperature increases. Thus, the change in temperature is proportional to the heat transfer.

The formula **$q = n C \Delta T$** represents the heat q required to bring about a **ΔT** difference in temperature of one mole of any matter. The constant **C** here is called the molar heat capacity of the body. Thus, the molar heat capacity of any substance is defined as the amount of heat energy required to change the temperature of 1 mole of that substance by 1 unit. It depends on the nature, size, and composition of the system.

Relationship Between Cp And Cv:

- The molar heat capacity C, at constant pressure, is represented by **C_P**.
- At constant volume, the molar heat capacity C is represented by **C_V**.

In the following section, we will find how C_P and C_V are related, for an ideal gas.

The relationship between C_P and C_V for an Ideal Gas

From the equation **$q = n C \Delta T$**, we can say:

At constant pressure P, we have

$$q_P = n C_P \Delta T$$

This value is equal to the change in enthalpy, that is,

$$q_P = n C_P \Delta T = \Delta H$$

Similarly, at constant volume V, we have

$$q_V = n C_V \Delta T$$

This value is equal to the change in internal energy, that is,

$qV = n\ CV\Delta T = \Delta U$

We know that for one mole (n=1) of an ideal gas,

$\Delta H = \Delta U + \Delta(pV)$ $= \Delta U + \Delta(RT) = \Delta U + R\ \Delta T$

Therefore, **$\Delta H = \Delta U + R\ \Delta T$**

Substituting the values of ΔH and ΔU from above in the former equation,

$CP\Delta T = CV\Delta T + R\ \Delta TCP = CV + R$

$CP - CV = R$

Calculation of W:

Defined as mechanical energy equal to the product of the force (F) applied to an object and the distance (d) that the object is moved:

$$w = F \times d$$

Work, like heat, results from interaction between a system and its surroundings. Chemical reactions can do two types of work:

Electrical work - When a reaction is used to drive an electric current through a wire.

e.g. a light bulb

Work of expansion - When a reaction causes a change in the volume of the system.

e.g. a gas pushing up a piston

The magnitude of work done when a gas expands is equal to the product of the pressure of the gas and the change in volume of the gas:

$$|w| = P\Delta V$$

Calculation of Q:

A form of energy associated with the random motion of the elementary particles in matter.

Heat capacity - The amount of heat needed to raise the temperature of a defined amount of a pure substance by one degree.

Specific heat - The amount of heat needed to raise the temperature of **one gram** of a substance by 1 °C (or 1 K)

SI unit for specific heat is joules per gram^{-1} Kelvin^{-1} (J/g-K)

Calorie - The specific heat of water = 4.184 J/g-K

Molar heat capacity - The amount of heat required to raise the temperature of **one mole** of a substance by 1 °C (or 1 K)

SI unit for molar heat capacity is joules per mole^{-1} Kelvin^{-1} (J/mol-K)

Btu (British thermal unit) - The amount of heat needed to raise the temperature of 1 lb water by 1 °F.

Note: The specific heat of water (4.184 J/g-K) is very large relative to other substances. The oceans (which cover over 70% of the earth) act as a giant "heat sink," moderating drastic changes in temperature. Our body temperatures are also controlled by water and its high specific heat.
Perspiration is a form of evaporative cooling which keeps our body temperatures from getting too high.

Thermochemistry:

Thermochemistry - A branch of thermodynamics which focuses on the study of heat given off or absorbed in a chemical reaction.

Temperature - An intensive property of matter; a quantitative measurement of the degree to which an object is either "hot" or "cold".

1. There are 3 scales for measuring temperature

- **Fahrenheit** - relative
  - 32 F is the normal freezing point temperature of water; 212 F is the normal boiling point temperature of water.
- **Celsius** (centigrade) - relative
  - 0 C is the normal freezing point temperature of water; 100 C is the normal boiling point temperature of water.
- **Kelvin** - absolute
  - 0 K is the temperature at which the volume and pressure of an ideal gas extrapolate to zero.

Conversion Factors for Temperature

$$K = {}^{\circ}C + 273.15$$

$$^{\circ}C = \frac{5}{9}(^{\circ}F - 32)$$

$$^{\circ}F = \frac{9}{5}(^{\circ}C) + 32$$

Relationship between Enthalpy of Reaction at Constant Volume (qv) And At Constant Pressure (qp):

We define the enthalpy change (ΔH) as the heat of a process when pressure is held constant: $\Delta H \equiv q$ at constant pressure
When a chemical reaction occurs, there is a characteristic change in enthalpy. The enthalpy change for a reaction is typically written after a balanced chemical equation and on the same line.

For example, when two moles of hydrogen react with one mole of oxygen to make two moles of water, the characteristic enthalpy change is 570 kJ. We write the equation as

$2 H_2(g) + O_2(g) \rightarrow 2 H_2O(\ell)$ $\Delta H = -570$ kJ

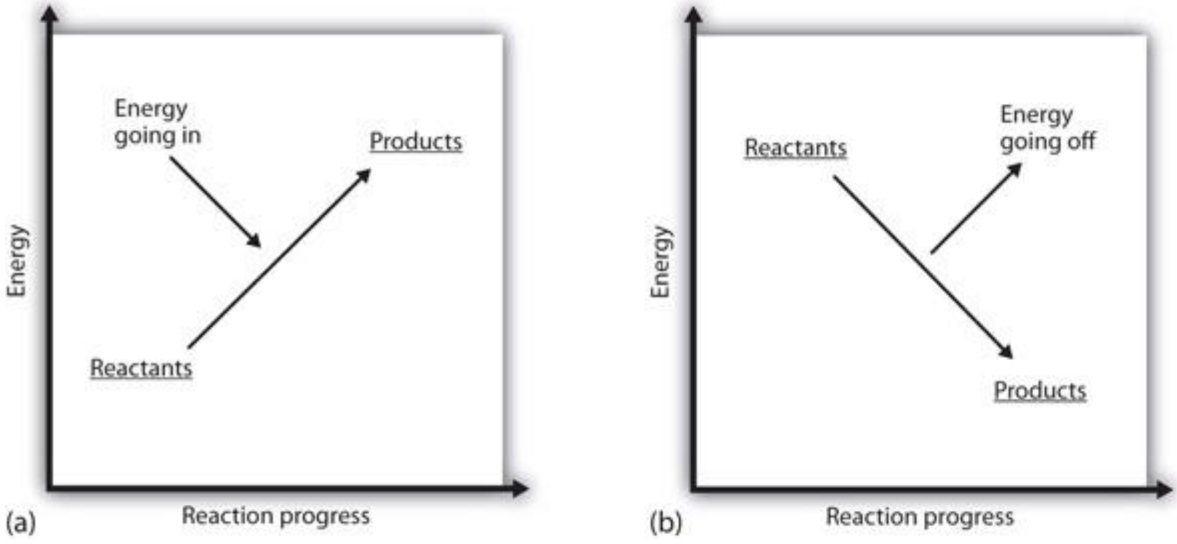
A chemical equation that includes an enthalpy change is called a thermochemical equation. A thermochemical equation is assumed to refer to the equation in molar quantities, which means it must be interpreted in terms of moles, not individual molecules.

You may have noticed that the ΔH for a chemical reaction may be positive or negative. The number is assumed to be positive if it has no sign; a + sign can be added explicitly to avoid confusion. A chemical reaction that has a positive ΔH is said to be endothermic, while a chemical reaction that has a negative ΔH is said to be exothermic.

What does it mean if the ΔH of a process is positive? It means that the system in which the chemical reaction is occurring is gaining energy. If one considers the energy of a system as being represented as a height on a vertical energy plot, the enthalpy change that accompanies the reaction can be diagrammed as in part (a) in Figure “Reaction Energy”: the energy of the reactants has some energy, and the system increases its energy as it goes to products. The products are higher on the vertical scale than the reactants. Endothermic, then, implies that the system *gains*, or absorbs, energy.

An opposite situation exists for an exothermic process, as shown in part (b) in Figure “Reaction Energy”. If the enthalpy change of a reaction is negative, the system is losing energy, so the products have less energy than the reactants, and the products are lower on the vertical energy scale than the reactants are. Exothermic, then, implies that the system *loses*, or gives off, energy.

Figure for Reaction Energy



(a) In an endothermic reaction, the energy of the system increases (i.e., moves higher on the vertical scale of energy).

(b) In an exothermic reaction, the energy of the system decreases (i.e., moves lower on the vertical scale of energy).

Temperature Dependence of Heat of Reaction:

It is often required to know thermodynamic functions (such as enthalpy) at temperatures other than those available from tabulated data. Fortunately, the conversion to other temperatures is not difficult.

At constant pressure

$dH=CpdT$ *(1)*

And so for a temperature change from $T1$ to $T2$

$\Delta H=\int T2T2CpdT$ *(2)*

The above equation is often referred to as *Kirchhoff's Law*. If *Cp* is independent of temperature, then

$\Delta H=Cp\Delta T$ *(3)*

If the temperature dependence of the heat capacity is known, it can be incorporated into the integralin Equation 2. A common *empirical* model used to fit heat capacities over broad temperature ranges is

$Cp(T)=a+bT+cT2$ *(4)*

After combining Equations 4 and 2, the enthalpy change for the temperature change can be foundobtained by a simple integration

$\Delta H=\int T2T1(a+bT+cT2)dT$ *(5)*

Solving the definite integral yields

$\Delta H=[aT+b2T2-cT]T2T1=a(T2-T1)+b2(T22-T21)-c(1T2-1T$ *(6)(7)*

This expression can then be used with experimentally determined values of *a*, *b*, and *c*, some ofwhich are shown in the following table

Kirchoff’s Equation:

Kirchhoff's Law describes the enthalpy of a reaction's variation with temperature changes. In general, enthalpy of any substance increases with temperature, which means both the products and the reactants' enthalpies increase. The overall enthalpy of the reaction will change if the increase in the enthalpy of products and reactants is different.

At constant pressure, the heat capacity is equal to change in enthalpy divided by the change in temperature.

$cp=\Delta H\Delta T$ (1)

Therefore, if the heat capacities do not vary with temperature then the change in enthalpy is a function of the difference in temperature and heat capacities.

The amount that the enthalpy changes by is proportional to the product of temperature change and change in heat capacities of products and reactants.

A weighted sum is used to calculate the change in heat capacity to incorporate the ratio of the molecules involved since all molecules have different heat capacities at different states.

$HTf=HTi+\int TfTicpdT$ (2)

If the heat capacity is temperature independent over the temperature range, then Equation 1 can be approximated as $HTf=HTi+cp(Tf-Ti)$ (3) With cp is the (assumed constant) heat capacity and HTi and HTf are the enthalpy at the respective temperatures.

Equation 3 can only be applied to small temperature changes, (<100 K) because over a larger temperature change, the heat capacity is not constant. There are many biochemical applications because it allows us to predict enthalpy changes at other temperatures by using standard enthalpy data.

Bond Energy and its Calculation From Thermochemical Data:

Bond energy of a bond is amount of energy required to break 1 mole of a bond in gaseous state or energy released when one mole of a bond is formed in gaseous state. In terms of bond energy, Heat reaction = Heat absorbed – Heat released = bond energies of reactants – bond energies of products.

Estimate the enthalpy change for the reaction

H_2 (g) + Cl_2 (g) → 2HCl (g) Given bond energy of H – H = 435 KJ mole^{-1}
Bond energy of Cl-Cl = 243 KJmole^{-1} Bond energy of H-Cl = 430 KJmole^{-1}

Sol:

The amount of energy released during formation of 2moles of H-Cl bond = 2 × 430 = 860 KJ H reaction = Energy absorbed – Energy released

= 618 – 860

= -182 KJ

Calculate the enthalpy change for the hydrogenation of ethane gas.

$CH_2 = CH_2$ (g) + H_2 (g) → $CH_3 – CH_3$ (g)

Given, bond energy of H -H bond = 435 KJ mole^{-1} Bond energy of C – H bond = 413 KJ mole^{-1} Bond energy of C -C bond = 347 KJ mole^{-1} Bond energy of C=C bond = 615 KJ mole^{-1}

The amount of energy absorbed during reaction

= 413 × 4 + 615 + 435

= 2702 KJ

Energy released during reaction

= 6 × 413 + 347

= 2825 KJ

H reaction = 2825 – 2702 KJ = -123 KJ

Integral and Differential Heats of Solution:

Here's a comprehensive explanation of integral and differential heats of solution:

Integral Heat of Solution ($\Delta\mathrm{Hsoln}$):

- Represents the **total enthalpy change** (heat absorbed or released) when **one mole of solute is dissolved in a specific amount of solvent** to form a solution of a certain concentration.
- It's a **macroscopic** property that considers the overall energy change of the entire solution process.
- It's often expressed as joules per mole (J/mol) or kilojoules per mole (kJ/mol).
- It **depends on the nature of the solute, the solvent, and the concentration of the final solution.**

Differential Heat of Solution ($\partial\Delta\mathrm{Hsoln}/\partial m$):

- Represents the **instantaneous enthalpy change** (heat absorbed or released) **per mole of solute** when an **infinitesimally small amount of solute is added** to a solution of a **particular concentration**.
- It's a **microscopic** property that measures the change in energy associated with each additional solute molecule at a specific point in the solution process.
- It's often expressed as joules per mole per kilogram of solvent (J/mol·kg) or kilojoules per mole per kilogram of solvent (kJ/mol·kg).
- It **varies with the concentration of the solution.**

Key Differences:

Feature	**Integral Heat of Solution**	**Differential Heat of Solution**
Amount of solute	Specific amount	Infinitesimal amount
Concentration	Fixed	Varies with addition
Measure	Total enthalpy change	Instantaneous enthalpy change
Representation	$\Delta\mathrm{Hsoln}$	$\partial\Delta\mathrm{Hsoln}/\partial m$

Relationship:

The differential heat of solution is the partial derivative of the integral heat of solution with respect to the molality of the solute. In other words, it's the slope of the integral heat of solution curve at a particular concentration.

Importance:

- Understanding these concepts is crucial in various fields, including:
- Thermochemistry
- Chemical thermodynamics
- Solution chemistry
- Industrial processes involving solutions
- Biological systems where solute transport and energy changes occur

Dilution:

When one mole of a substance is dissolved in a specified quantity of solvent in a large number of steps the enthalpy change per mole of solid for each step is called the differential heat of solution. Sometimes it is desirable to define another enthalpy term known as **enthalpy of dilution.** The heat of dilution is the difference between two integral heats of solutions.

Considering example**:** If some ammonium chloride or glucose is added to water in a test tube the tube becomes cooler. On the other hand if some solid NaOH is added to the test tube the water becomes quite warm. These are examples of a common experience that when solids are dissolved in water heat is either absorbed or evolved.

$Na^+ OH^- (s) + H2O (l) \rightarrow Na^+ (aq) + OH^- (aq)$; $\Delta H = -40 \text{ kJ mol}^{-1}$ $NH4^+ NO3^- (s) + H2O (l) \rightarrow NH4^+ (aq) + NO3^- (aq)$; $\Delta H = +26 \text{ kJ mol}^{-1}$
The heat of a solution of NaOH in water, the heat of solution of 1.0 mole of NaOH in 5 moles of water and in 200 moles of water are respectively – 37.8 and -42.3 kJ. Thus, in the above example of enthalpy of solution of NaOH the difference between the two values, – 4.5 kJ would be the enthalpy of dilution.

On many occasions it is essential to know the enthalpy of solution at infinite dilution. If we keep on diluting a solution by gradual addition of the solvent there will be heat change at each dilution.

Finally a stage will come when any further dilution produces no thermal change. This stage is called the state of infinite dilution. The enthalpy of solution at infinite dilution is defined as:

"The enthalpy change when one mole of a substance is dissolved in such a large volume of solvent so that any further dilution produces no thermal effect".

The integral heat of solution reaches a limiting value at infinite dilution. Thus if 1.0 mole of $HC1$ is dissolved in a large volume of water so that no heat change is observed when more water is added one can write

$$\mathbf{HCl\,(g) + aq \rightarrow HC1(aq);\ \ \Delta H^{0} = -\,75.1\ kJ}$$

UNIT V

CHEMICAL KINETICS

RATE OF REACTION:

The rate of reaction or reaction rate is the speed at which reactants are converted into products. When we talk about chemical reactions, it is a given fact that rate at which they occur varies by a great deal. Some chemical reactions are nearly instantaneous, while others usually take some time to reach the final equilibrium.

This article aims to help students learn about and understand what exactly is the rate of reaction for a given chemical compound.

This article aims to help students learn about and understand what exactly is the rate of reaction for a given chemical compound.

As per the general definition, the speed with which a reaction takes place is referred to as the rate of a reaction.

For example, wood combustion has a high reaction rate since the process is fast and rusting of iron has a low reaction rate as the process is slow.

Chemical kinetics is the study of the rates of chemical reactions and the factors that influence them. It's a fascinating branch of chemistry, delving into the dynamics of how molecules interact and rearrange themselves to form new products.

To explore the rate of a reaction, we can delve into various aspects:

1. **Factors Affecting Rate:** Numerous factors can influence the pace of a reaction, like:

- **Reactant Concentration:** Generally, increasing the concentration of reactants leads to a faster reaction due to more frequent collisions between molecules.
- **Temperature:** Higher temperatures typically increase the rate by providing more kinetic energy to overcome the activation energy barrier.
- **Pressure (for gas-phase reactions):** Increasing pressure in gas-phase reactions can push molecules closer together, potentially speeding up the collision rate.
- **Surface Area (for heterogeneous reactions):** Involving a solid and a fluid, increasing the surface area of the solid reactant can provide more contact points for the reaction to occur.

- **Catalyst Presence:** Catalysts can lower the activation energy barrier, thus accelerating the reaction without being consumed themselves.

2. **Rate Laws and Expressions:** Rate laws mathematically express the relationship between the rate of a reaction and the concentrations of its reactants. Rate expressions, derived from rate laws, provide numerical values for the rate constant, which reflects the inherent reactivity of the system.
3. **Reaction Mechanisms:** Understanding the step-by-step sequence of elementary reactions that constitute a complex reaction helps explain its overall rate and identify potential rate-determining steps.
4. **Order of Reaction:** The order of a reaction refers to the dependence of the rate on the reactant concentrations raised to their respective exponents in the rate law. Determining the reaction order helps predict how the rate changes with concentration variations.

Chemical kinetics finds applications in diverse fields like industrial processes, environmental science, medicine, and even astrochemistry. Delving deeper into this realm unveils the intricate dance of molecules as they transform, revealing the secrets of reaction rates and their governing principles.

RATE EQUATION:

What is a rate equation?

- In chemical kinetics, the rate equation (or rate law) is a mathematical expression that describes how the **rate of a reaction** depends on the **concentrations of the reactants**.
- It's essential for understanding and predicting how reactions proceed over time.

General form of a rate equation:

Rate = k[A]^m[B]^n...

- **Rate:** The speed at which the reaction occurs, usually expressed in units of concentration per unit time (e.g., M/s).
- **k:** The **rate constant**, a proportionality constant that depends on factors like temperature and the nature of the reactants. It's specific to a particular reaction.
- **[A], [B], ...:** The molar concentrations of the reactants.
- **m, n, ...:** The **reaction orders** with respect to each reactant, indicating how the concentration of that reactant affects the rate.

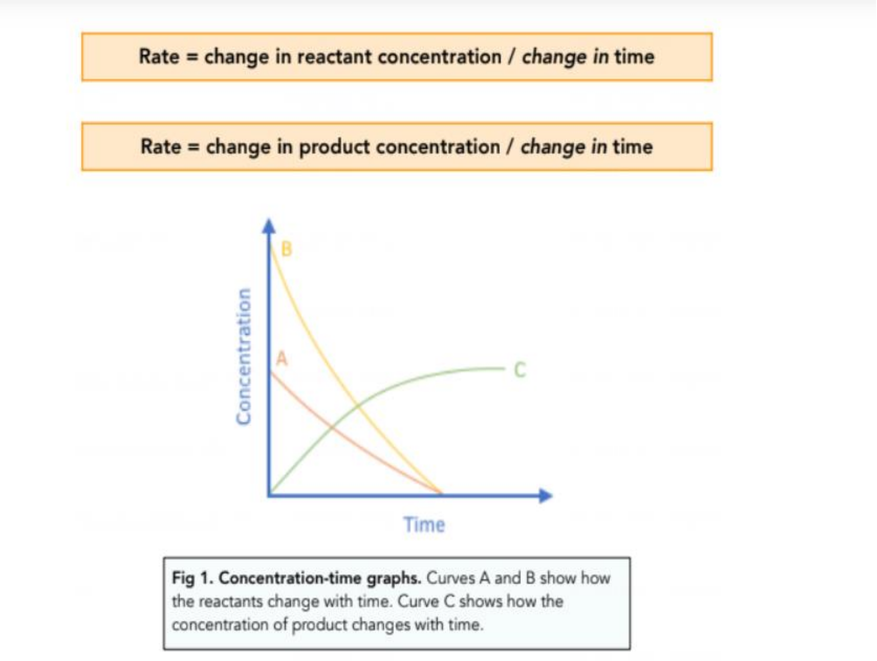
Determination of rate equation:

- The rate equation can't be deduced from the balanced chemical equation but must be determined experimentally.
- This involves measuring the reaction rate at different initial concentrations of reactants and analyzing the data.

Common types of rate equations:

1. **Zero-order reactions:** Rate is independent of reactant concentrations. Rate = k. (Example: decomposition of certain catalysts)
2. **First-order reactions:** Rate depends on the concentration of one reactant raised to the first power. Rate = k[A]. (Example: radioactive decay)
3. **Second-order reactions:** Rate depends on the concentration of one reactant raised to the second power, or the concentrations of two reactants each raised to the first power. Rate = k[A]^2 or k[A][B]. (Example: combustion of hydrogen and oxygen)

Image example:



Rate = change in reactant concentration / *change in* time

Rate = change in product concentration / *change in* time

Fig 1. Concentration-time graphs. Curves A and B show how the reactants change with time. Curve C shows how the concentration of product changes with time.

Rate Equations – Measuring Rate of Reaction

graph showing how reaction rate changes with reactant concentration for different reaction orders

Importance of rate equations:

- **Understanding reaction mechanisms:** Rate equations provide insights into the steps involved in a reaction mechanism.
- **Predicting reaction rates:** They allow us to calculate how fast a reaction will occur under different conditions.
- **Optimizing reaction conditions:** Rate equations guide the selection of optimal conditions for desired reaction rates (e.g., in industrial processes).
- **Designing catalysts:** They can inform the design of catalysts to speed up or slow down reactions.

Order and Molecularity of Reaction:

The molecularity of a reaction refers to the number of atoms, molecules, or ions which must undergo a collision with each other in a short time interval for the chemical reaction to proceed. The key differences between molecularity and reaction order are tabulated below.

Molecularity	Order of Reaction
It is always a whole number	It can be a whole number or a fraction.
It must be determined experimentally	It can be determined from the balanced chemical equation
Is only applicable in simple reactions	The reaction order is applicable in all chemical reactions

It can be noted that when the order of reaction is a fraction, the reaction is generally a chain reaction or follows some other complex mechanism. An example of a chemical reaction with a fractional reaction order is the pyrolysis of acetaldehyde.

RATE LAWS:

The rate law (also known as the rate equation) for a chemical reaction is an expression that provides a relationship between the rate of the reaction and the concentrations of the reactants participating in it.

Expression

For a reaction given by:

aA + bB → cC + dD

Where a, b, c, and d are the stoichiometric coefficients of the reactants or products, the rate equation for the reaction is given by:

$$\textbf{Rate a } [A]^{x}[B]^{y} \Rightarrow \textbf{Rate} = k[A]^{x}[B]^{y}$$

Where,

- [A] & [B] denote the concentrations of the reactants A and B.
- x & y denote the partial reaction orders for reactants A & B (which may or may not be equal to their stoichiometric coefficients a & b).
- The proportionality constant 'k' is the rate constant of the reaction.

Rate Laws: Describing Reaction Speed

- **Definition:** Rate laws are mathematical expressions that relate the rate of a chemical reaction to the concentrations of its reactants.
- **Purpose:** They provide essential insights into reaction mechanisms, allow prediction of reaction rates under different conditions, and aid in understanding factors that influence reaction speeds.

Key Concepts:

1. **Rate Expression:**
   - Represents the general form of a rate law: rate = k[A]^m[B]^n
   - k: rate constant, specific to a reaction at a given temperature
   - [A], [B]: molar concentrations of reactants A and B
   - m, n: exponents (orders) determined experimentally, reflecting reaction mechanism
2. **Order of Reaction:**
   - Sum of exponents in the rate law (m + n in the example above)
   - Determines how concentration changes affect reaction rate
   - Common orders: zeroth, first, second, and sometimes fractional
3. **Determining Rate Law and Order:**
   - Experimentally obtained by conducting reactions at different initial concentrations

- Measuring initial rates and analyzing data to find exponents that yield a consistent rate constant

Examples:

- **First-order reaction:** rate = k[A] (e.g., radioactive decay)
- **Second-order reaction:** rate = k[A]^2 or rate = k[A][B] (e.g., some decomposition reactions)
- **Zeroth-order reaction:** rate = k (rare, independent of reactant concentrations)

Importance:

- **Understanding Reaction Mechanisms:** Rate laws provide clues about reaction steps and how molecules interact.
- **Predicting Reaction Rates:** Allow estimation of reaction rates under various conditions, crucial for industrial processes and chemical engineering.
- **Optimizing Reaction Conditions:** Guide adjustments in concentration, temperature, or catalysts to achieve desired reaction speeds.

REACTION ORDERS

The sum of the partial orders of the reactants in the rate law expression gives the overall order of the reaction.

If Rate = $k[A]^x[B]^y$; overall order of the reaction (n) = $x+y$

The order of a reaction provides insight into the change in the rate of the reaction that can be expected by increasing the concentration of the reactants. For example:

- If the reaction is a zero-order reaction, doubling the reactant concentration will have no effect on the reaction rate.
- If the reaction is of the first order, doubling the reactant concentration will double the reaction rate.
- In second-order reactions, doubling the concentration of the reactants will quadruple the overall reaction rate.
- For third-order reactions, the overall rate increases by eight times when the reactant concentration is doubled.

What is a reaction order?

Simply put, it tells you how the rate of a reaction changes with respect to the concentration of the reactants. For example, a reaction of order 1 means the rate is directly proportional to the concentration of one reactant. Doubling the concentration would double the rate, and vice versa.

Common reaction orders:

- **Zero order:** The rate is independent of reactant concentration. Imagine a race car speeding at a constant pace, regardless of how many laps it's done.
- **First order:** The rate is proportional to the concentration of one reactant. Think of a single raindrop falling – the rate of raindrops hitting the ground depends only on how many drops are falling, not how hard it's raining.
- **Second order:** The rate is proportional to the square of the concentration of one reactant, or to the product of the concentrations of two reactants. Picture a game of bumper cars – the crash rate increases rapidly as more cars are added.

Determining reaction order:

Scientists use various methods to determine reaction orders, like running experiments with different initial concentrations and analyzing the data. It's like figuring out the secret recipe of a chemical reaction!

The world of reaction orders:

Understanding reaction orders has countless applications, from optimizing industrial processes to designing effective drugs. It's like having a cheat code for predicting and controlling chemical reactions.

RATE CONSTANTS:

Rearranging the rate equation, the value of the rate constant 'k' is given by: $k = \text{Rate}/[A]^x[B]^y$

Therefore, the units of k (assuming that concentration is represented in mol.L^{-1} or M and time is represented in seconds) can be calculated via the following equation.

$$\mathbf{k = (M.s^{-1})*(M^{-n}) = M^{(1-n)}.s^{-1}}$$

Chemical kinetics, the study of reaction rates, is a fascinating branch of chemistry. Rate constants play a crucial role in understanding how fast reactions occur and under what conditions.

To delve deeper into this topic, what specific aspects of rate constants are you interested in? Perhaps you'd like to explore:

- **The factors influencing rate constants:** Temperature, concentration, catalyst presence, and reaction mechanism all play a part.
- **Units of rate constants:** Understanding the units (e.g., $L\ mol^{-1}\ s^{-1}$) helps interpret their meaning and compare reaction rates.
- **Different types of rate constants:** Depending on the reaction order, we have first-order, second-order, and even higher-order rate constants.
- **Applications of rate constants:** From predicting reaction times in industrial processes to understanding biological processes, rate constants have diverse applications.

The units of the rate constants for zero, first, second, and nth-order reactions are tabulated below.

Reaction Order	**Units of Rate Constant**
0	$M.s^{-1}$ (or) $mol.L^{-1}.s^{-1}$
1	s^{-1}
2	$M^{-1}.s^{-1}$ (or) $L.mol^{-1}.s^{-1}$
N	$M^{1-n}.s^{-1}$ (or) $L^{(-1+n)}.mol^{(1-n)}.s^{-1}$

Differential Rate Equations

Differential rate laws are used to express the rate of a reaction in terms of the changes in reactant concentrations (d[R]) over a small interval of time (dt). Therefore, the differential form of the rate expression provided in the previous subsection is given by:

$$-d[R]/dt = k[A]^x[B]^y$$

Differential rate equations can be used to calculate the instantaneous rate of a reaction, which is the reaction rate under a very small time interval. It can be noted that the ordinary rate law is a differential rate equation since it offers insight into the instantaneous rate of the reaction.

Integrated Rate Equations

Integrated rate equations express the concentration of the reactants in a chemical reaction as a function of time. Therefore, such rate equations can be employed to check how long it would take for a given percentage of the reactants to be consumed in a chemical reaction. It is important to note that reactions of different orders have different integrated rate equations.

Integrated Rate Equation for Zero-Order Reactions

The integrated rate equation for a zero-order reaction is given by:

$kt = [R0] – [R]$ (or) $k = ([R0] – [R])/t$

Where,

- [R0] is the initial concentration of the reactant (when t = 0)
- [R] is the concentration of the reactant at time ‘t’
- k is the rate constant

DERIVATION OF FIRST ORDER RATE CONSTANT:

The derivation of the first-order rate constant involves relating the rate of the reaction to the concentration of the reactant and then mathematically manipulating the equation to extract the constant. Here's a breakdown of the steps:

1. Rate Law of a First-Order Reaction:

- A first-order reaction involves only one reactant, and the rate of the reaction is directly proportional to the concentration of that reactant raised to the power of 1. This can be expressed as:

$\text{Rate} = -d[A]/dt = k[A]$

where:

- **Rate:** the change in concentration of A with respect to time (negative indicates a decrease in concentration)
- **[A]:** the concentration of reactant A at time t
- **k:** the rate constant of the reaction

2. Integration of the Rate Law:

- To isolate k, we need to integrate the rate equation above. This can be done using separation of variables:

$d[A]/[A] = -k\,dt$

Integrating both sides:

$\int d[A]/[A] = -\int k\,dt$
$\ln[A] = -kt + C$

where C is the integration constant.

3. Determining the Integration Constant:

- At the initial time (t = 0), the concentration of A is $[A]_0$. Substituting this into the equation:

$\ln[A]_0 = -k(0) + C$

$C = \ln[A]_0$

Substituting this value of C back into the general equation:

$\ln[A] = -kt + \ln[A]_0$

4. Extracting the Rate Constant:

- Rearranging the equation to isolate k:

$k = (\ln[A]_0 - \ln[A]) / t$

This final equation provides the expression for the first-order rate constant, k. It relates the initial concentration of the reactant ($[A]_0$), the concentration of the reactant remaining at any time t ([A]), and the time elapsed (t).

The integrated rate law for first-order reactions is:

$kt = 2.303\log([R0]/[R])$ (or) $k = (2.303/t)\log([R0]/[R])$

Integrated Rate Equation for Second-Order Reactions

For second-order reactions, the integrated rate equation is:

$kt = (1/[R]) – (1/[R0])$

Example

For the reaction given by $2NO + O2 \rightarrow 2NO2$, The rate equation is: $Rate = k[NO]^2[O2]$ **Find the overall order of the reaction and the units of the rate constant.**

The overall order of the reaction = sum of exponents of reactants in the rate equation = 2+1 = 3The reaction is a third-order reaction. Units of rate constant for 'nth' order reaction = $M^{(1-n)}.s^{-1}$ Therefore, units of rate constant for the third-order reaction = $M^{(1-3)}.s^{-1} = M^{-2}.s^{-1} = L^2.mol^{-2}.s^{-1}$

Example

For the first-order reaction given by $2N2O5 \rightarrow 4NO2 + O2$ the initial concentration of N2O5 was 0.1M (at a constant temperature of 300K). After 10 minutes, the concentration of N2O5 was found to be 0.01M. Find the rate constant of this reaction (at 300K).

From the integral rate equation of first-order reactions:

k = (2.303/t)log([R0]/[R])

Given, t = 10 mins = 600 s

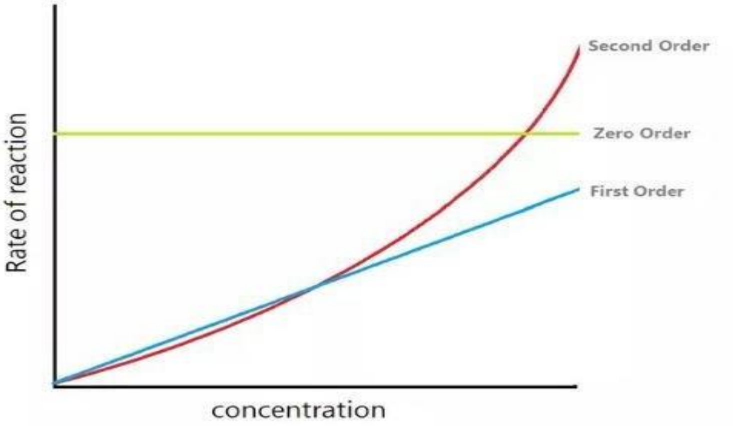
Initial concentration, [R0] = 0.1M Final concentration, [R] = 0.01M
Therefore, rate constant, k = (2.303/600s)log(0.1M/0.01M) = 0.0038 s^{-1} The rate constant of this equation is 0.0038 s^{-1}

Characteristics of zero order:

- The rate of reaction is independent of the concentration of the reactants in these reactions.
- A change in the concentration of the reactants has no effect on the speed of the reaction
- Examples of these types of reactions include the enzyme-catalyzed oxidation of CH3CH2OH (ethanol) to CH3CHO (acetaldehyde).

First order reaction:

- The rates of these reactions depend on the concentration of only one reactant, i.e. the order of reaction is 1.
- In these reactions, there may be multiple reactants present, but only one reactant will be of first-order concentration while the rest of the reactants would be of zero-order concentration.
- Example of a first-order reaction: **2H2O2 → 2H2O + O2**



PSEUDO-FIRST ORDER REACTIONS

- In a pseudo-first order reaction, the concentration of one reactant remains constant and is therefore included in the rate constant in the rate expression.
- The concentration of the reactant may be constant because it is present in excess when compared to the concentration of other reactants, or because it is a catalyst.
- Example of a pseudo-first order reaction: **$CH3COOCH3 + H2O \rightarrow CH3COOH + CH3OH$**
  (this reaction follows pseudo-first order kinetics because water is present in excess).

Pseudo-First Order Reactions: A Disguise in the Chemical World

Pseudo-first order reactions are fascinating phenomena in the world of chemistry where a reaction masquerades as a simpler one. While they might appear to follow the rules of a first-order reaction, they hold a hidden secret: their true nature lies in a higher order, often second-order!

Here's how it works:

- **The Key Ingredient:** Imagine a reaction with two reactants, A and B. In a true second-order reaction, the rate depends on the concentration of both A and B. But in a pseudo-first order reaction, one of the reactants, let's say B, is present in a **large excess** compared to A. This means the concentration of B barely changes throughout the reaction.
- **The Masking Act:** Due to the constant concentration of B, its contribution to the rate becomes negligible. The reaction rate then solely depends on the changing concentration of A, just like in a first-order reaction. This gives the illusion of a simpler order, making the reaction appear to be first-order.
- **The Hidden Truth:** Despite the disguise, the true nature of the reaction can be revealed through various methods, such as analyzing the rate law at different initial concentrations of both reactants.

Here are some key points to remember about pseudo-first order reactions:

- **They are often second-order reactions in disguise.**
- **The excess reactant acts as a constant concentration "background" for the reaction.**
- **The rate law simplifies to a first-order expression.**

- **They exhibit exponential decay of reactant concentration, similar to true first-order reactions.**

Understanding pseudo-first order reactions has several advantages:

- **Simpler calculations:** The first-order rate law makes it easier to analyze the reaction rate and predict its behavior.
- **Design of experiments:** We can manipulate the initial concentrations to create pseudo-first order conditions for studying complex reactions.
- **Modeling and simulation:** These reactions are easier to model and simulate due to their simplified rate law.

Examples of pseudo-first order reactions include:

- **Hydrolysis of esters in acidic solutions:** The large excess of H+ ions acts as the constant concentration reactant.
- **Decomposition of radioactive isotopes:** The constant concentration of the radioactive isotope makes the decay appear first-order.
- **Enzymatic reactions:** When the enzyme concentration is much higher than the substrate concentration, the reaction rate becomes pseudo-first order with respect to the substrate.

SECOND ORDER REACTIONS:

- **What defines a second-order reaction:** It's a chemical reaction where the rate depends on the concentration of the reactants raised to a power that sums to two.

- **The two main types of second-order reactions:** Reactions where the rate depends on the square of the concentration of one reactant, and reactions where the rate depends on the product of the concentrations of two different reactants.

- **Some common examples of second-order reactions:** The decomposition of nitrogen dioxide, the hydrolysis of esters, and the formation of dimers.

- **How to determine the rate law of a second-order reaction:** You can use experiments to measure the reaction rate at different initial concentrations of the reactants, and then plot the data to see how the rate changes with concentration.

- How to calculate the half-life of a second-order reaction: **The half-life is the time it takes for half of the reactants to be consumed, and it depends on the initial concentration and the rate constant.**

- When the order of a reaction is 2, the reaction is said to be a second-order reaction.
- The rate of these reactions can be obtained either from the concentration of one reactant squared or from the concentration of two separate reactants.
- The rate equation can correspond to **$r = k[A]^2$** or **$r = k[A][B]$**
- Example of a second-order reaction: **$NO_2 + CO \rightarrow NO + CO_2$**

Derivation of time for half change (t1/2) with examples:

The half-life of a reaction, t1/2, is the amount of time needed for a reactant concentration to decrease by half compared to its initial concentration. The concepts of half life plays a key role in the administration of drugs into the target, especially in the elimination phase, where half life is used to determine how quickly a drug decrease in the target after it has been absorbed in the unit of time (sec, minute, day,etc.) or elimination rate constant ke (minute^{-1}, hour^{-1}, day^{-1},etc.). It is important to note that the half-life is varied between different type of reactions.

ZERO ORDER KINETICS

Zero-order kinetics, a fascinating realm in the world of chemical reactions, beckons you! I'm here to guide you through this intriguing concept, unraveling its secrets and delving into its applications.

But before we embark on this journey, let's set the stage:

Imagine a chemical reaction where the rate doesn't depend on the concentration of the reactants. That's the essence of zero-order kinetics. It's like a party where the number of guests doesn't influence the flow of fun! The reaction proceeds at a constant pace, unfazed by the crowd.

So, what makes this peculiar behavior tick? Often, it involves some limiting factor, like the availability of a surface or the rate of a physical process like diffusion. Think of it as a bottleneck controlling the traffic, not the number of cars on the road.

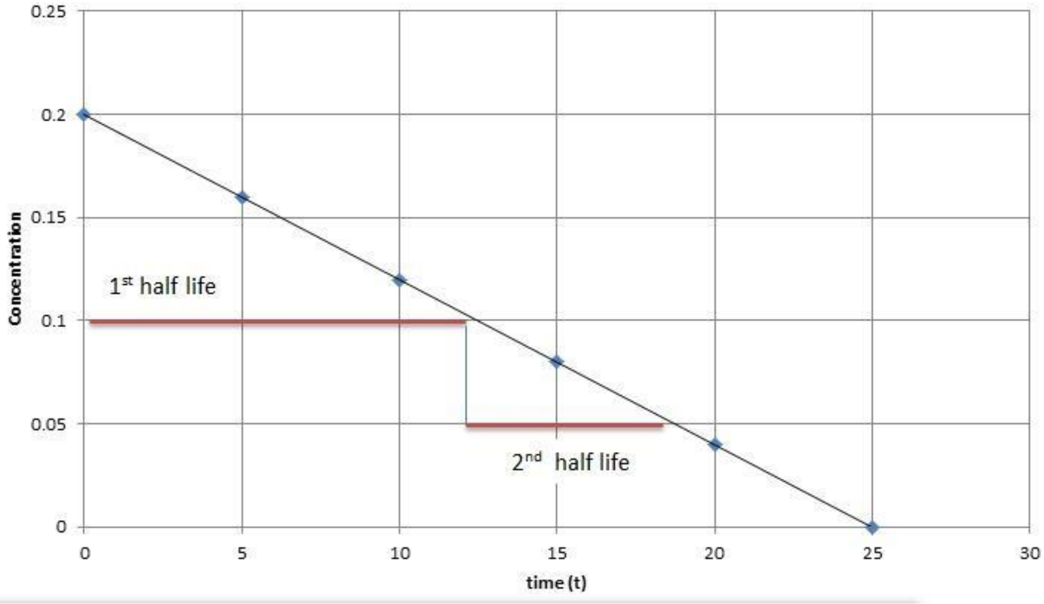
Now, let's delve into the practicalities:

- **Equations:** Zero-order kinetics is governed by a simple equation where the rate is a constant. It's like a straight line on a graph, a steady march of progress over time.

- **Examples:** From the decomposition of certain solid materials to the enzymatic breakdown of certain molecules, zero-order reactions play a role in various natural and technological processes.
- **Applications:** Understanding zero-order kinetics helps us predict the behavior of such reactions, which has applications in fields like catalysis, environmental remediation, and even drug delivery.

But the journey doesn't end there! Zero-order kinetics can intertwine with other reaction orders, creating complex mechanisms and fascinating dynamics. We can explore these intricacies and delve deeper into the captivating world of chemical kinetics if you'd like.

In zero-order kinetics, the rate of a reaction does not depend on the substrate concentration. In other words, saturating the amount of substrate does not speed up the rate of the reaction. Below is a graph of time (t) vs. concentration [A] in a zero order reaction, several observation can be made: the slope of this plot is a straight line with negative slope equal negative k, the half-life of zero order reaction decrease as the concentration decrease.



We learn that the zero order kinetic rate law is as followed, where [A] is the current concentration, [A]0 is the initial concentration, and k is the reaction constant and t is time:

$[A]=[A]0-kt$ (1)

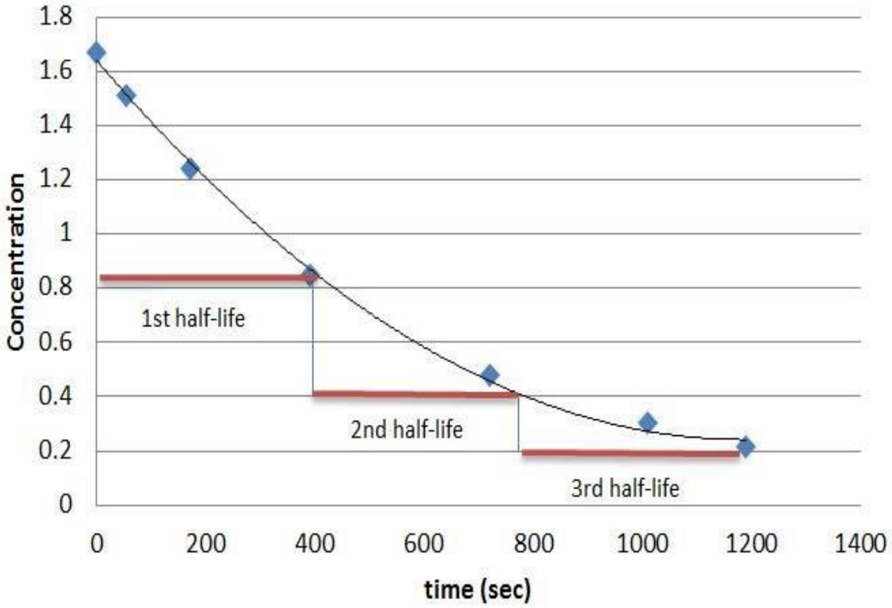
In order to find the half life we need to isolate t on its own, and divide it by 2. We would end up with a formula as such depict how long it takes for the initial concentration to dwindle by half:

$t1/2=[A]02k$ (2)

The $t1/2$ formula for a zero order reaction suggests the half-life depends on the amount of initial concentration and rate constant.

FIRST ORDER KINETICS

In First order reactions, the graph represents the half-life is different from zero order reaction in a way that the slope continually decreases as time progresses until it reaches zero. We can also easily see that the length of half-life will be constant, independent of concentration. For example, it takes the same amount of time for the concentration to decrease from one point to another point.



In order to solve the half life of first order reactions, we recall that the rate law of a first order reaction was:

$[A]=[A]0e-kt$ (3)

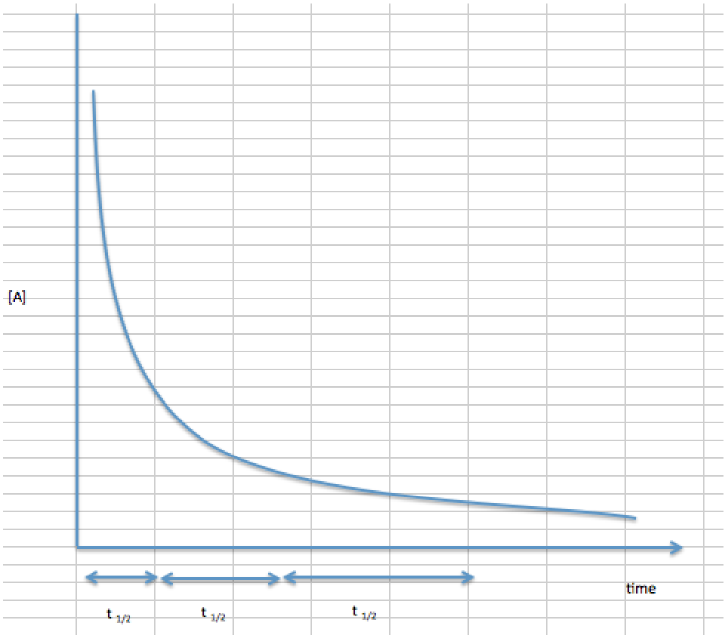
To find the half life we need to isolate t and substitute [A] with $[A]0/2$, we end up with an equation looking like this:

$t1/2=\ln 2/k\approx 0.693k$ (4)

The formula for t1/2 shows that for first order reactions, the half-life depends solely on the reaction rate constant, k. We can visually see this on the graph for first order reactions when we note that the amount of time between one half life and the next are the same. Another way to see it is that the halflife of a first order reaction is independent of its initial concentration.

SECOND ORDER REACTIONS

Half-life of second order reactions shows concentration [A] vs. time (t), which is similar to first order plots in that their slopes decrease to zero with time. However, second order reactions decrease at a much faster rate as the graph shows. We can also note that the length of half-life increase while the concentration of substrate constantly decreases, unlike zero and first order reaction.



In order to solve for half life of second order reactions we need to remember that the rate law of a second order reaction is:

$1/[A]=kt+1/[A]0$ (5)

As in zero and first order reactions, we need to isolate T on its own:

$t1/2=1/k[A]0$ (6)

This replacement represents half the initial concentration at time, t (depicted as t1/2). We then insert the variables into the formula and solve for t1/2. The formula for t1/2 shows that for second order reactions, the half-life only depends on the initial concentration and the rate constant.

Second-order reactions are a fascinating and important class of chemical reactions! I'd be happy to discuss them with you. What specifically would you like to know about them?

Here are some topics I can cover:

- **Definition and characteristics of second-order reactions:** We can explore what makes a reaction second-order, compare them to other reaction orders, and discuss their key features.
- **Types of second-order reactions:** There are two main types, depending on the number of reactants involved: 1) reactions with one reactant squared in the rate law (e.g., 2A → products) and 2) reactions with the product of two reactant concentrations in the rate law (e.g., A + B → products).
- **Rate laws and kinetics of second-order reactions:** We can delve into the mathematical equations that describe the rate of these reactions, how they change with concentration, and how to determine the rate constant.
- **Examples of second-order reactions:** From decomposition reactions like NO2 to NO and O2 to enzyme-catalyzed reactions in biology, there are numerous real-world examples to explore.
- **Applications of understanding second-order reactions:** Knowing the kinetics of these reactions helps us analyze their behavior in various contexts, predict their outcomes, and optimize processes involving them.

METHODS OF DETERMINATION OF ORDER OF REACTIONS:

There are several different methods which can be followed in order to determine the reaction order. Some of these methods are described in this subsection.

Determining the order of a reaction is crucial in understanding its kinetics and predicting its behavior. Several methods can be employed, each with its own advantages and limitations. Here are some common methods:

1. Initial Rate Method:

- This method involves measuring the initial rate of the reaction at different initial concentrations of one or more reactants while keeping others constant.
- Analyzing the relationship between the initial rate and concentration can reveal the order with respect to each reactant. For example, doubling the concentration and observing a doubled rate suggests a first-order dependence.
- This method is versatile and applicable to various reaction orders.

2. Integration Method:

- This method utilizes the integrated form of the rate equation for different reaction orders.
- By plotting the concentration data against time in specific forms (e.g., ln([A]) vs. t for first-order), a linear relationship confirms the assumed order and provides the rate constant.
- This method requires knowledge of the possible rate equation forms beforehand.

3. Half-Life Method:

- This method focuses on measuring the half-life (time taken for reactant concentration to halve) at different initial concentrations.
- For first-order reactions, the half-life remains constant regardless of the initial concentration. However, it changes proportionally with initial concentration for other orders.
- This method is simple but only applicable to first-order reactions.

4. Graphical Method:

- This method involves plotting the concentration data against time in various transformed forms based on the suspected order.
- For example, a straight line on a plot of ln([A]) vs. t confirms a first-order reaction.
- This method provides a visual confirmation of the order but can be subjective in interpretation.

5. Differential Method:

- This method directly analyzes the differential form of the rate equation.
- Examining the exponents of reactant concentrations in the rate equation reveals the individual and overall reaction orders.
- This method is efficient but requires prior knowledge of the rate equation.

The choice of method depends on factors like the available data, reaction complexity, and desired accuracy. Often, a combination of methods provides more reliable confirmation of the reaction order.

Initial Rates Method

- First, the natural logarithm form of the power-law expression is obtained. It is given by: **ln r** = ln k + x.ln[A] + y.ln[B] + ….
- The partial order corresponding to each reactant is now calculated by conducting the reaction with varying concentrations of the reactant in question and the concentration of the other reactants kept constant.
- If the partial order of A is being determined, the power-law expression of the rate equation now becomes **ln r = x.ln[A] + C**, where C is a constant.
- A graph is now plotted by taking 'ln r' as a function of ln[A], the corresponding slope is the partial order, given by x.

Integral Method

- The order of reaction obtained from the initial rates method is usually verified using this method.
- The measured concentrations of the reactants are compared with the integral form of the rate law.
- For example, the rate law for a first-order reaction is verified if the value for ln[A] corresponds to a linear function of time (integrated rate equation of a first-order reaction: ln[A] = -kt + ln[A]0).

Differential Method

- This method is the easiest way to obtain the order of reaction
- First, the rate expression of the reaction is written ($r = k[A]^x[B]^y$..)
- The sum of the exponents x+y+… gives the final value of the reaction order.

Apart from these methods, there exist other ways to obtain the reaction order, such as the method of flooding in which the concentration of a single reactant is measured when all the other reactants are present in huge excess.

Experimental Methods:

Colorimetry Experimental Methods:

Calorimetry is the science associated with determining the changes in energy of a system bymeasuring the heat exchanged with the surroundings.

Calorimetry labs are frequently performed in order to determine the heat of reaction or the heat offusion or the heat of dissolution or even the specific heat capacity of a metal.

A calorimeter is a device used to measure the quantity of heat transferred to or from an object. Most students likely do not remember using such a *fancy piece of equipment* known as a calorimeter. Fearnot; the reason for the lack of memory is not a sign of early Alzheimer's. The more sophisticated cases include a lid on the cup with an inserted thermometer and maybe even a stirrer.

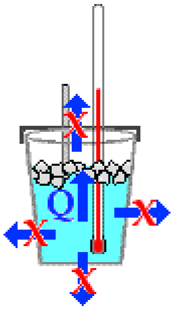
Coffee Cup Calorimetry

So how can such simple equipment be used to measure the quantity of heat gained or lost by a system? We have learned on the previous page, that water will change its temperature when it gainsor loses energy. And in fact, the quantity of energy gained or lost is given by the equation

$$Q = m_{water} \bullet C_{water} \bullet \Delta T_{water}$$

where C_{water} is 4.18 J/g/°C. So if the mass of water and the temperature change of the water in thecoffee cup calorimeter can be measured, the quantity of energy gained or lost by the water can becalculated.

The assumption behind the science of calorimetry is that the energy gained or lost by the water is equal to the energy lost or gained by the object under study. So if an attempt is being made to determine the specific heat of fusion of ice using a coffee cup calorimeter, then the assumption is that the energy gained by the ice when melting is equal tothe energy lost by the surrounding water. It is assumed that there is a heat exchange between the iceand the water in the cup and that no otherobjects are involved in the heat exchanged. This statement could be placed in equation form as



The heat exchanged in a calorimeter should be between the water and the system; heat should not be lost to the surrounding air.

Qice = - Qsurroundings = -Qcalorimeter

The role of the Styrofoam in a coffee cup calorimeter is that it reduces the amount of heat exchange between the water in the coffee cup and the surrounding air. The value of a lid on the coffee cup is that it also reduces the amount of heat exchange between the water and the surrounding air. The more that these other heat exchanges are reduced, the more true that the above mathematical equation will be. Any error analysis of a calorimetry experiment must take into consideration the flow of heat from system to calorimeter to other parts of the *surroundings*. And any design of a calorimeter experiment must give attention to reducing the exchanges of heat between the calorimeter contents and the *surroundings*.

POLARIMETRY EXPERIMENTAL METHODS:

A **polarimeter** is a scientific instrument used to measure the angle of rotation caused by passing polarized light through an optically active substance.

Some chemical substances are optically active, and polarized (uni-directional) light will rotate either to the left (counter-clockwise) or right (clockwise) when passed through these substances. The amount by which the light is rotated is known as the angle of rotation. The angle of rotation is basically known as observed angle.

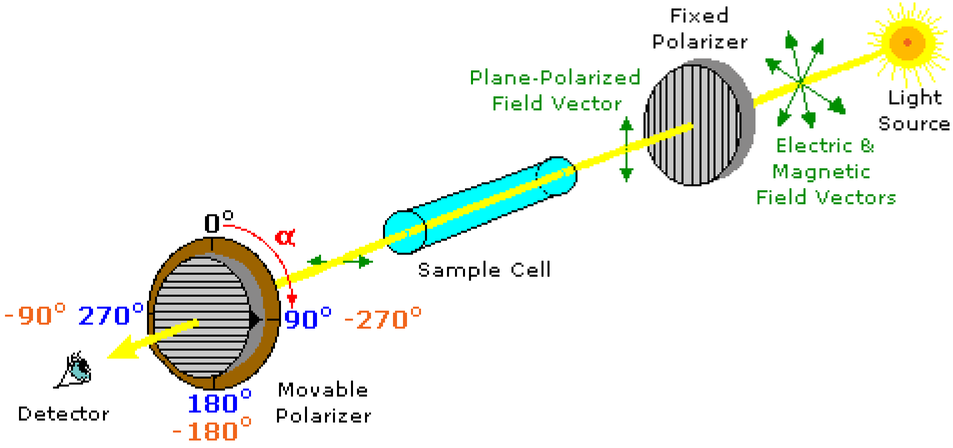
Because many optically active chemicals such as tartaric acid, are stereoisomers, a polarimeter can be used to identify which isomer is present in a sample – if it rotates polarized light to the left, it is a levo-isomer, and to the right, a dextro-isomer. It can also be used to measure the ratio of enantiomers in solutions.

The optical rotation is proportional to the concentration of the optically active substances in solution. Polarimetry may therefore be applied for concentration measurements of enantiomer-pure samples. With a known concentration of a sample, polarimetry may also be applied to determine the specific rotation (a physical property) when characterizing a new substance.

By the same token, if the specific rotation of a sample is already known, then the concentration and/or purity of a solution containing it can be calculated.

Most automatic polarimeters make this calculation automatically, given input on variables from the user.

Plane-polarized light is created by passing ordinary light through a polarizing device, which may be as simple as a lens taken from polarizing sun-glasses. Such devices transmit selectively only that component of a light beam having electrical and magnetic field vectors oscillating in a single plane. The plane of polarization can be determined by an instrument called a **polarimeter**, shown in the diagram below.



Monochromatic (single wavelength) light, is polarized by a fixed polarizer next to the light source. A sample cell holder is located in line with the light beam, followed by a movable polarizer (the analyzer) and an eyepiece through which the light intensity can be observed. In modern instruments an electronic light detector takes the place of the human eye. In the absence of a sample, the light intensity at the detector is at a maximum when the second (movable) polarizer is set parallel to the first polarizer (α = 0°). If the analyzer is turned 90° to the plane of initial polarization, all the light will be blocked from reaching the detector.

Polarimetry Experimental Methods:

Polarimetry is a broad field with various experimental methods used to measure and analyze the polarization state of light. To provide the most relevant information, I need more context about the specific area of interest within polarimetry.

Here are some examples of different polarimetry methods:

- **Ellipsometry:** Measures the change in polarization state upon reflection from a surface, providing information about the thickness and refractive index of thin films.
- **Mueller matrix polarimetry:** Characterizes the complete polarization transformation properties of a sample.
- **Scattering polarimetry:** Studies the polarization of light scattered by particles or materials.
- **Optical activity polarimetry:** Measures the rotation of the plane of polarization due to the chirality of molecules.
- **Fluorescence polarization anisotropy:** Determines the rotational dynamics of molecules based on the polarization of emitted fluorescence.

Once you provide more details about your specific area of interest in polarimetry (e.g., type of sample, desired information), I can offer a more focused response on relevant experimental methods, instrumentation, and data analysis techniques.

EFFECT OF TEMPERATURE ON REACTION RATE:

Temperature has a significant impact on the rate of chemical reactions, generally following the principle: **as temperature increases, so does the reaction rate**. This phenomenon can be explained through two key factors:

1. Increased Kinetic Energy: When you raise the temperature, the molecules of the reactants gain more kinetic energy. They move faster and collide with each other more frequently. This increases the chance of successful collisions, where reactants have the correct orientation and sufficient energy to overcome the activation energy barrier and form products.

2. Activation Energy: Every chemical reaction has an activation energy barrier, a minimum energy required for the reactants to undergo the reaction and form products. Increasing the temperature provides more energy to the molecules, making it easier for them to reach the activation energy and proceed with the reaction.

The relationship between temperature and reaction rate can be quantified by the **Arrhenius equation:**

$k = A * \exp(-Ea/RT)$

where:

- k is the rate constant
- A is the pre-exponential factor (frequency factor)
- Ea is the activation energy
- R is the gas constant
- T is the absolute temperature

This equation shows that the rate constant (k) increases exponentially with increasing temperature (1/T) and is also influenced by the activation energy (Ea) and the pre-exponential factor (A). Reactions with lower activation energies are more sensitive to temperature changes and their rates increase more rapidly with increasing temperature.

Here are some specific examples of how temperature affects reaction rates:

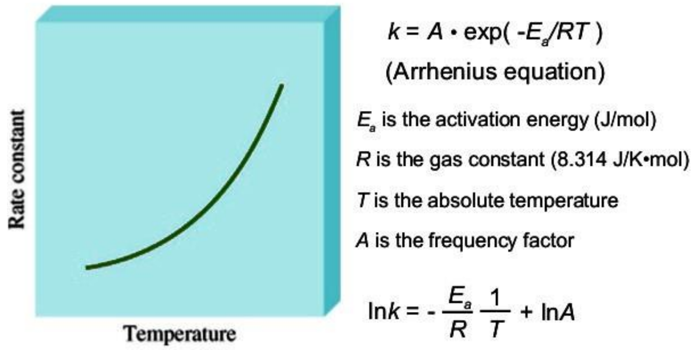
- **Cooking:** Food cooks faster at higher temperatures because the chemical reactions involved in cooking, like protein denaturation and browning, occur more rapidly.
- **Rusting:** Metal rusts faster in humid and warm environments compared to dry and cold conditions because the oxidation reaction between the metal and oxygen is accelerated by higher temperatures.
- **Photosynthesis:** Plants perform photosynthesis more efficiently in warmer temperatures as the enzymes involved in the process have higher activity.

It's important to note that **increasing temperature indefinitely can also have negative consequences**:

- Some reactions might become uncontrollable and lead to unwanted side products or even explosions.
- High temperatures can break down or denature molecules, such as enzymes, hindering their function and slowing down the reaction.

Temperature is one of the parameters that can affect the rate of a chemical reaction considerably. We have often seen milk boiling on a gas stove. The rate at which a specific quantity of milk boils depends on the flame of the stove. If the flame height is maximum, the milk boils in less time and if the flame height is minimum, the milk takes more time to boil. Here the flame height resembles temperature.

Temperature Dependence of the Rate Constant



If the temperature is high, the milk attains its boiling point in less time and if the temperature is low, the milk takes more time to attain its boiling point. The boiling of milk is not the only reaction that gets affected by temperature. Most of the chemical reactions show a change in their reaction rate with the varying in temperature.

It has been observed that the rate constant for a chemical reaction gets doubled for every 10^{o}C risein temperature. Until 1889, there was no fixed way to physically measure the temperature dependence of the rate of a chemical reaction. In 1889, Svante Arrhenius extended the work of J.H van't Hoff and proposed an equation that related temperature and the rate constant for a reaction quantitatively. The proposed equation was named as Arrhenius Equation.

The Arrhenius equation is a fundamental concept in chemical kinetics, describing the relationship between the rate of a chemical reaction and its temperature. It states that the rate constant (k) of a reaction increases exponentially with increasing temperature. Here's the equation:

k = A * exp(-Ea/RT)

where:

- **k** is the rate constant (measured in units like M^-1 s^-1)
- **A** is the pre-exponential factor (a constant specific to the reaction)

- **Ea** is the activation energy (the minimum energy required for a reaction to proceed, measured in Joules per mole)
- **R** is the gas constant (8.314 J mol^-1 K^-1)
- **T** is the absolute temperature (in Kelvin)

Interpretation of the equation:

- **A** represents the frequency of collisions between reactant molecules.
- **Ea** represents the energy barrier that must be overcome for a collision to be successful and lead to a reaction product.
- **R** relates the temperature scale to the energy scale.
- **e** is the base of the natural logarithm.

Applications and importance:

- The Arrhenius equation is used to:
  - Predict the rate of a reaction at different temperatures.
  - Calculate the activation energy of a reaction.
  - Understand the effect of temperature on reaction mechanisms.
- It has vast applications in various fields, including:
  - Chemical engineering
  - Materials science
  - Environmental science
  - Biology

CONCEPT OF ACTIVATION ENERGY:

Activation energy is defined as the minimum amount of extra energy required by a reacting molecule to get converted into product. It can also be described as the minimum amount of energy needed to activate or energize molecules or atoms so that they can undergo a chemical reaction or transformation.

SI Unit of Activation Energy

Activation energy is denoted by E_a. It is usually measured in joules (J) and or kilojoules per mole (kJ/mol) or kilocalories per mole (kcal/mol).
Activation energy depends on two factors.

Activation energy is a fundamental concept in chemistry and physics that describes the minimum amount of energy required to initiate a reaction or process. Imagine it like a small hill that reactants need to climb over before they can reach the other side and form products. Without enough energy, they'll get stuck at the bottom, unable to react.

Here's a breakdown of the concept:

What it is:

- The minimum extra energy needed to convert reactants into products in a chemical reaction.
- The energy required to overcome an energy barrier (like the hill mentioned earlier) between the initial state of the reactants and the final state of the products.
- Often represented by the symbol Ea.

Importance:

- Determines the rate of a reaction: Higher activation energy means a slower reaction, as fewer reactant molecules will have enough energy to overcome the barrier.
- Explains why some reactions require external energy sources like heat or light to get started.
- Plays a crucial role in various fields, including biochemistry, materials science, and catalysis.

Visualization:

Imagine two balls representing reactant molecules at the bottom of a valley. The valley floor represents their initial energy state. The top of the hill in the middle is the transition state, where the reactants have absorbed enough energy to be ready to react and form products. The other side of the hill represents the lower energy state of the products.

Factors affecting activation energy:

- Nature of the reactants: Strong bonds generally require higher activation energy to break.
- Reaction mechanism: Different reaction pathways can have different activation energies.
- Presence of a catalyst: Catalysts can lower the activation energy barrier, making the reaction faster.

Examples:

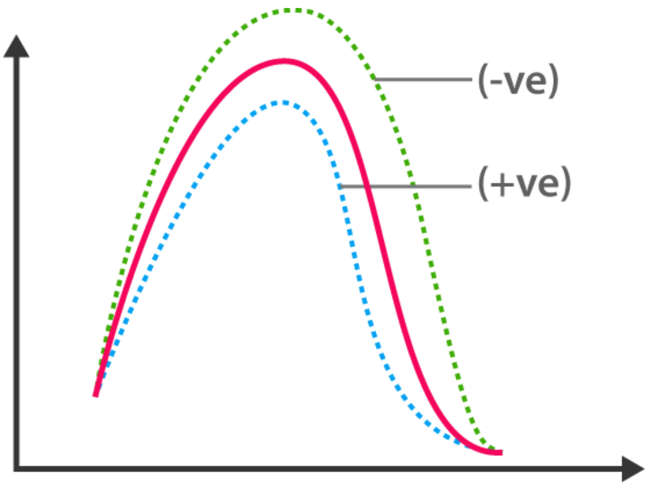
- Burning wood: Requires heat (activation energy) to break the bonds in the wood and start the combustion reaction.
- Digestion: Enzymes act as catalysts to lower the activation energy of biochemical reactions in our bodies.
- Nuclear fusion: Requires extremely high temperatures and pressures (activation energy) to overcome the repulsion between nuclei and initiate the fusion reaction.

1. Nature of Reactants

In the case of ionic reactant, the value of (E_a) will be low because there is an attraction between reacting species. While in the case of covalent reactant the value of E_a will be high because energy is required to break the older bonds.

2. Effect of Catalyst

Positive catalyst provides such an alternate path in which the value of E_a will be low, while the negative catalyst provides such an alternate path in which the value of E_a will be high.



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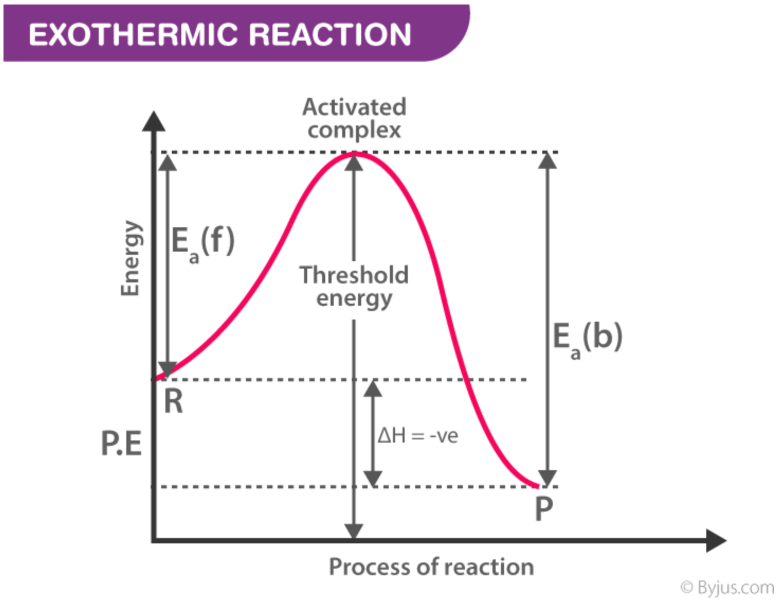
Note: Activation energy does not depend upon the temperature, pressure, volume, concentration, or coefficients of reactant.

ACTIVATION ENERGY EXAMPLES

EXOTHERMIC REACTION



Activation energy for Forward reaction (Ea)f Activation energy for Forward reaction (Ea)b

(Ea)f < (Ea)b

(ROR)f > (ROR)b

ΔH = (Ea)f – (Ea)b

ΔH = -ve value

(Ea)f = ΔH Only one can be possible for Exothermic Reaction (Ea)f > ΔH

(Ea)f < ΔH

Endothermic Reaction

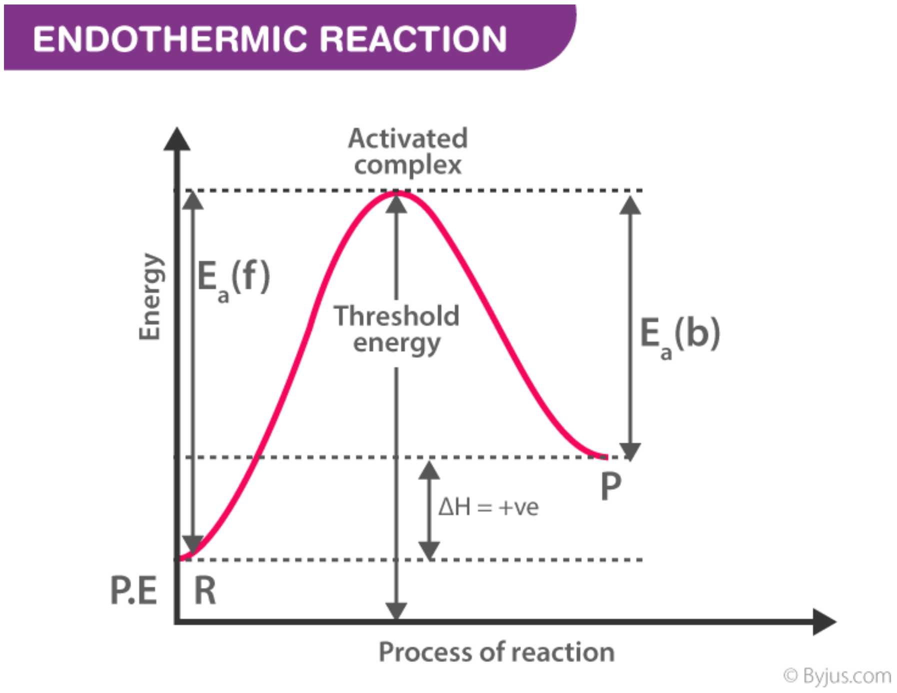
(Ea)f > (Ea)b

(ROR)f < (ROR)b

ΔH = (Ea)b – (Ea)f

ΔH = +ve value

(Ea)f > ΔH (Always)… .universal



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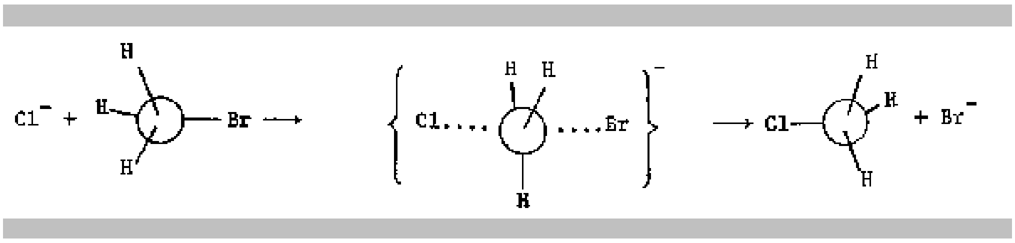
ENERGY BARRIER:

During the course of a reaction considerable redistribution of electrons may occur. Consider, for example, the reaction of CH3Br with Cl^- in water at 298K.



As the bimolecular reaction occurs:

(i) There is angle bending: the initially pyramidal CH3 grouping become planar;

(ii)There is bond-making and breaking: a partial CBr bond is weakened. The energy released by the formation of the partial CCl bond will not fully compensate for the other two (endothermic) changes and yet there is no lower energy pathway from reactants to products.

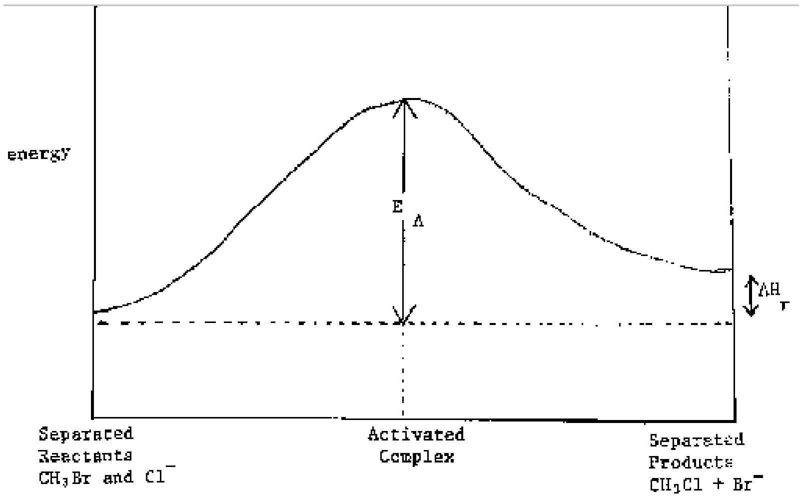
The reactants can get to the point of highest potential energy (the "activated complex" or "transition state" - in curly braces above) only if they initially have sufficient kinetic energy to turn into the potential energy of the activated complex.

The activated complex can not be isolated; it is that arrangement of reactants which can proceed to products without further input of energy.

It is often useful to make a schematic plot of the total energy (enthalpy) of the combined reactant molecules during the various stages of the chemical reaction. The points on the plot which we can pinpoint are:

- the difference between the average energy of the products and the average energy of the reactants, Hreaction (~ + 25 kJ mol^{-} for CH3Br + Cl^{-}) and
- the activation energy (obtained experimentally; 103 kJ mol^{-} for CH3Br + Cl^{-}).

If we assume the total energy varies smoothly with the course of the reaction we obtain the following "energy profile":



It is important to note that there will be more than one way for the reactants to interact and so pass to the products. However, there can only be one minimum energy pathway and essentially all of the reaction will occur via this pathway.

The term "energy barrier" can have different meanings depending on the context. To give you the most relevant information, I need some more information from you.

Here are some possibilities:

- **Physics and Chemistry:** In physics and chemistry, an energy barrier is a potential field that prevents particles or molecules from undergoing a certain process unless they are given enough energy to overcome the barrier. Examples include activation energy in chemical reactions, potential energy barriers in electronic devices, and the potential energy barrier between two atoms forming a bond.

- **Biology:** In biology, energy barriers can exist in various processes like protein folding, enzyme activity, and cellular transport. Understanding these barriers helps us understand how these processes occur and how they can be regulated.
- **Metaphor:** Energy barrier can also be used metaphorically to describe any obstacle or challenge that needs to be overcome before achieving something. This could be anything from starting a new job to writing a book.

ARRHENIUS EQUATION:

An elementary bimolecular reaction originates from a collision between two reactants. Whether or not a collision results in a chemical reaction is determined by the energy of the reactants and their orientation. The total energy of the two reactants must be in excess of the activation energy, Ea, and the reactants must be in a favorable orientation for the chemical reaction to occur. While there are many different orientations possible for the collisions, usually not all of them will result in a chemical reaction. For most reactions, if the orientation is not correct, the reactants will bounce off of each other without a chemical reaction.

Reaction Rate

The rate of a bimolecular reaction, between the reactants A and B is expressed as,

$Rate=k[A][B]$

where k is the reaction's rate constant and [A] and [B] are the reactants' concentrations. The reaction rate represents the "speed" of the chemical reaction and is equal to the magnitude of the change in the concentration of A or B per unit time. Thus, the reaction rate has units of concentration/time. Because one B molecule reacts for every A molecule, the loss rates of A and B are equal. The activation energy is illustrated in the following diagram. The difference in the activation energies for the forward and reverse reactions equals the change in the internal energy for the chemical reaction; i.e., $\Delta Erxn=Efa-Era$

Arrhenius equation! This fundamental formula in physical chemistry describes the relationship between temperature and the rate of chemical reactions. It's a cornerstone of understanding reaction kinetics and predicting how reactions will behave under different temperature conditions.

What would you like to know about the Arrhenius equation? I can explain its components, applications, limitations, or even guide you through solving problems using it. Just let me know what you have in mind!

Here are some things I can tell you about the Arrhenius equation:

- **The formula:** k = A * exp(-Ea/RT), where k is the reaction rate constant, A is the pre-exponential factor, Ea is the activation energy, R is the gas constant, and T is the absolute temperature.
- **Meaning of the terms:**
    - **k:** How fast the reaction occurs, measured in units like M^-1 s^-1.
    - **A:** The frequency of collisions between reactant molecules, influenced by factors like their shapes and sizes.
    - **Ea:** The minimum energy required for colliding molecules to overcome the energy barrier and react, measured in Joules per mole.
    - **R:** Universal gas constant, with a value of 8.314 J/mol*K.
    - **T:** Absolute temperature, measured in Kelvin.
- **Applications:**
    - Predicting reaction rates at different temperatures.
    - Understanding the effect of temperature on reaction mechanisms.
    - Determining activation energies from experimental data.
    - Developing catalysts to lower activation energies and increase reaction rates.
- **Limitations:**
    - Assumes a simple one-step reaction mechanism.
    - Does not account for complex reaction mechanisms with multiple steps.
    - May not be accurate for reactions with very high or very low activation energies.

THEORIES OF REACTION RATES

COLLISION THEORY:

The collision theory explains that gas-phase chemical reactions occur when molecules collide with sufficient kinetic energy. The collision theory is based on the kinetic theory of gases; therefore only dealing with gas-phase chemical reactions are dealt with. Ideal gas assumptions are applied. Furthermore, we also are assuming:

1. All molecules are traveling through space in a straight line.
2. All molecules are rigid spheres.
3. The reactions concerned are between only two molecules.
4. The molecules need to collide.

Ultimately, the collision theory of gases gives the **rate constant** for bimolecular gas-phase reactions; it is equal to the rate of successful collisions. The rate of successful collisions is proportional to the *fraction of successful collisions* multiplied by the overall *collision frequency*.

Collision theory is a principle of chemistry that explains how the rate of a chemical reaction depends on the frequency and effectiveness of collisions between the reacting particles.

Key points of the collision theory:

1. **Collision:** For a reaction to occur, the reacting particles (atoms or molecules) must collide with each other. Just bumping into each other isn't enough, though.
2. **Activation energy:** The colliding particles must have enough energy, called the activation energy, to break the bonds in the reactants and form new bonds in the products. Imagine the activation energy as a hump that the particles need to overcome for the reaction to take place.
3. **Orientation:** The colliding particles must also be oriented correctly for the reaction to occur. Think of it like trying to fit two puzzle pieces together; they only fit if they are lined up in the right way.

Factors affecting the rate of a reaction according to collision theory:

- **Concentration of reactants:** The more reactant particles there are, the more likely they are to collide, and the faster the reaction will occur.
- **Temperature:** Increasing the temperature increases the kinetic energy of the particles, making them move faster and collide more frequently and forcefully. This can increase the rate of the reaction.
- **Presence of a catalyst:** A catalyst can lower the activation energy required for the reaction, making it more likely that collisions will be successful. This can also increase the rate of the reaction.

DERIVATION OF RATE CONSTANT OF BIMOLECULAR REACTION:

The derivation of the rate constant for a bimolecular reaction can be approached through different methods, each offering varying levels of complexity and rigor. Here, we'll explore two common approaches:

1. Collision Theory:

This method starts with the basic idea that the rate of a reaction depends on the frequency of successful collisions between reactant molecules. Here's the breakdown:

a) Effective collision rate:

- Imagine a reaction A + B -> products. We need to consider the rate at which A and B molecules collide with the correct orientation and sufficient energy (activation energy) for the reaction to occur. This is called the effective collision rate, Z.
- Z can be expressed as: Z = P * Z_max, where:
  - P is the probability of a collision having the correct orientation and energy (usually a small value).
  - Z_max is the maximum collision rate, which can be calculated based on the kinetic theory of gases and depends on the reactant concentrations and their velocities.

b) Fraction of successful collisions:

- Not all collisions will be successful in forming products. Only a fraction, f, will overcome the activation energy barrier and proceed to reaction.

c) Rate constant:

- Combining the above, the rate of the reaction (d[products]/dt) can be written as: d[products]/dt = k * [A] * [B], where:
  - k is the rate constant, a proportionality constant that reflects the overall efficiency of the reaction.
  - [A] and [B] are the concentrations of reactants A and B.
- We can now define the rate constant k as: k = Z * f. This relates the microscopic details of successful collisions (frequency and probability) to the macroscopic observable rate of the reaction.

2. Transition State Theory:

This method takes a more sophisticated approach by considering the existence of a metastable intermediate state called the transition state, which lies at the peak of the energy barrier between reactants and products.

a) Reaction coordinate and transition state:

- Imagine the reaction progress as movement along a reaction coordinate, with an energy profile showing the reactants, transition state, and products. The transition state represents the configuration of the reactants with the minimum energy required for the reaction to proceed.

b) Rate of crossing the transition state:

- The rate of the reaction is then determined by the rate at which reactant molecules reach and cross the transition state. This rate can be expressed as: k = k_BT * h^-1 * exp(-Ea/RT), where:
    - k_B is the Boltzmann constant.
    - h is Planck's constant.
    - Ea is the activation energy.
    - R is the gas constant.
    - T is the temperature.

c) Relationship to collision theory:

- Transition state theory and collision theory are connected. The pre-exponential factor k_BT * h^-1 can be interpreted as the effective collision rate (Z_max) multiplied by a transmission coefficient that accounts for the probability of successfully crossing the transition state (f).

Visualizations:

- To visualize the reaction coordinate and transition state, you can imagine a ball rolling down a valley with a hump. The reactants are at one end, the products at the other, and the transition state is the top of the hump. The faster the ball rolls, the more likely it is to overcome the hump and reach the products.
- You can also find various interactive simulations and animations online that depict the concepts of collision theory and transition state theory for different reactions.

These are just two of the main approaches to derive the rate constant for a bimolecular reaction. The choice of method depends on the level of detail and accuracy needed, as well as the specific information available about the reaction.

An elementary bimolecular reaction originates from a collision between two reactants. Whether or not a collision results in a chemical reaction is determined by the energy of the reactants and their orientation. The total energy of the two reactants must be in excess of the activation energy, E_a, and the reactants must be in a favorable orientation for the chemical reaction to occur. While there are many different orientations possible for the collisions, usually not all of them will result in a chemical reaction. For most reactions, if the orientation is not correct, the reactants will bounce off of each other without a chemical reaction.

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$$\Delta Erxn=Efa-Era$$

Failure of Collision Theory:

The following are the drawbacks of collision theory.

- This theory does not advance any explanation for the abnormally high rates that are observed sometimes.
- This theory cannot be applied to reversible reactions with complete success.
- It does not take into account the fact that proper molecule orientation is the requirement for a chemical reaction to occur. Active collision does not occur due to lack of proper orientation and therefore the experimentally observed frequency is less than determined based on the theory of collision.
- The theory of collision states that the reaction frequency is proportional to the total number of collisions per cc per second.
- It does not take into account the fast reactions where reactant molecules react despite having much less energy than the activation energy. These reactions are described by quantum mechanics, which means the reaction happens as a result of electrons being exchanged between reactant molecules.

LINDEMANN’S THEORY OF UNIMOLECULAR REACTION:

The Lindemann mechanism, sometimes called the Lindemann-Hinshelwood mechanism, is a schematic reaction mechanism. It breaks down a stepwise reaction into two or more elementary steps, then it gives a rate constant for each elementary step.

The rate law and rate equation for the entire reaction can be derived from this information. Lindemann mechanisms have been used to model gas phase decomposition reactions. Although the net formula for a decomposition may appear to be first-order (unimolecular) in the reactant, a Lindemann mechanism may show that the reaction is actually second-order (bimolecular).

A Lindemann mechanism typically includes an activated reaction intermediate, labeled A* (where A can be any element or compound). The activated intermediate is produced from the reactants only after a sufficient activation energy is applied. It then either deactivates from A* back to A, or reacts with another (dis)similar reagent to produce yet another reaction intermediate or the final product.

Unimolecular reactions are chemical reactions where a single molecule breaks down into smaller molecules or atoms.

Lindemann's theory, proposed in 1922 by Frederick A. Lindemann, explains the rates of these reactions. It assumes that a molecule must first be excited to an **activated state** (A*) with sufficient energy to overcome the **activation barrier** and proceed to the products. This excitation can occur through collisions with other molecules.

The theory proposes two main steps:

1. **Activation:** A molecule (A) gains enough energy from a collision to become an activated molecule (A*). This is a **bimolecular** step, meaning it depends on the concentration of both A and the collision partner (M).

2. **Reaction or Deactivation:** The activated molecule (A*) can either:
   - ○ **React:** If it retains enough energy for a sufficient time, it will decompose into products (P). This is a **unimolecular** step, independent of the concentration of other molecules.
   - ○ **Deactivate:** If it loses its excess energy through a collision with another molecule, it returns to its original state (A).

Lindemann's theory predicts that the rate of a unimolecular reaction depends on:

- **The rate of activation:** This is determined by the collision frequency and the probability of a collision transferring enough energy to excite a molecule to the activated state.
- **The rate of deactivation:** This is determined by the collision frequency and the probability of a collision removing enough energy from an activated molecule to deactivate it.
- **The rate of reaction:** This is determined by the probability of an activated molecule decomposing before it gets deactivated.

The theory can be used to explain the observed pressure dependence of unimolecular reaction rates. At low pressures, the rate of deactivation is slow, so most activated molecules react before they collide with another molecule. Therefore, the rate is proportional to the concentration of the reactant molecule (first-order dependence). At high pressures, the rate of deactivation is fast, so most activated molecules are deactivated before they react. Therefore, the rate becomes independent of the reactant concentration (zero-order dependence).

Limitations of Lindemann's theory:

- It assumes a single activated state, whereas in reality, there may be multiple excited states with different energies.
- It neglects the possibility of energy transfer between molecules without reaction.
- It does not account for the role of internal vibrations and rotations in the activation process.

Despite these limitations, Lindemann's theory remains a valuable tool for understanding the rates of unimolecular reactions and has been extended to develop more sophisticated models.

COMPARISON OF COLLISION THEORY AND ABSOLUTE REACTION RATE THEORY (ARRT).

Both collision theory and ARRT aim to explain and predict the rates of chemical reactions. However, they differ in their level of detail and sophistication. Here's a comparison:

Collision Theory:

- **Simplistic approach:** Focuses on the collision of reactant molecules with sufficient kinetic energy and proper orientation.
- **Key features:**
  - **Collision frequency:** Assumes gas molecules collide frequently.
  - **Activation energy:** Only successful collisions with energy exceeding the activation energy lead to reaction.
  - **Ignores intermediate states:** Doesn't consider the formation of any temporary intermediates during the reaction.
- **Predictions:**
  - Overestimates reaction rates, particularly for complex reactions.
  - Provides a qualitative understanding of factors affecting reaction rates.

Absolute Reaction Rate Theory (ARRT):

- **More complex:** Incorporates ideas from thermodynamics, statistical mechanics, and quantum mechanics.
- **Key features:**
  - **Transition state:** Introduces a high-energy intermediate state called the transition state (TS).
  - **Equilibrium between reactants and TS:** Assumes equilibrium between reactants and the TS.
  - **Rate constant expression:** Relates the rate constant to the partition functions of reactants, TS, and products.
- **Predictions:**
  - More accurate than collision theory, especially for complex reactions.
  - Provides a deeper understanding of the factors influencing reaction rates (e.g., entropy, bond strengths).
  - Can be used to calculate the rate constant from thermodynamic and structural data.

Comparison summary:

Feature	**Collision Theory**	**Absolute Reaction Rate Theory (ARRT)**
Complexity	Simplistic	More complex
Focus	Collisions with sufficient energy	Transition state formation and equilibrium
Intermediate states	Ignored	Considers a high-energy intermediate (TS)
Predictions	Overestimates rates, qualitative understanding	More accurate, quantitative predictions
Strengths	Easy to understand, provides basic insights	More accurate, deeper understanding, calculates rates
Weaknesses	Oversimplification, inaccurate for complex reactions	More complex, requires detailed knowledge of thermodynamics and statistical mechanics

In conclusion, ARRT is a more refined and accurate theory compared to collision theory. However, collision theory remains valuable for its simplicity and ability to provide a basic understanding of reaction rates. The choice of which theory to use depends on the desired level of detail and accuracy.

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