Lecture Based
Modules for Bridge Course in
Chemistry

PREFACE

Globalization of the world economy and higher education are driving profound changes in engineering education system. Worldwide adaptation of Outcome Based Education framework and enhanced focus on higher order learning and professional skills necessitates paradigm shift in traditional practices of curriculum design, education delivery and assessment. AICTE has also taken various quality initiatives for strengthening the technical education system in India. These initiatives are essential for promoting quality education in our institutions in the country so that our students passing out from these institutions may match the pace with global standards.

A quality initiative by AICTE is 'Revision of Curriculum'. Recently, AICTE has released an outcome based Model Curriculum for various Undergraduate degree courses in Engineering & Technology which are available on AICTE website. A three-week mandatory induction program is developed as a part of the model curriculum for the first year UG Engineering students which helps students joining the first year of the college from diverse backgrounds to get adjusted in the new environment of the institution.

Education is primarily conceived by students as one simple remembering facts by rote. However, Science education also requires clear understanding of science concepts and a proper logical thinking or a constructive thinking by students. We all know that the students seeking admission in an undergraduate degree engineering program have passed their 10+2 in science but it was felt that a student joining an engineering program after 10+2 require reinforcement of fundamental science concepts i.e. basic science courses in Physics, Chemistry and Mathematics. To support the students, gain better understanding, AICTE decided to initiate the task of development of bridge courses in Physics, Chemistry and Mathematics and it was entrusted to IIT-BHU. These bridge courses aim to accelerate the students' knowledge in these subjects acquired at 10+2 level; and also bridge the gap between the school science syllabus and the level needed to understand their applications to engineering concepts. Therefore, it was decided that after completion of the 3-week mandatory induction programme introduced for the first year UG engineering students, bridge course in basic Physics, Chemistry and Mathematics may be taken up by universities/institutions for the students for the remaining part of the semester. The concerned University/institution has a flexibility to adopt these modules on bridge courses by adjusting teaching hours accordingly.

The lecture based modules in Physics, Chemistry and Mathematics have been developed by a team of respective Course Coordinators from Indian Institute of Technology, Banaras Hindu University. AICTE approved institutions may utilize these modules *'Lecture Based Modules for Bridge Courses - Physics, Chemistry and Mathematics'* for teaching students to help bridge the gap of their studies of 10+2 and UG level.

(Prof. Anil D. Sahasrabudhe)
Chairman, AICTE

ACKNOWLEDGEMENT

Curriculum plays a crucial role in enabling quality learning for our young learners in our society i.e. students. An effective curriculum not only enables a student's learning process & knowledge acquired but also supports students to overcome their inhibitions and aids in their holistic development. AICTE in 2018 released a Model Curriculum for various Undergraduate degree courses in Engineering & Technology. This curriculum is equipped with making students industry ready, allow internships for hands on experience, learn about Constitution of India, Environment science etc. Induction program has been included as a mandatory program for the first year engineering students to get acquainted and get accustomed to this new environment in the college. a curriculum needs to be consistent and sustainable and it has been noticed that students joining an engineering program required to strengthen their concepts in science subjects i..e Physics, Chemistry and Mathematics building a better foundation during the first semester itself. AICTE therefore decided to develop lecture based bridge courses in basic science subjects i..e Physics, Chemistry and Mathematics for students,. The lecture based modules in Physics, Chemistry and Mathematics have been developed by IIT-BHU. This task has been accomplished by a team of respective Course Coordinators under Prof Indrajit Sinha, Department of Chemistry, IIT BHU as Overall Coordinator.

AICTE places on record its acknowledgement and appreciation to Dr. Indrajit Sinha, Department of Chemistry, IIT-BHU as overall coordinator; and respective course coordinators and their team of faculty members at IIT-BHU for developing these lecture based modules for bridge courses:

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Institutions may adjust teaching hours to utilize these modules *'Lecture based Modules for Bridge Courses - Physics, Chemistry and Mathematics'* to bridge the gap of 10+2 and UG level.

(Prof. Rajive Kumar)
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CHEMISTRY MODULES

(For AICTE Approved Colleges)

Prepared by

Department of Chemistry

Indian Institute of Technology

(Banaras Hindu University)

Varanasi – 221005

Preface

The genesis of this module lies in the Induction Program first conceived and started by IIT(BHU) on 2016 on mass scale for about 1000 students. The fact is that the students are overburdened and stressed out due to a hectic high school life. To refresh their creative mind, they were exposed to month long diverse credit courses like Physical Education, Human Values and Creative Practices, as well as several non-credit informal activities. In a welcome step the AICTE has proposed to extend this program to the Engineering Colleges affiliated to them.

In fact, purpose of this module is to bridge the gap between what the students need to know before they can start taking the advanced courses in the college level and what they are actually aware of from the intermediate level. Consequently, after the completion of the 3-weeks induction program, it is proposed that (besides other subjects) bridge courses in basic Physics, Chemistry and Mathematics should be taught to these students for the rest of the semester. The bridge courses will cover typical weaknesses of students in science at the 10+2 level.

The modules in Chemistry are prepared keeping in mind that an hour of discussion will bring all the students in the same stage such that they can cope up with the courses in their college level, that requires the concepts of different topics in Chemistry. The modules are made as interactive sessions between the students and the instructors. Furthermore, we have discussed those topics which harder to understand. At the end of the discussion teacher may also take a small test to understand how much the students followed the class.

We are grateful to the faculty members who contributed to make these modules: Prof. R. B. Rastogi, Prof. A. K. Mukherjee, Prof. M. A. Quraishi, Prof. V. Srivastava, Prof. Y. C. Sharma, Prof. D.Tiwari, Prof. K. D. Mandal, Dr. I. Sinha, Dr. S. Singh, Dr. M. Malviya of the Department of Chemistry who devoted their valuable time to prepare the modules.

Department of Chemistry
IIT(BHU)

Module 1 on Coordination Chemistry

Ist Lecture: Importance of coordination chemistry, Types of complexes, Classification of Ligands.

2nd Lecture: Crystal Field Theory to explain nature of bonding in octahedral complexes.

3rdLecture: Crystal Field Theory to explain nature of bonding in tetrahedral, tetragonally distorted octahedral and square planar complexes.

4thLecture: Magnetic properties of all types of complexes.

5thLecture: Color of complexes, Interpretation of Intensity of absorption bands in various complexes.

Module 2 on Organic Chemistry

Lecture 1
Introduction to Reaction Intermediates: Carbocations: Generation, stability, reactions and applications in synthetic organic chemistry, Exercise

Lecture 2
Free Radicals: Generation, stability, examples and applications in synthetic organic chemistry, Exercise.

Lecture 3 & 4
Carbenes and Nitrenes: Generation, stability, examples and applications in synthetic organic chemistry, Exercise

Lecture 5
Ylides: Generation, stability, examples and applications in synthetic organic chemistry, Exercise

Lecture 6
Organic Reactions without formation of intermediates: Diels-Alder reaction, S_N2 and E2 reactions, their applications, Exercise

Module 3
Thermodynamics and Equilibrium   3 lectures

Module 4
Basics of Electrochemistry   2 lectures

Module 5
Chemical Kinetics   4 lectures

Pre Module Test on Coordination Chemistry

1. Out of the following compounds select the coordination compounds-

   (i)AgCl, Ag(NH$_3$)$_2$Cl, AgNO$_3$

   (ii) FeSO$_4$, FeSO$_4$. (NH$_4$)$_2$SO$_4$.6H$_2$O, KFeCl$_4$

   (iii) KCl, KCl.MgCl$_2$.6H$_2$O, K$_3$Co(NO$_2$)$_6$

2. Calculate oxidation state of metal ion in the following coordination compounds -

   (i)[Fe(CN)$_6$]$^{4-}$ and [Fe(CN)$_6$]$^{3-}$

   (ii)[Co(NH$_3$)$_5$ Cl] Cl$_2$ and [Co(NH$_3$)$_5$ Cl$_2$] Cl

   (iii) Ni(CO)$_4$ and [NiCl$_4$]$^{2-}$

3. How many geometrical isomers do you predict for the coordination compounds given below -

   MX$_6$, MX$_5$, MX$_4$Y$_2$ and MX$_3$Y$_3$

4. Give one example each for homoleptic and heteroleptic coordination compounds.

5. Write the formula for (i)nitrito ligand as nitrito- N and nitrito- O
   (ii) thiocyanato and isothiocyanato –ligands

6. Write the formula for the following coordination compounds-
   (i)   Diammine chloridonitritito-N-platinum (II)
   (ii)   Mercury(I) tetrathiocyanatocobaltate (III)
   (iii)   Dichlorobis(ethane-1,2-diamine)cobalt(III) chloride

7. Write the IUPAC names of the following coordination compounds-
   (i)   [(Ag(NH$_3$)$_2$] [Ag(CN)$_2$]
   (ii)   K$_2$Zn(OH)$_4$
   (iii)   K$_3$[Al(C$_2$O$_4$)$_3$]

8. How will you identify[[Co(NH$_3$)$_5$SO$_4$] Br and [Co(NH$_3$)$_5$ Br] SO$_4$?

9. Using valence bond theory show hybridization in the following coordination compounds-

   [Co(NH$_3$)$_6$]$^{3+}$, [CoCl$_4$]$^{2-}$ and [CoF$_6$]$^{3-}$

10. Using valence bond theory can you explain reddish violet color of [Ti (H$_2$O)$_6$]$^{3+}$?

Coordination Chemistry

First Lecture

Coordination Chemistry plays a vital role in various fields, for example, in the natural world, medicines, catalysts and analytical chemistry etc. In the natural world, complexes of iron, hemoglobin, myoglobin and cytochromes are known as oxygen transport, oxygen storage and electron transport molecules respectively. Some complexes of iron, zinc, copper and molybdenum are involved in enzymatic processes in biological systems. Medicines like cis-platin and carboplatin are used as anticancer drugs. Some 3d metal Schiff base complexes are known for their antitumor activity. Many industrial catalysts are metal complexes like Ziegler Natta catalyst ($TiCl_3$ and AlR_3 for polymerization of alkene) Rh (I) complexes of diphosphine, sulfide clusters of iron, Fe-Mo and Ru-Mo etc. In analytical chemistry, separation of metal ions, Ag^+- Hg_2^{2+}, Cu^{2+}- Cd^{2+}, Ni^{2+}- Co^{2+} etc. is achieved by complex formation reactions. Quantitative estimation of Ca^{2+} and Mg^{2+} ions is performed titrimetrically using ethylene diamine tetra acetic acid. The concentration of metal ions, Cu^{2+}, Co^{2+}, Zn^{2+} and Ni^{2+} etc. is determined gravimetrically as their stable complexes.

Thus, metal complexes are very much important in our daily life, it seems essential to carry out a detailed study to understand their chemistry. The conditions under which an octahedral complex is high spin or low spin, are being discussed. Similarly, how to predict that a metal M forming a complex ML_4 should have tetrahedral geometry or square planar geometry through extreme distortion of octahedral geometry, is being discussed. An

account of magnetic properties of complexes, calculation of magnetic moments along with concept of color and intensity of absorption bands is being given in detail.

Coordination Complex

A coordination complex consists of a central atom or ion which is usually metallic and is called coordination center and a surrounding array of bound molecules or ions that are in turn, known as ligands or complexing agents. Ligands are Lewis bases containing at least one pair of electrons to donate to a metal atom or ion.

Nature of complex

Depending on the charge, a complex may be cationic, anionic or neutral.

$[Fe\,(H_2O)_6]^{2+}$ cationic complex

$[Fe(CN)_6]^{4-}$ anionic complex

$[Ni(CO)_4]$ neutral complex

Coordination Number(Ligancy)

Number of atoms, ions or molecules that a central atom or ion holds as its nearest neighbors in a complex or coordination compound or in a crystal is known as coordination number. In the above complexes, it is 6, 6 and 4 respectively.

Metal is usually a transition metal. Transition metals are-

1. Small, highly charged ions with variable oxidation states

2. Possess vacant /filled orbitals of right energy to accept electrons

3. High crystal field stabilization energy

Hard acids- possess small size, high positive oxidation state, cations with s^2p^6 electronic configuration like H^+, Li^+, Na^+, K^+, Ca^{2+}, Al^{3+}, BF_3 are Hard acids and have lowest – unoccupied molecular orbitals (LUMO) of high energy.

Soft acids- Comparatively larger size, low oxidation state, cations with pseudo inert gas configuration $s^2p^6d^{10}$ like Cu^+. Au^+, Tl^+, Hg^{2+}, Cd^{2+}, BH_3. Soft acids have LUMO of lower energy than hard acids.

Ligands are classified in various ways-

1. On the basis of charge, ligand may be neutral anionic and cationic

    Anionic- halide ion, CN^-

    Cationic- NO^+, $[N_2H_5]^+$

    Neutral – NH_3, H_2O

2. On the basis of ligand field strength

    I^-, Br^-, Cl^-, F^-, H_2O - weak field ligands

    CN^-, CO, *o*-dipyridyl, 1,10 phenanthroline, ethylene diamine, ammonia, pyridine - strong field ligands
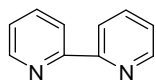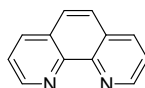
o- dipyridyl   1,10 phenanthroline

3. On the basis of number of coordinating sites

    Mono dentate- NH_3, H_2O

Ambidentate- monodentate ligands with different sites of bonding -SCN⁻ -NCS⁻

Bidentate - *o*-dipyridyl, 1,10 phenanthroline, ethylene diamine

Multi dentate- Terpyridine - tridentate

Ethylene diamine tetra acetic acid -hexa dentate

Bidentate and multidentate ligands are also known as chelating ligands and form more stable complexes than monodentate ligands

4. On the basis of nature of bonding-

   π donor – C_2H_4, first donation occurs from π electrons of ethylene to vacant orbital of metal ion and second back donation from metal filled d orbitals to vacant antibonding orbitals of ethylene.

   σ donor- NH_3, H_2O, lone pair of electrons are donated to vacant orbital of the metal ion.

5. Hard and Soft ligands

   Hard ligands- F, O, N donors- H_2O, NH_3, OH^-, F^-, Cl^-, $(CH_3COO)^-$, $(CO_3)^{2-}$. These are highly electronegative, have low polarizability and associated with vacant orbitals of high energy which are inaccessible.

   Hard bases have highest occupied molecular orbitals (HOMO) of low energy.

   Soft ligands- I, S, P donors- I^-, R_3P, R_2S, CO, C_2H_4, C_6H_6, H^-, SCN^-. These are less electronegative, have high polarizability and have easily accessible vacant low lying orbitals. Soft bases have HOMO of higher energy than hard bases.

   The affinity of soft acids and bases is mainly covalent in nature while that of hard acid and hard bases for each other is mainly ionic in nature.

Problems

1. Silver is found in nature as silver sulfide, explain.

Soft acids combine with soft bases, Ag^+ is soft acid and S^{2-} is soft base.

2. Carbonyl complexes are formed with the low oxidation states of metal, justify.

Metal in low oxidation state is electron rich and can easily be involved in back donation to vacant antibonding molecular orbitals of the ligand.

Exercise

1. Compare nature of bonding in metal complexes of CO and ethylene.

2. Name a complex of benzene.

3. Discuss stability of $[CaEDTA]^{2-}$, (EDTA= ethylene diamine tetra acetic acid) on the basis of Hard Soft Acid Base Principle (HSAB principle).

4. The ions Ni^{2+}, Pt^{2+} and Pd^{2+} belong to the same group but complexes of with S, P containing ligands are much known for the latter two ions.

5. Out of $[Cr(NH_3)_6]^{3+}$ and $[Cr(en)_3]^{3+}$ complexes, which one is more stable and why?

6.

Second Lecture

There are three theories to explain Nature of bonding in complexes.

- Valence bond theory

- Crystal Field Theory

- Molecular orbital Theory

Here Crystal field theory is being discussed.

Crystal Field Theory is one of the most important theory for explaining nature of bonding in coordination compounds. It deals with electrostatic interactions between metal ion and the ligands forming complexes with varying geometries like octahedral, tetrahedral, square planar etc. According to this theory, the donor electrons of the incoming ligands due to their negative charges attract the positively charged metal ion. Besides this, there is repulsive interaction between d electrons present on the metal ion and the ligands. Certain assumptions are taken while dealing with CFT-

1. The ligands are treated as point charges. In fact, this is not practically true since sometimes the size of ligand particularly when it is sulfur or phosphorus donating ligands, is approximately similar to the size of metal ion.

2. The interactions between metal ion and ligand are treated as purely electrostatic, no covalent interactions are considered. This again is not true, some of the observations cannot be explained without invoking covalent interactions.

3. Upon complexation, the degeneracy of d -orbitals is destroyed. In isolated gaseous metal ion, all of the five d-orbitals are degenerate. When spherically symmetrical field of ligand approaches the metal ion, d-orbitals still remain degenerate, although their energy level is raised a little bit. Usually the complexes formed by transition metal ions are octahedral, tetrahedral or square planar, the field provided by the ligands is not at all spherically symmetrical therefore d-orbitals are unequally affected by the ligands.
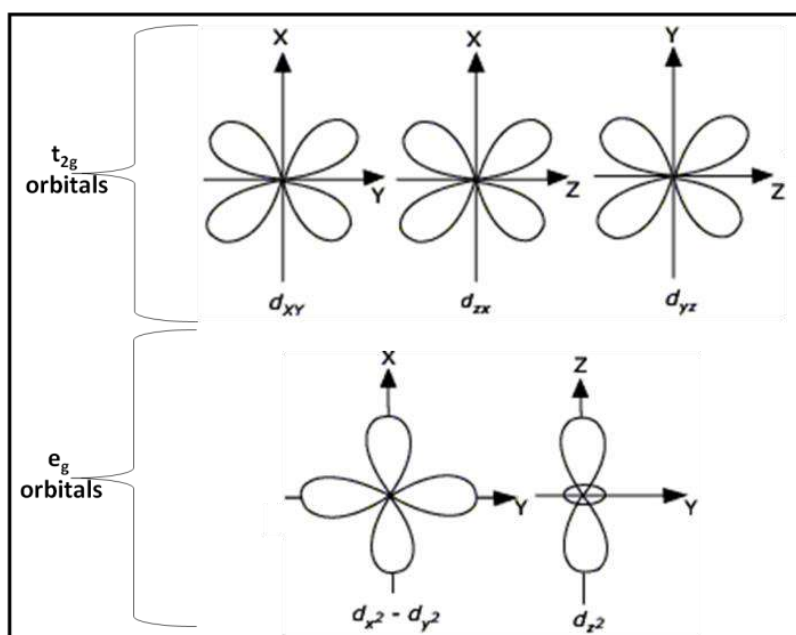
Figure 1. Shapes of d-orbitals

Octahedral Complexes

In octahedral complexes, the ligand approach is along the axes. As a result, the d-orbitals where electron density is oriented along the axes, dx^2-y^2 and dz^2 are repelled much more by the ligands while the orbitals dxy, dxz, dyz having electron density oriented in between the axes are repelled lesser by the ligands. Thus two sets of orbitals e_g and t_{2g}, doubly and triply degenerate respectively, are formed.

Noticeable features

1. The mean of these two sets of orbitals is zero and represented as Bari center.

2. The energy gap between these two sets of orbitals is known as Δ_0, crystal field splitting parameter under the influence of octahedral field of ligands.
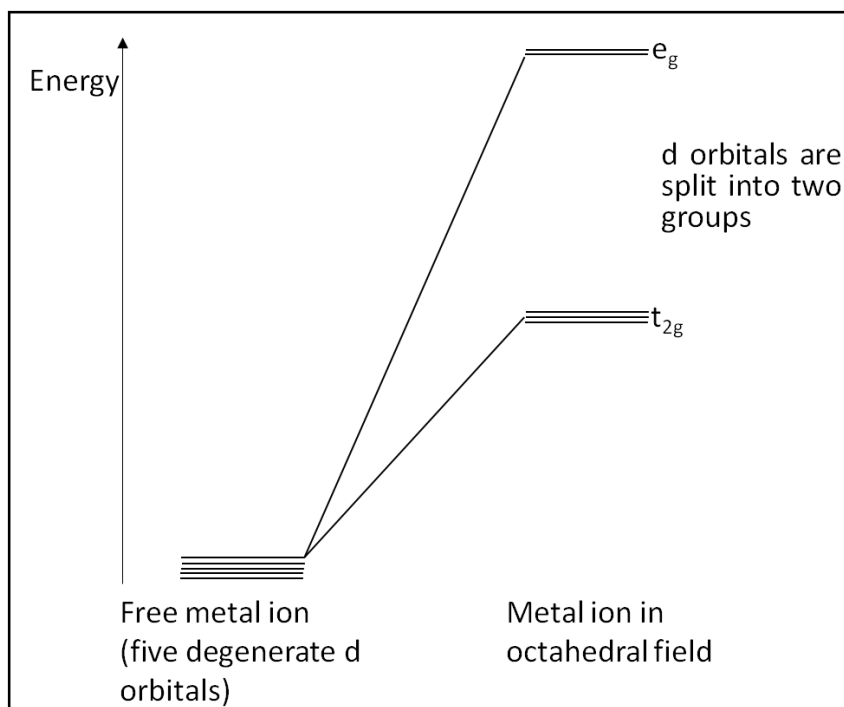
Figure 2. Crystal Field splitting of energy levels in an octahedral field of ligands

3. The value of Δ_0 in the complex $[Ti(H_2O)_6]^{3+}$ has been experimentally found as 20,300 cm^{-1} or 243 kj/mol (1 kj/mol=83.7cm^{-1}) from the absorption spectrum in the visible region showing band at 500 nm or 5000A^0.

4. The magnitude of Δ_0 depends on mainly on field strength of ligand, oxidation state of metal and down the group from 3d to 4d or 5d metals.

5.a. The ligands arranged in order of increasing ligand field strength constitute **spectro-chemical series**-

$$I^- < Br^- < S^{2-} < SCN^- < Cl^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < pyridine$$

$$< NH_3 < \text{ethylene diamine} < o\text{-dipyridyl} < 1,10\text{-phenanthroline} < NO_2^- < CN^- < CO$$

The Ligand with higher field, like CO or CN^- would produce more splitting or larger energy gap while I^- being weakest would produce minimum energy gap.

b. With increase in oxidation state of 3d metal ions from +2 to +3 there is almost 50% increase in Δ_0.

c. Descending in a group, for example 3d to 4d series, Δ_0 increases by approximately 30%.

Crystal Field Stabilization Energy (CFSE) and Pairing (P) Energy

The CFSE is defined as net gain in energy achieved by preferential filling of electrons in lower lying d orbitals over the energy of complete random occupancy of electrons in all five d orbitals. It is 2 to10% of actual bond energy. The energy required to pair the electrons in the same orbital is known as Mean Pairing energy and it is constant for the same metal ion.

Noticeable features

1. When magnitude of Δ_0 is higher than P, electrons tend to pair in the lower lying orbital thus spin paired or low spin complexes are formed. On the other hand, if Δ_0 is less than P, high spin or spin free complexes are formed. If Δ_0 is approximately equal to P, single temperature changes may affect spin changes. Sum of CFSE and P gives Total Stabilization Energy(TSE).

d^n system	electronic distribution	CFSE	P	TSE
d^0	$t_{2g}^0 eg^0$	zero		
d^1	$t_{2g}^1 eg^0$	$-0.4\ \Delta_0$		
d^2	$t_{2g}^2 eg^0$	$-0.4\ \Delta_0 \times 2 = -0.8\ \Delta_0$		
d^3	$t_{2g}^3 eg^0$	$-0.4\ \Delta_0 \times 3 = -1.2\ \Delta_0$		
d^4	$t_{2g}^3 eg^1$(high spin)	$-0.4\ \Delta_0 \times 3 + 0.6\ \Delta_0 = -0.6\ \Delta_0$		
d^4	$t_{2g}^4 eg^0$(low spin)	$-0.4\ \Delta_0 \times 4 = -1.6\ \Delta_0$	P	$-1.6\ \Delta_0 + P$
d^5	$t_{2g}^3 eg^2$(high spin)	$-0.4\ \Delta_0 \times 3 + 0.6\ \Delta_0 \times 2 = $ Zero		
d^5	$t_{2g}^5 eg^0$(low spin)	$-0.4\ \Delta_0 \times 5 = -2.0\ \Delta_0$	2P	$-2.0\ \Delta_0 + 2P$
d^6	$t_{2g}^4 eg^2$(high spin)	$-0.4\ \Delta_0 \times 4 + 0.6\ \Delta_0 \times 2 = -0.4\ \Delta_0$		
d^6	$t_{2g}^6 eg^0$ (low spin)	$-0.4\ \Delta_0 \times 6 = -2.4\ \Delta_0$	2P	$-2.4\ \Delta_0 + 2P$
d^7	$t_{2g}^5 eg^2$(high spin)	$-0.4\ \Delta_0 \times 5 + 0.6\ \Delta_0 \times 2 = -0.8\ \Delta_0$		
d^7	$t_{2g}^6 eg^1$(low spin)	$-0.4\ \Delta_0 \times 6 + 0.6\ \Delta_0 = -1.8\ \Delta_0$	P	$-1.8\ \Delta_0 + P$
d^8	$t_{2g}^6 eg^2$	$-0.4\ \Delta_0 \times 6 + 0.6\ \Delta_0 \times 2 = -1.2\ \Delta_0$		
d^9	$t_{2g}^6 eg^3$	$-0.4\ \Delta_0 \times 6 + 0.6\ \Delta_0 \times 3 = -0.6\ \Delta_0$		
d^{10}	$t_{2g}^6 eg^4$	$-0.4\ \Delta_0 \times 6 + 0.6\ \Delta_0 \times 4 = $ Zero		

2. For d^4 and d^7 low spin systems only one P is added in CFSE to get TSE because only one electron is to be paired in the same orbital, rest are paired in natural configuration while for d^5 and d^6 low spin systems twice of pairing energy is required to be added to get TSE.

3. The 3d metals form high and low spin complexes, on the other hand 4d and 5d metals having very high CFSE form low spin complexes.

Problems

1. Calculate CFSE for the complex $[Cr\ (H_2O)_6]^{2+}$

Chromium in ground state is $[Ar]3d^5\ 4s^1$, in +2 state, will be a d^4 system with $t_{2g}^3 eg^1$ configuration of electrons because H_2O is a weak field ligand. CFSE will be therefore

$$-0.4\ \Delta_0 X\ 3 + 0.6\ \Delta_0 = -0.6\ \Delta_0$$

2. Calculate TSE for $[Fe(CN)_6]^{4-}$

Iron in ground state is $[Ar]3d^6 4s^2$, in +2 state it will be a d^6 system with $t_{2g}^6 eg^0$ configuration of electrons because CN^- is a strong field ligand. Therefore, TSE will be

$$-0.4 \Delta_0 X 6 + 2P = -2.4 \Delta_0 + 2P$$

Since it is $t_{2g}^4 eg^2$ by the configuration itself, only 2 electrons have to be paired.

Exercise

1. An aqueous solution of titanium chloride shows zero magnetic moment. Write down its formula assuming it to be an octahedral complex in aqueous solution.

   $[Ti (H_2O)_6] Cl_4$, a d^0 configuration.

2. Calculate CFSE and TSE for the following complexes-

   $[Co(CN)_6]^{4-}$, $[Ti(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{3+}$, $[Cr(H_2O)_6]^{2+}$, $[Cr(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, $[Mn(CN)_6]^{4-}$, $[MnF_6]^{4-}$, $[Fe(1,10phenanthroline)_3]^{3+}$, $[Fe(H_2O)_6]^{2+}$, $[Fe(dipyridyl)_3]^{3+}$, $[Fe(dipyridyl)_3]^{2+}$, $[FeF_6]^{3-}$, $[Fe(H_2O)_6]^{3+}$.

3. Give correct order for the energy gap between two sets of d orbitals in the following complexes-

   $[CrCl_6]^{3-}$, $[Cr(H_2O)_6]^{3+}$, $[Cr(en)_3]^{3+}$ $[Cr(CN)_6]^{3-}$.

4. Give correct order for energy gap between two sets of d levels in the following complexes –

   a. $[Fe (H_2O)_6]^{2+}$, $[Fe (H_2O)_6]^{3+}$

   **b.** $[Co(NH_3)_6]^{3+}$, $[Rh(NH_3)_6]^{3+}$, $[Ir(NH_3)_6]^{3+}$

   5.Iron (II) in deoxy hemoglobin is paramagnetic but in oxyhemoglobin, it is diamagnetic, explain.

Third Lecture

Tetrahedral Complexes

In tetrahedral geometry, the ligand approach is in between the axes. The e_g orbitals lie exactly between L-M-L bond, as a result, e_g-M-L bond angle is 109^0 28'/2, 54^o44' while t_{2g}-M-L bond angle comes to be 35^016' (90^0-54^044').
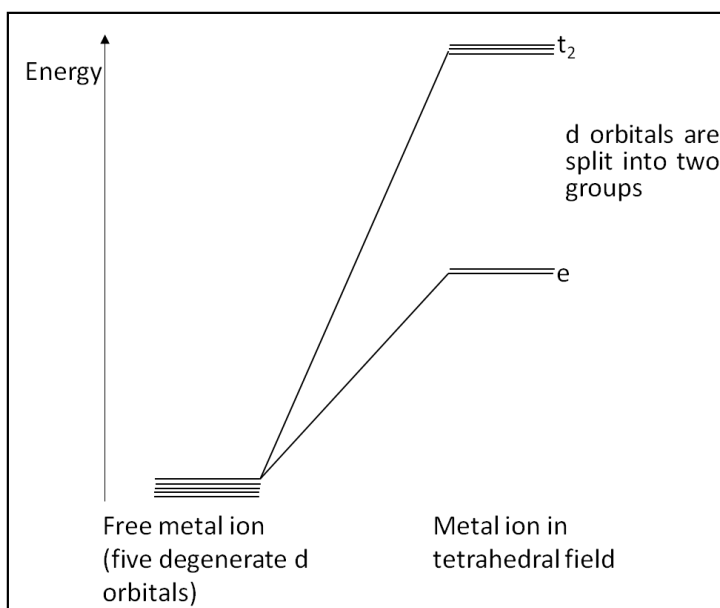
Figure 3. Splitting of d orbitals in a tetrahedral field of ligands

Noticeable features

1. The t_{2g} orbitals are closer than e_g orbitals and therefore get repelled more than e_g orbitals.

2. It can simply be stated that the d orbital splitting diagram in tetrahedral complexes is just inverse of octahedral complexes.

3. The g subscript should be omitted in tetrahedral complexes as these are never symmetrical.

4. The crystal Field Splitting parameter Δ_t is 4/9 of Δ_0.

   It is 2/3 of Δ_0 due to number of ligands being 4 and 6 in tetrahedral and octahedral complexes respectively and 2/3 of Δ_0 due to approach of ligands, t_2-M-L bond angle $35^0 16$' and e-M-L bond angle $54^0 44$'.

5. Tetrahedral complexes are high spin complexes as the energy gap between two sets of orbitals is roughly half of octahedral complexes.

d^n system	electronic distribution	CFSE
d^0	$e^0 t_2^0$	Zero
d^1	$e^1 t_2^0$	$-0.6\ \Delta_t$
d^2	$e^2 t_2^0$	$-0.6\ \Delta_t \times 2 = -1.2\ \Delta_t$
d^3	$e^2 t_2^1$	$-0.6\ \Delta_t \times 2 + 0.4\ \Delta_t = -0.8\ \Delta_t$
d^4	$e^2 t_2^2$	$-0.6\ \Delta_t \times 2 + 0.4 \times 2\ \Delta_t = -0.4\ \Delta_t$
d^5	$e^2 t_2^3$	$-0.6\ \Delta_t \times 2 + 0.4 \times 3\ \Delta_t =$ Zero
d^6	$e^3 t_2^3$	$-0.6\ \Delta_t \times 3 + 0.4\ \Delta_t \times 3 = 0.6\ \Delta_t$
d^7	$e^4 t_2^3$	$-0.6\ \Delta_t \times 4 + 0.4 \times 3 = -1.2\ \Delta_t$
d^8	$e^4 t_2^4$	$-0.6\ \Delta_t \times 4 + 0.4 \times 4\ \Delta_t = -0.8\ \Delta_t$
d^9	$e^4 t_2^5$	$-0.6\ \Delta_t \times 4 + 0.4 \times 5\ \Delta_t = -0.4\ \Delta_t$
d^{10}	$e^4 t_2^6$	$-0.6\ \Delta_t \times 4 + 0.4 \times 6\ \Delta_t =$ Zero

6. As evident from the above data CFSE in tetrahedral complexes is much smaller than octahedral complexes, these should not be energetically favored. Since tetrahedral complexes are very much known to exist, their formation can be possible under the conditions when loss in CFSE is meagre.

   A. Metal is in low oxidation state like in $Ni(CO)_4$, Ni is in zero oxidation state.

   B. Ligand is weak field, for example Cl^- in $[MnCl_4]^{2-}$.

C. Metal ion with d^0, d^5(weak field) or d^{10} configurations [MnO_4]⁻, [$MnCl_4$]²⁻ and [$ZnCl_4$]²⁻ respectively where CFSE is zero in octahedral field.

D. In tetrahedral complexes the bond angle being 109^028' is larger than that in octahedral complexes,90^0. Therefore, bulky ligands may form tetrahedral complexes as have lesser steric hindrance.

E. The configurations of metal ions where symmetrical filling of electrons in degenerate orbitals is present, may form tetrahedral complexes. For example, $e^0t_2{}^0$, $e^2t_2{}^0$, $e^2t_2{}^3$, $e^4t_2{}^3$, $e^4t_2{}^6$.

Problem

1. **Should tetrahedral geometry be favored in [MnO₄]⁻ and [MnO₄]³⁻ ?**

   It will be favored because their electronic configurations are $e^0t_2{}^0$ and $e^2t_2{}^0$ respectively. There is no asymmetrical filling of electrons in these configurations.

Exercise

1. Out of the following configurations, which configurations are regular for tetrahedral geometry?

   $e^2\,t_2{}^3$, $e^2\,t_2{}^2$, $e^4\,t_2{}^4$, $e^2\,t_2{}^1$ and $e^4\,t_2{}^5$

2. Calculate CFSE for the following complexes-

   [$FeCl_4$]⁻, [FeO_4]²⁻, [$NiCl_4$]²⁻, [MnO_4]⁻, [CrO_4]²⁻, [MnO_4]²⁻, [CrO_4]³⁻, [$Ti(H_2O)_6$]³⁺, [MnO_4]³⁻, [VCl_4]⁻, [$MnCl_4$]²⁻, [$CoCl_4$]²⁻ , [$ZnCl_4$]²⁻.

Tetragonal distortion of Octahedral Complexes (Jahn Teller Distortion)

Asymmetrical filling of degenerate d orbitals of a metal ion results in unequal repulsion with incoming ligands which causes distortion in geometry. Practically, distortion in geometry is observed when e_g orbitals which point directly at ligands, are asymmetrically filled. The t_{2g} orbitals do not point directly at ligands, asymmetrical filling of electrons in them does not give observable distortion. Thus high spin $d^4(t_{2g}^3 eg^1)$, low spin $d^7(t_{2g}^6 eg^1)$ and $d^9(t_{2g}^6 eg^3)$ configurations result in Jahn Teller distortion as e_g orbitals are asymmetrically filled. Among e_g orbitals, the electron in dz^2 experiences repulsion from two ligands but that in dx^2-y^2 experiences repulsion from four ligands. Therefore, the electron tends to be present in dz^2. Since the electron lies in dz^2 orbital the ligand approaching towards it, will be more repelled as compared to vacant dx^2-y^2 orbital. Consequently, two of the bond lengths along Z –axis will be longer than the rest four. This is known as **tetragonal elongation or Z-ou**t **distortion**. On the other hand, if the electron is placed in dx^2-y^2 orbital, reverse would occur and bond lengths along z axis are shorter than the rest four. This would result in **tetragonal compression or Z-in type of distortion**.
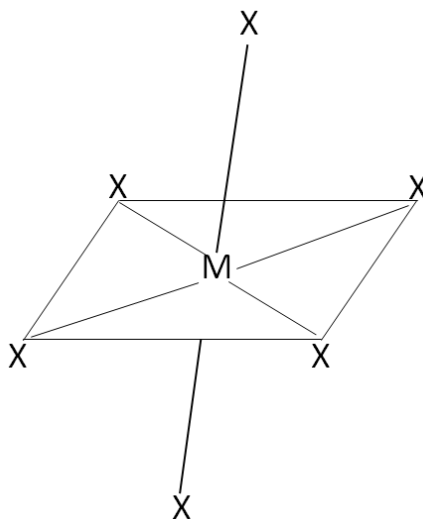
**Figure 4.** Tetragonal elongation or Z-out distortion
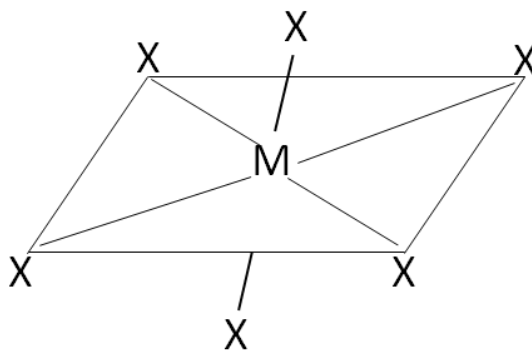
Figure 5. Tetragonal compression or Z-in distortion

Square Planar Complexes

In a complex, like $[Ni(H_2O)_6]^{2+}$ with $t_{2g}^6 eg^2$ configuration and symmetrical filling of electrons in both t_{2g} and e_g orbitals, no distortion is observed. In presence of strong field ligands like CN^-, electron in dz^2 is being repelled by two ligands while that in $dx^2\text{-}y^2$ is repelled by four ligands. As a result, energy of $dx^2\text{-}y^2$ increases and that of dz^2 decreases. The electrons present singly in $dx^2\text{-}y^2$ and dz^2 are paired up in dz^2 and $dx^2\text{-}y^2$ becomes

vacant, therefore four ligands can now approach along x, y directions but experience too much repulsion along z direction. Consequently, square planar complex is formed instead of octahedral complex.
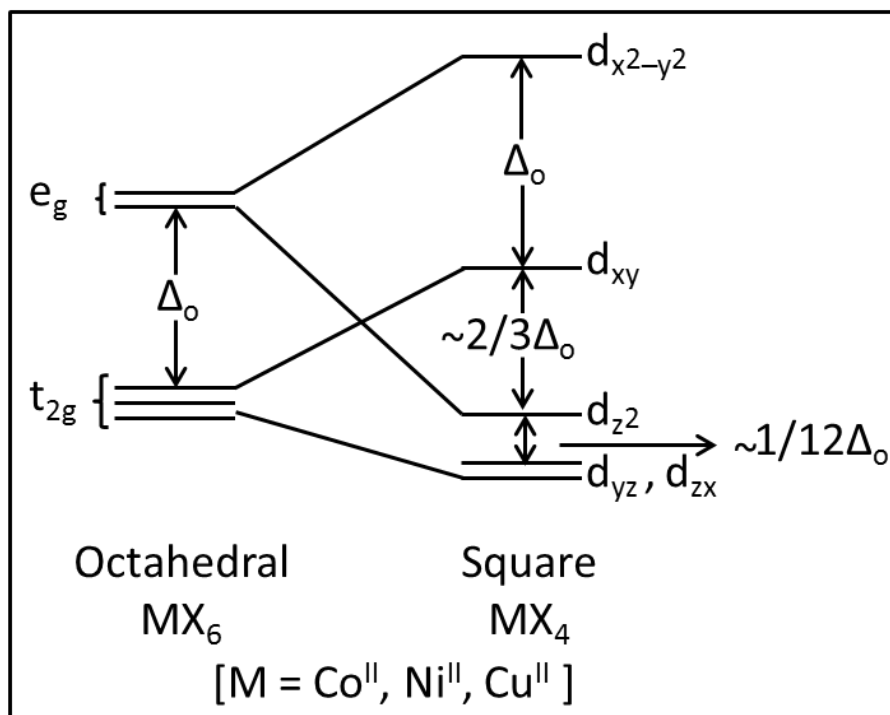
Figure 6. Square Planar complexes

Problems

1. Predict the possibility of Jahn Teller distortion of Fe $^{2+}$ ion in [Fe $(H_2O))_6]^{2+}$

Fe(II) ion with electronic distribution as $t_{2g}^4 eg^2$ showing asymmetrical filling of t_{2g} but symmetrical filling of electrons in e_g orbitals will not show any distortion in the complex [Fe $(H_2O)_6]^{2+}$.

2. The complex [Fe(CN)₆]⁴⁻ is easily formed but [Ni(CN)₆]⁴⁻ is not formed, instead [Ni(CN)₄]²⁻ is formed.

The complex $[Fe(CN)_6]^{4-}$ with CN^- as strong field ligand, will have $t_{2g}^6 eg^0$ electronic distribution. Ligand can approach easily along z direction as there will be no repulsion in z direction due to vacant e_g orbitals. However, in case of Ni (II) ion with $t_{2g}^6 eg^2$ configuration, CN^- being strong field ligand causes pairing of electrons in dz^2 orbital and dx^2-y^2 orbital becomes vacant. This happens because the electrons would feel repulsion from four ligands if these are in dx^2-y^2 orbital and would feel repulsion from two ligands if these are in dz^2 orbital. Therefore, electrons prefer to be in the dz^2 orbital and ligand entry along this direction is not favored. As a result, **$[Ni(CN)_4]^{2-}$ is formed instead of $[Ni(CN)_6]^{2-}$.**

Exercise

1. Draw d-orbitals splitting patterns with filling of electrons in the appropriate d orbitals in the following complexes

   (a). $d^{7,}$ octahedral low spin and high spin

   (b). d^7, tetrahedral

   (c). d^8, square planar

   (d). d^9, octahedral with tetragonal distortion

2. Calculate in units of Δ_0, the difference in CFSE between complexes (a) and (b).

3. Which of the following complexes would undergo Jahn Teller distortion-

   (a). $[Cr (H_2O)_6]^{2+}$, $[Cr(CN)_6]^{4-}$

   (b). $[Co (H_2O)_6]^{2+}$, $[Co(NH_3)_6]^{3+}$

   (c). $[Cu (H_2O)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$

4. With Cl⁻ as weak field ligand, Ni(II) forms tetrahedral complex $[NiCl_4]^{2-}$ but Pd (II) and Pt(II) belonging to the same group form square planar complexes$[PdCl_4]^{2-}$ and $[PtCl_4]^{2-}$ respectively, explain.

Fourth Lecture

Magnetic properties of complexes

Magnetic moment in Bohr Magneton can be calculated using the formula- $\mu_s = g[S(S+1)]^{1/2}$,

Where μ_s = Spin only magnetic moment, S = Total spin quantum number, g = Spectroscopic splitting factor and its value for free electron is 2.0023. The formula may be simplified as

$$\mu_s = [n(n+2)]^{1/2}$$

where n is number of unpaired electrons.

Accordingly, μ_s can be calculated for the value of n ranging from 1 to 7 as 1.73 BM (1), 2.83 BM (2), 3.87BM (3), 4.90BM (4), 5.97BM (5), 6.93 BM (6) and 7.94(7).

When orbital contribution of magnetic moment is included, the formula becomes-

$$\mu_{s+l} = [4S(S+1)+L(L+1)]^{1/2}$$

where L = Total angular momentum quantum number and μ_{s+l} is total magnetic moment including spin and orbital magnetic moments

Orbital contribution is partially quenched, it is observed in those cases only where an orbital can be transformed into an equivalent orbital by rotation. This is not possible at all in case of e_g orbitals as the shapes of dx^2-y^2 and dz^2 orbitals are different, however, t_{2g} orbitals having same shape can easily be transformed into each other provided it is not half or full filled. Accordingly, in octahedral complexes the configurations $t_{2g}^1 eg^0$, $t_{2g}^2 eg^0$, $t_{2g}^4 eg^0$, $t_{2g}^5 eg^0$, $t_{2g}^4 eg^2$, $t_{2g}^5 eg^2$ should have orbital contribution. Similarly, in tetrahedral complexes the configurations $e^2 t_2^1$, $e^2 t_2^2$, $e^4 t_2^4$, $e^4 t_2^5$ will show orbital contribution.

Problem

1. Out of [Ni (H₂O)₆]²⁺, [NiCl₄]²⁻ both having oxidation state of Ni as +II which will show higher magnetic moment?

[Ni (H₂O)₆]²⁺ (t₂g⁶ eg²) will not show orbital contribution having 6 electrons in t₂g orbital but [NiCl₄]²⁻ (e⁴t₂⁴) will have orbital contribution because there are 4 electrons in t₂ orbital. Therefore, magnetic moment will be higher in the latter case.

Exercise

1. Calculate the spin only magnetic moment of the following complexes-

[FeCl₄]⁻, [FeO₄]²⁻, [NiCl₄]²⁻, [MnO₄]⁻, [CrO₄]²⁻, [MnO₄]²⁻, [CrO₄]³⁻, [Ti(H₂O)₆]³⁺,

[MnO₄]³⁻, [VCl₄]⁻, [MnCl₄]²⁻, [CoCl₄]²⁻, [ZnCl₄]²⁻, [Co(CN)₆]⁴⁻, [Ti(H₂O)₆]³⁺,

[V(H₂O)₆]³⁺, [Cr(H₂O)₆]²⁺, [Cr(CN)₆]⁴⁻, [Fe(CN)₆]³⁻, [Mn(CN)₆]⁴⁻, [MnF₆]⁴⁻, [Fe(1,10 phenanthroline)₃]³⁺, [Fe(H₂O)₆]²⁺, [Fe(dipyridyl)₃]³⁺, [Fe(dipyridyl)₃]²⁺, [FeF₆]³⁻, [Fe(H₂O)₆]³⁺, [Fe(1,10 phenanthroline)₃]²⁺.

2. Which of the following complexes will have orbital contribution to the magnetic moment and why?

a. [Fe(CN)₆]³⁻ and [Fe(CN)₆]⁴⁻

b. [Fe (H₂O)₆]³⁺ and [Fe (H₂O)₆]²⁺

c. [Cr (H₂O)₆]²⁺, [Cr(CN)₆]⁴⁻

4. The complex [CoF₆]³⁻ is paramagnetic, while [Co(CN)₆]³⁻ is diamagnetic, explain.

**5.** The complex Na₂[Ni(CN)₂Br₂] has zero magnetic moment, predict its geometry.

Fifth Lecture

Color of complexes

Color of complex may be due to crystal defect, d-d transition or charge transfer. It is relevant here to discuss about d-d transition and charge transfer.

d-d transition

As discussed, in all the complexes d orbitals split into two sets of orbitals depending upon the approach of ligands. The electron in the lower lying orbital is excited to higher energy level by absorption in visible region of the spectrum, the transmitted light is colored with the complementary color of the light absorbed. According to Newton's disc, a complex absorbing in yellow region will appear violet or vice versa. Similarly, complex which absorbs in red region will appear green and vice versa. Thus, the observed color of a complex is dependent on the region of visible light where it absorbs, which in turn, will depend upon the magnitude of energy gap between two sets of d orbitals. As discussed earlier, the energy gap depends on strength of ligand, oxidation state of metal, geometry of the complex and the nature of metal whether it belongs to 3d/4d/5d series.
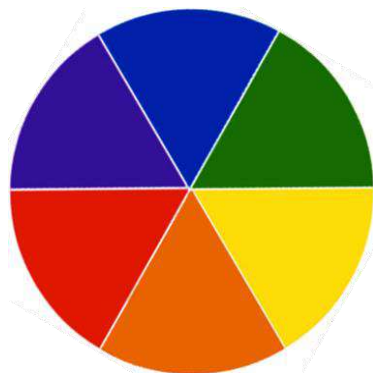
Figure 6. Newton's Disc

Problem

1. An aqueous solution of $[Ti(H_2O)_6]^{3+}$ is reddish violet in color, turns colorless in presence of excess of CN^- ions.

$[Ti(H_2O)_6]^{3+}$ absorbs in yellow green region of visible light and appears reddish violet. When H_2O ligand (weak field) is replaced by CN^- (very strong field ligand) the energy gap becomes very high, as a result complex absorbs in UV region and turns colorless.

2. $[Co(H_2O)_6]^{2+}$ is pink but $[CoCl_4]^{2-}$ is blue.

$[Co(H_2O)_6]^{2+}$ is octahedral complex, energy gap is higher than $[CoCl_4]^{2-}$ which is tetrahedral. Therefore, $[CoCl_4]^{2-}$ will absorb in lower energy region.

Intensity of color and absorption of bands

Intense color of a complex means high intensity of bands in its absorption spectrum. For allowed transitions intensity of absorption bands would be high, for forbidden transitions it has to be very low and for partially forbidden it is in between. Intensity of absorption bands is measured by the parameter molar absorption coefficient ε which is defined as absorbance of a solution of concentration 1mole/litre and thickness of the cell as 1 cm (unit litre/mol/cm).

Laporte orbital selection rule

This rule states that those transitions are allowed transitions which have change in l values

i.e. $$\Delta l = \neq 0$$

Accordingly, s to p and p to d are allowed transitions but d-d transitions are forbidden transitions. These become partially allowed when complex lacks center of symmetry, i.e. when x, y, z axes are replaced by -x, -y, -z respectively, the same configuration is not reached. ML_6, trans-ML_4X_2 types of complexes will possess center of symmetry but ML_5X or cis-ML_4X_2 complexes will lack center of symmetry. Tetrahedral complexes are never symmetrical and always lack center of symmetry. When a complex is non-centrosymmetric, there is d-p mixing, therefore it is no more now a pure d-d transition.

The ML_6 type of complexes gain some intensity as the ligands are most of the time out of their centrosymmetric equilibrium position due to vibration of M-L bond.

Spin selection rule

This rule states that those transitions are allowed which do not have change in spin.

$$\Delta s = 0$$

Problems

1. The intensity of absorption bands in $[CoCl_4]^{2-}$ is almost hundred times greater than in $[MnCl_4]^{2-}$.

Here both the complexes are tetrahedral, both lack center of symmetry and transitions are partially orbital allowed. Co^{2+} in tetrahedral geometry, $e^4t_2^3$ will be spin allowed while Mn^{2+}, $e^2t_2^3$ will be a spin forbidden transition. Spin forbidden transitions are 100 times weaker than that of spin allowed transitions.

2. The intensity of absorption band is much weaker in $[Mn(H_2O)_6]^{2+}$ as compared to that in case of $[Ti(H_2O)_6]^{3+}$

Both the complexes are ML_6 type, so transitions will be orbital forbidden, Ti^{3+}, $t_{2g}^1 e_g^0$ will be spin allowed but Mn^{2+}, $t_{2g}^3 e_g^2$ will be spin forbidden. Therefore, intensity of absorption band is much weaker in the latter.

Exercise

1. Mention the complex which exhibits the lowest energy electronic absorption-

   $[NiCl_4]^{2-}$, $[Ni(CO)_4]$, $[Ni (H_2O)_6]^{2+}$, $[Ni(CN)_4]^{2-}$

2. Which of the following complexes will show minimum intensity in their absorption bands- $[Cr (H_2O)_6]^{2+}$, $[Mn(H_2O)_6]^{2+}$, $[V(H_2O)_6]^{2+}$ and $[Co(H_2O)_6]^{2+}$

3. Give reason for stronger intensity of absorption band in $[Co(NH_3)_5 Cl]^{2+}$ than $[Co(NH_3)_6]^{3+}$

4. Give correct order for the energy of absorption in the following complexes-

   $[CrCl_6]^{3-}$, $[Cr (H_2O)_6]^{3+}$, $[Cr(en)_3]^{3+}$ $[Cr(CN)_6]^{3-}$.

5. Arrange the following complexes in order of decreasing intensity of their absorption bands-

   a. $[CoCl_4]^{2-}$, $Co (H_2O)_6]^{2+}$

   b. $[CoCl_4]^{2-}$, $[FeCl_4]^-$

   c. $[Fe(CN)_6]^{3-}$, $Fe (H_2O)_6]^{3+}$

   d. $[Cr (H_2O)_6]^{2+}$, $[Cr(H_2O)_5Cl]^{2+}$

   e. $[Fe (H_2O)_6]^{2+}$ and $Fe (H_2O)_6]^{3+}$

6. A complex $[CoL_6]^{3+}$ is red colored while $[CoL'_6]^{3+}$ is green colored. Which ligand L or L' has larger Crystal Field Stabilization energy?

7. Why are Ti^{4+} and Zn^{2+} complexes white?

8. The complex $[Co (CN)_6]^{3-}$ is pale yellow. In which part of the electromagnetic radiation does it absorb? If in place of CN^- ions NH_3 is used as a ligand, will the shift in absorbance of radiation be towards blue or red region of electromagnetic radiation?

9. An aqueous solution of $[Ti(H_2O)_6]^{3+}$ reddish violet in color, turns colorless in presence of excess of CN^- ions.

10. The color of $CuSO_4.5H_2O$ is blue, what will be the color of its anhydrous compound?

Charge transfer transitions

1. These transitions are from filled orbitals of Ligand to vacant orbitals of Metal or from filled orbitals of Metal to vacant orbitals of Ligand. These transitions involve two entities, metal and ligand while d-d transitions are within the metal ion itself therefore, are not governed by the above selection rules.

2. Intensity of charge transfer bands is very high. For example, molar absorption coefficient value of $[TiCl_6]^{2-}$ is 10,000 litre/mol/cm.

3. Charge transfer bands sometimes, mask the d-d transition bands due to their high intensity.

Problems-

1. **Explain Formation of Ni(CO)₄ on the basis of CFT**

    Here Ni is in zero oxidation state, its formation cannot be explained just on electrostatic interaction between M ion and ligands. The covalent interaction has to be considered to explain the complex formation.

2. **Explain Intense color of KMnO₄ on the basis of CFT**

    Intense color of $KMnO_4$ is due to charge transfer and cannot be explained without covalent interaction. In CFT, assumption has been taken that interactions between M ion and ligands are purely electrostatic.

Exercise

1. Intensity of absorption band in $[TiCl_6]^{2-}$ is much higher than $[TiCl_6]^{3-}$, explain.

2. Compare the Intensity of absorption bands in $[MnO_4]^{2-}$ and $[MnO_4]^{-}$.

Reference Books

1. Concise Inorganic Chemistry by J. D. Lee, 5th Edition 2014, ELBS with Chapman & Hall.

2. Advanced Inorganic chemistry by F. A. Cotton and G. Wilkinson, 6th Edition 2007, A Wiley Inter science publication.

Pretest on Organic Chemistry Module

1. Which of the following is a permanent electron displacement effect?
a) Inductomeric
b) Electromeric
c) Inductive
d) All of the mentioned

2. Which of the following is application of inductive effect?
a) Bond length
b) Dipole moment
c) Strength of carboxylic acids
d) All of the mentioned

3. Due to presence of C – X polar bond in alkyl halide, alkyl halides are
a) More reactive than corresponding alkane
b) Less reactive than corresponding alkane
c) Equally reactive as corresponding alkane
d) None of the mentioned

4. Hyperconjugation involves the delocalisation of
a) σ bond orbital
b) π bond orbital
c) Both σ and π bond orbital
d) None of the mentioned

5. Larger the number of hyperconjugation structures, the stability of free radicals will
a) Increase
b) Decrease
c) Remain same
d) None of the mentioned

6. The compound that can be most readily sulphonated is
a) Benzene

b) Toluene

c) Nitrobenzene

d) Chlorobenzene

7. Which of the following is a temporary effect brought into play at the requirement of attacking reagent?

a) Inductive effect

b) Mesomeric effect

c) Electromeric effect

d) Inductomeric effect

8. Select the correct statement from the following option

a) When multiple bond is present between two different atoms, electromeric shift towards the more electronegative atom takes place

b) When multiple bond is present between two similar atoms, the first possibility is symmetric alkenes or alkynes

c) When multiple bond is present between two similar atoms, the second possibility is asymmetric alkenes or alkynes

d) All of the mentioned

9. Select the correct statement from the following option.

a) Conjugate effect is stronger than (-I) effect

b) Conjugate effect is weaker than (-I) effect

c) Conjugate effect is same as (-I) effect

d) None of the mentioned

10. When the complete transfer of π-electrons take place away from the atom at the requirement of attacking agent, it is called

a) (-E) effect

b) (+E) effect

c) (-I) effect

d) (+I) effect

11. The positively charged and electron deficient compounds which have a tendency to

form a bond by accepting the electron pair are known as

a) **Electrophiles**

b) Nucleophiles

c) Homophiles

d) All of the mentioned

12. Which of the following molecule will show highest dipole moment?

a) CH_3Cl

b) CH_3Br

c) CH_3F

d) **CH_3I**

Module

On

Organic Chemistry

Carbocation Intermediate

Outline

1.Definition

2. Generation of Carbocations (See Attachment)

3.Characteristics features of carbocation

4.Stability

5.Reactions of carbocation and Synthetic Application

1. Definition

Corbonium ion are positively charged species containg a carbon atom having six electrons in three bonds. On the carbon atom lacks apair of electron in the its valancy shell.

Carbonium ions are classified as primary, secondary or tertiary depending upon the nature of the carbon atom bearing the positive charge.

2. Generation of Carbocations

Generation of carbocations

Carbocations are produced by heterolytic cleavage of covalent bonds in which the leaving group takes away both bonding electrons of the covalent bond. Some of the reactions in which carbocations are formed are summarized below:
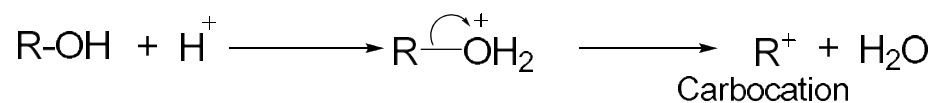
(1) Ionization of alkyl halides in polar solvents.

$$R-X \longrightarrow R^+ + :X^-$$
Carbocation

$$(CH_3)_3C-Cl \xrightarrow{\text{Ionization}} (CH_3)_3C^+ + :Cl^-$$
Carbocation
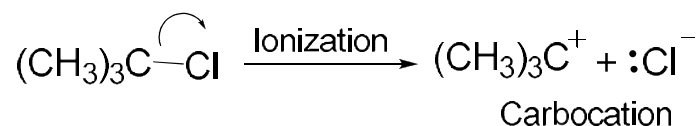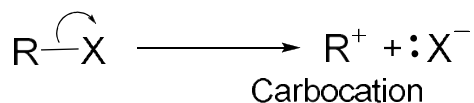
(2)By protonation of unsaturated compounds such as alkenes, carbonyl compounds and nitriles.

$$R-\underset{\underset{H}{|}}{C}=CH_2 + H^+ \xrightarrow{\text{Mark. Addition}} R-\overset{+}{C}H-CH_3$$

tert-Butyle Carbocation
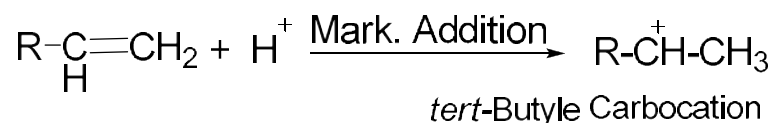
(3) By protonation of alcohols followed bydehydration.

$$R-OH + \overset{+}{H} \longrightarrow R\overset{+}{\frown}OH_2 \longrightarrow R^+ + H_2O$$

Carbocation

(4) By deamination of primary aliphatic amines with nitrous acid.

$$R-NH_2 \xrightarrow[-2H_2O]{HNO_2} R\overset{+}{\frown}N\equiv N \longrightarrow R^+ + N_2$$
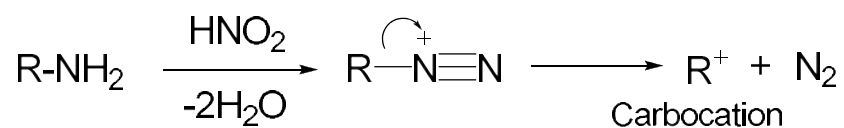
Carbocation

(5) By action of super acids on alkyl flourides.

$$R-F + SbF_5 \xrightarrow{FSO_3H} R^+ + SbF_6^-$$
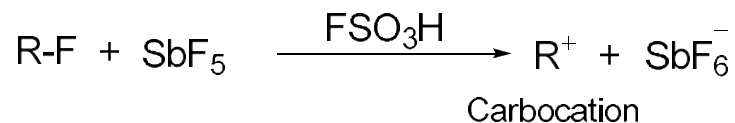
Carbocation

3. Characteristic features of carbocation:

a.it lacks a pair of electron in its valancy shell.

b.most of corboniumions cannot be isolated they are shart livedand have a strong tendency to complete the octet.

c. carbonium ions aretend to active more stable arrangement.

 for eg:primary to secondary to tertiary corbonium ion rearrangement.

d. Carbocation can be classified as Primary secondary and tertiary
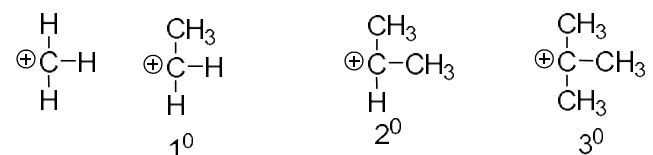
4. Stability of carbocation:

According to laws of physics the stability of charged species/systems increase by dispersal of its charge.more the aessibility of dispersal of charge, more will be the stability of the corbonium ion. Mainly two effects are responsible for the dispersal of the charge (a) hyperconjugation and (b) resonance.

Hyperconjugation: explains the stability of all alkyl carbonium ions by the dispersal of the sigma electron of the adjacent C-H or C-C bond into the empty p orbital +ve charge carrying C atom. +ve charge may disperse on adjacent C-C and C-H bonds.

Resonance: It explains the stability of all types of corbonium ions the +ve charge is delocalized over adjacent atoms having alternate single and double bonds in their molecular structure.

Structure of corbonium ion: The carbon atom of a carbocation is sp^2hybridised and three sp^2hybrid orbitals are used in forming bonds to three substituents so one p-orbital remains unused and vacant.the cabocation has planar structure having all three bonds in one plane with bond angle 120° between them, sp^2hybridisation, planar structure with 120°bond angle between orbitals are necessary condition for the stabilization of carbocation.
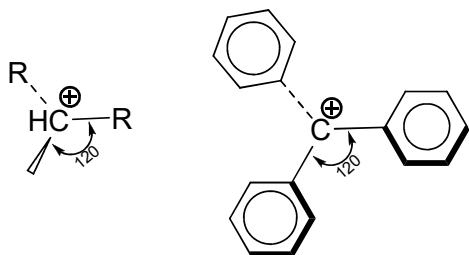
Hyperconjugation-

Resonance- Fig
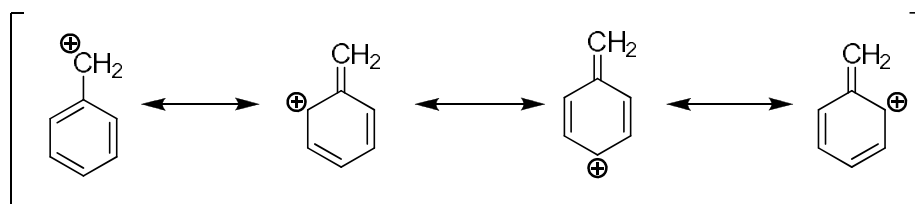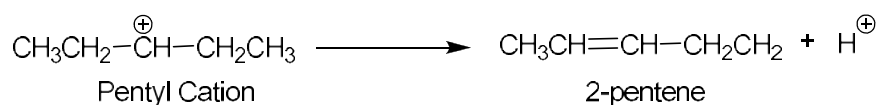

Canonical structures of benzyl cation

$$CH_2=CH-\overset{\oplus}{CH_2} \longleftrightarrow \overset{\oplus}{CH_2}-\underset{H}{C}=CH_2$$

Canonical structures of allyl cation

5. Reactions of carbocation:

A carbocation may undergo following types of reactions-

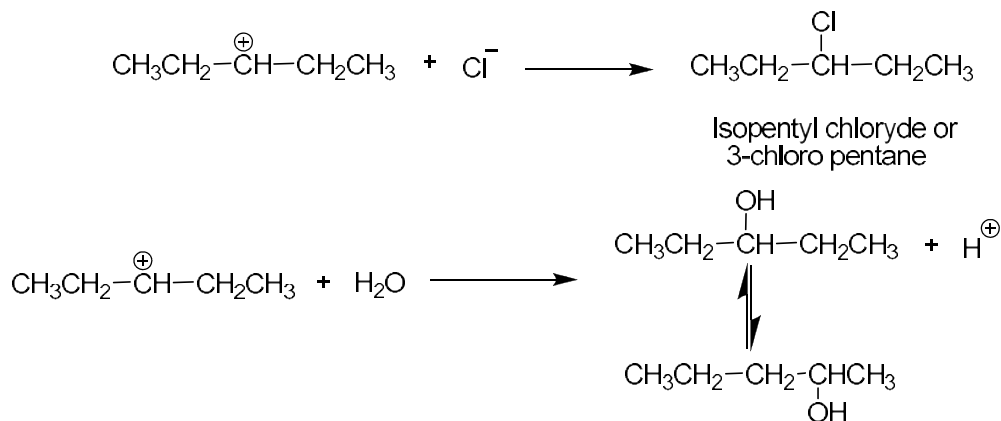**a .Deprotonation**- A carbocation may eliminate a H^+ to give an alkene.

For ex-

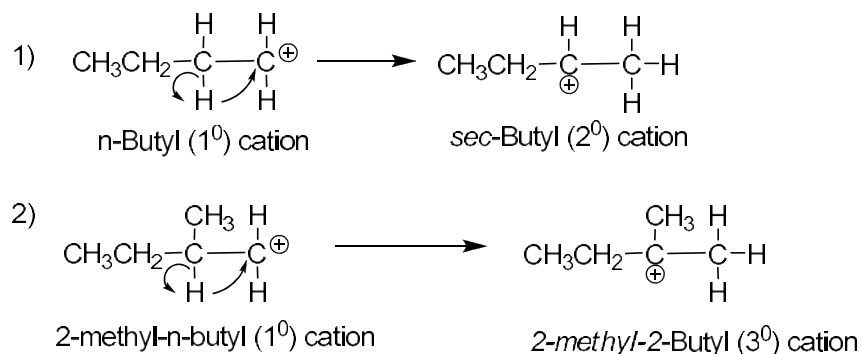$$CH_3CH_2-\overset{\oplus}{CH}-CH_2CH_3 \longrightarrow CH_3CH=CH-CH_2CH_2 + H^{\oplus}$$
Pentyl Cation   2-pentene

b. Reaction with neucleophile- A carbocation may combine with other basic molecule or a –ve ion.

For ex-

$$CH_3CH_2-\overset{\oplus}{CH}-CH_2CH_3 + Cl^- \longrightarrow CH_3CH_2-\underset{Cl}{CH}-CH_2CH_3$$

Isopentyl chloryde or
3-chloro pentane

$$CH_3CH_2-\overset{\oplus}{CH}-CH_2CH_3 + H_2O \longrightarrow CH_3CH_2-\underset{OH}{CH}-CH_2CH_3 + H^{\oplus}$$

$$CH_3CH_2-CH_2-\underset{OH}{CHCH_3}$$

c.Rearrangement -A carbocation may rearrange to a more stable corbocation.in rearrangement,+ve charge of carbon get a pair of e⁻ from neighbouring C-atom which can better hold +ve charge, leading to formation of a new corbocation (on the basis of stability due to hyperconjugation and resonance).

For ex-

1)
$$CH_3CH_2-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}{}^{\oplus} \longrightarrow CH_3CH_2-\underset{\oplus}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$$
n-Butyl (1^0) cation   *sec*-Butyl (2^0) cation

2)
$$CH_3CH_2-\underset{H}{\overset{CH_3}{C}}-\underset{H}{\overset{H}{C}}{}^{\oplus} \longrightarrow CH_3CH_2-\underset{\oplus}{\overset{CH_3}{C}}-\underset{H}{\overset{H}{C}}-H$$
2-methyl-n-butyl (1^0) cation   *2-methyl*-2-Butyl (3^0) cation

d. Addition with alkene- A carbocation may add to an alkene to form a bigger carbocation.this is also called propogation of carbocation

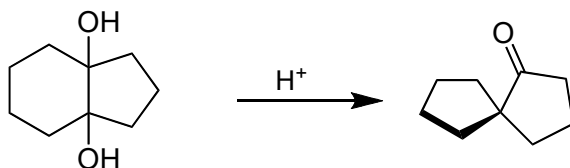4)   CH₃—C(CH₃)=CH₂ + ⊕C(CH₃)₃   ⟶   CH₃—C(CH₃)₂—C(H₂)⊕—C(CH₃)₃
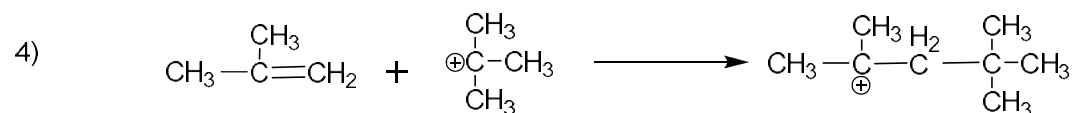
e. Hydride transfer reaction- A carbocation may abstract an hydride ion from an alkane this is also called hydride transfer reqaction.
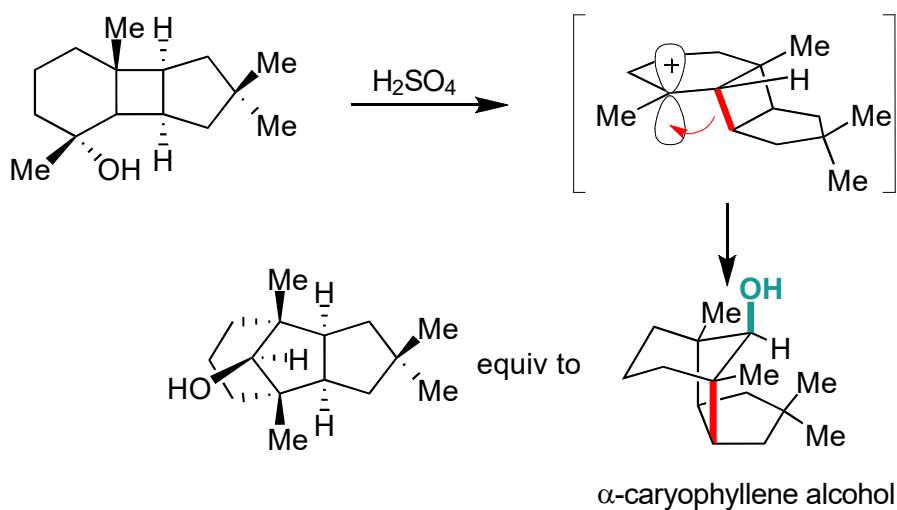
For ex-

5)   CH₃—C⊕(CH₃)—CH₂-CH₂CH₃ + HC(CH₃)₂CH₃ (Isobutane)   ⟶   CH₃CH(CH₃)—CH₂-CH₂CH₃ + ⊕C(CH₃)₃
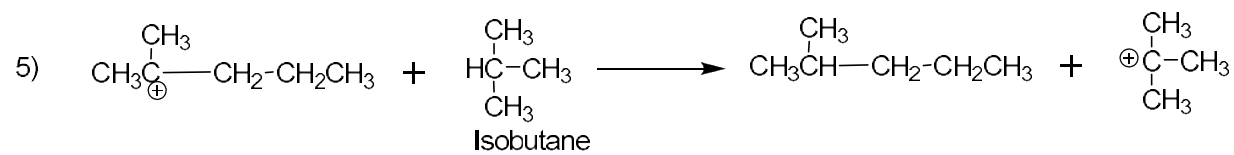
Synthetic Application:

Pinacol rearrangement (Driving force is the formation of C=O)

Demjanov-rearrangement (Driving force: relief of ring strain)

α-caryophyllene alcohol

Questions:

1   The stability of $1°, 2°, 3°$ and benzyl carbocations is of the order

      (a) $1° > 2° > 3° >$ benzyl   (b) benzyl $> 3° > 2° > 1°$

      (c) $3° > 2° > 1° >$ benzyl (d) $3° >$ benzyl $> 2° > 1°$

2   Relative stabilities of the following carbocation will be in order
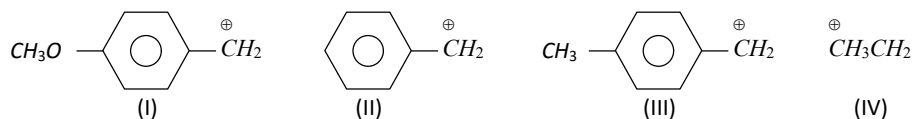
      (I)   (II)   (III)   (IV)

      (a) I < II < III < IV   (b) IV < III < II < I

      (c) IV < II < III < I   (d) II < IV < III < I

3   The product obtained in the reaction $CH_3 - \underset{\underset{H}{|}}{C} - \underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{CH}} - CH_3 \xrightarrow[\Delta]{H_2SO_4}$ is

      (a) $CH_3 - \underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH = CH_2$ (b) $CH_3 - \overset{\overset{CH_3}{|}}{C} = CH - CH_3$

      (c) $CH_2 = \overset{\overset{CH_3}{|}}{C} - CH_2 - CH_3$ (d) None of these
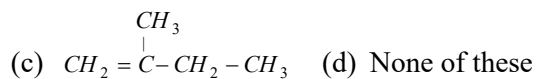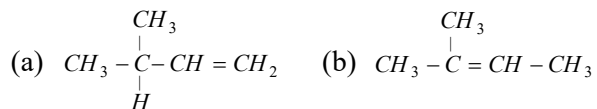
4.   Which of the following intermediate is unstable?
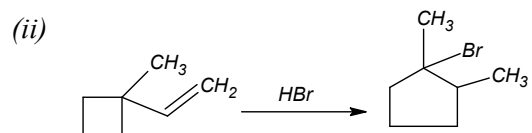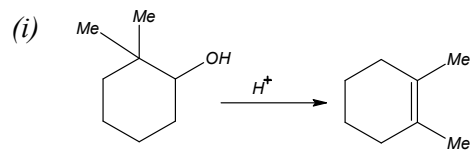

      (a)   (b)
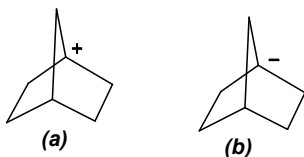
5.   Arrange the following carbocation in the order of decreasing stability

      (I)   (II)   (III)
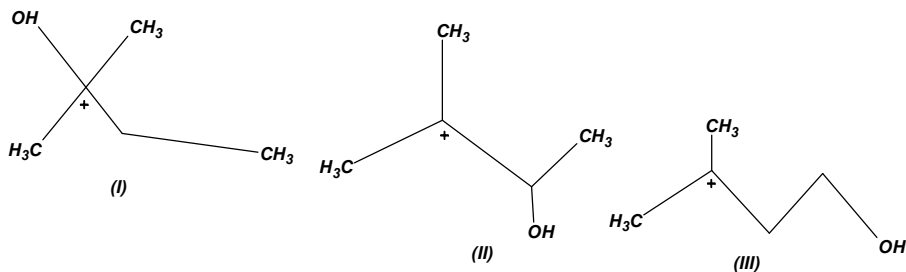
6.   Why $CH_3 - O - \overset{+}{C}H_2$ is more stable than $CH_3CH_2\overset{+}{C}H_2$ while both are primary

carbocations?

7.   Give the mechanism

(i)

(ii)

Free Radicals

Outlines:

1.4.1   Generation of free radicals

1.4.2   Stability of free radicals

1.4.3   Reactions of free radicals

1.4.4   Applications in synthetic organic chemistry

Definition of Free Radicals: Chemical species carrying an odd or unpaired electrons are called free radicals. For example,

 1 H_3 $_6H_5$ C_6H_5 H_2 $(C_6H_5)_3$

Free radicals are formed by homolytic fission of the covalent bond. Free radicals have planar sp^2 hybridized structure. They are highly reactive reaction intermediates. The high reactivity of free radicals is due to tendency of the odd electrons to pair up with another available electron.
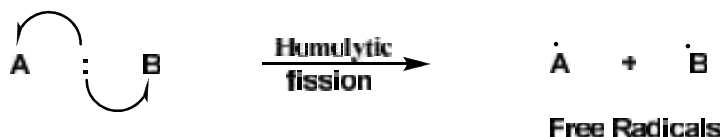
Stability of the free radicals:

The stability of the free radicals can be explained on the basis of hyperconjugation and resonance effect.

The stability of simple alkyl free radicals follows the sequence: tertiary > secondary > primary > methyl, i.e.
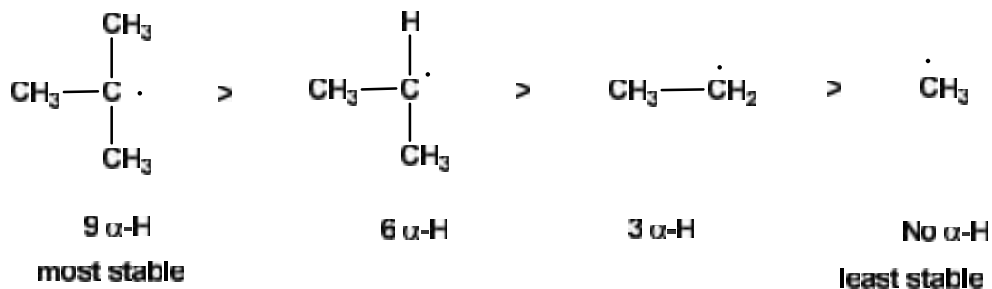
This order of stability can be easily explained on the basis of hyperconjugation effect. In general, greater the number of -hydrogens, greater is the number of hyperconjugative structures and hence more stable is the free radical. Thus, tert-butyl free radical with nine -hydrogens and hence nine hyperconjugation structures is more stable than isopropyl free radical with six -hydrogens and hence six hyperconjugation structures which, in turn, is more stable than ethyl free radical with three -hydrogens and hence three hyperconjugation structures while methyl free radical with no -hydroconjugative structures is the least stable.

The stability of the free radicals also increases by resonance possibilities. Thus, allylic and benzylic free radicals are more stable and less reactive than the simple alkyl radicals. This is due to the delocalization of the unpaired electrons over the orbital system in each case.

The stability of a radical increases as the extent of delocalization increases. Therefore, Ph_2C is more stable than $PhCH_2$ and Ph_3C is steel more stable due to larger number of resonating structures. The stability of Ph_3C is explained by the delocalization of the unpaired electron. The extent of delocalization is maximum in Ph_3C than in Ph_2CH or even in $PhCH_2$.
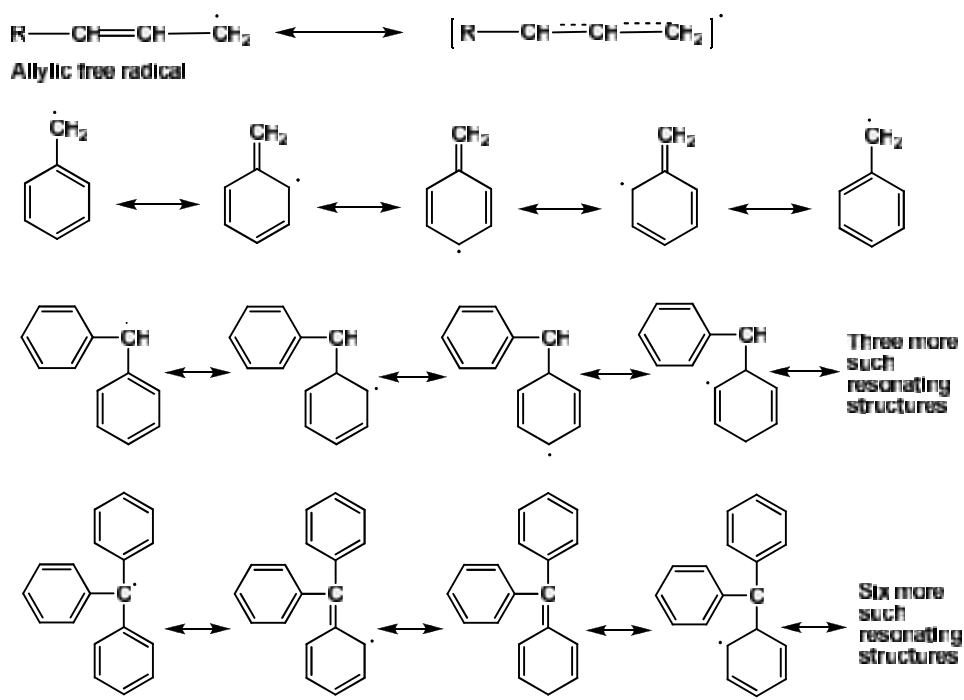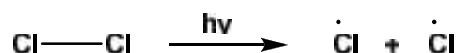
Generation of free radicals:

(a) Photolysis

(i) Photolysis of Acetone

Acetone
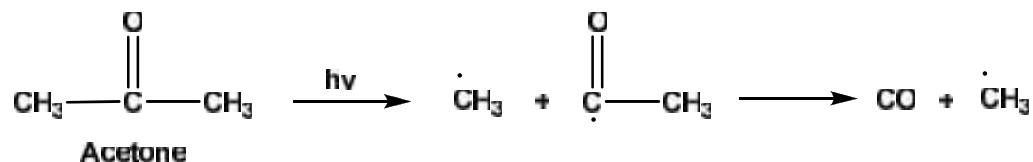
(ii) The photolysis of halogen molecules gives chlorine free radicals.

(iii) Photolysis can also cleave strong bonds that are difficult to cleave by thermolysis.
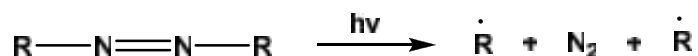
(iv) Photolysis of acyl peroxide gives alkyl free radicals as follows:

(b) Thermolysis

In this method, the organic substrate is heated at suitable temperature. Following are some examples of thermolysis.

(i)

Benzoyl peroxide

(ii)

Azobisisobutyronitrile
(AIBN)

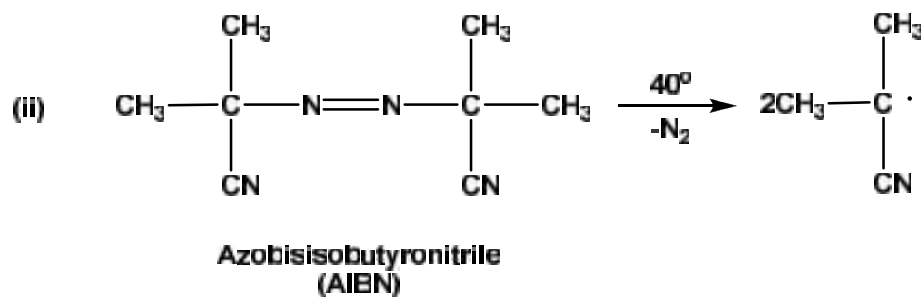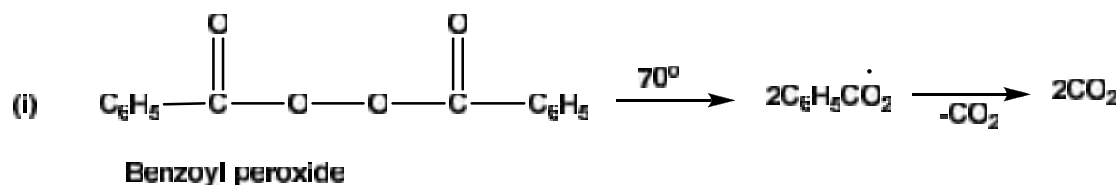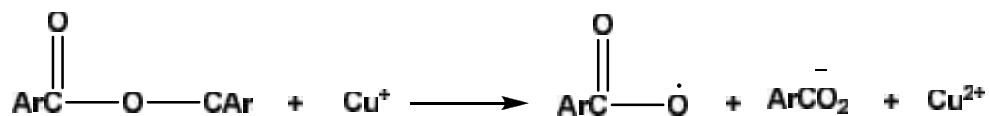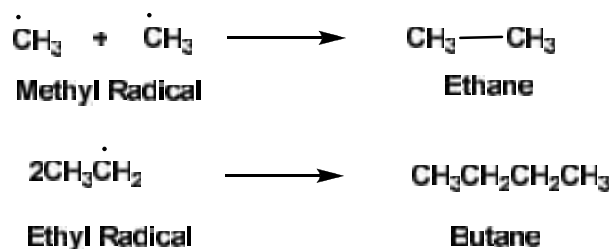**(c)** In redox reactions there is one-electron transfer in generating the free radicals. The source of one-electron transfer is the metal ion (e.g. Cu^+, Fe^{2+} etc.). Thus Cu^+ ions are used for the decomposition of acyl peroxides.

$$\underset{\displaystyle \text{ArC}}{\overset{\displaystyle O}{\parallel}}\!\!-\!O\!-\!\underset{\displaystyle}{\overset{\displaystyle O}{\parallel}}\text{CAr} \;+\; Cu^+ \longrightarrow \underset{\displaystyle \text{ArC}}{\overset{\displaystyle O}{\parallel}}\!\!-\!\dot{O} \;+\; Ar\overset{-}{C}O_2 \;+\; Cu^{2+}$$

Reactions of free radicals

(a) Recombination

The free alkyl radicals may recombine to form hydrocarbons.

$$\dot{C}H_3 \;+\; \dot{C}H_3 \longrightarrow CH_3\!-\!CH_3$$
Methyl Radical $\qquad\qquad$ Ethane

$$2CH_3\dot{C}H_2 \longrightarrow CH_3CH_2CH_2CH_3$$
Ethyl Radical $\qquad\qquad$ Butane

The reaction is used in the termination step in free radical polymerization for the production of polymers.

(b) Disproportionation

At higher temperature the alkyl radical may undergo disproportionation. The ethyl radical disproportionate (i.e. one radical CH_3CH_2˙ takes up hydrogen from another free radical) to give ethylene and ethane.

$$CH_3\dot{C}H_2 \;+\; CH_3\dot{C}H_3 \longrightarrow CH_2\!=\!CH_2 \;+\; CH_3CH_3$$
Ethyl Radicals $\qquad\qquad$ Ethylene $\qquad$ Ethane
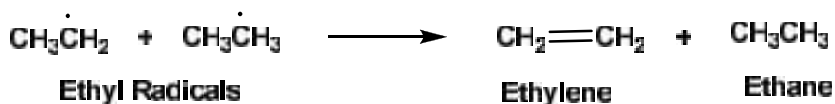
(c) Reaction with olefins

The alkyl radicals react with olefins to form a new free radicals.

$$\dot{C}H_3 \;+\; CH_2\!=\!CH_2 \longrightarrow CH_3\!-\!CH_2\!-\!\dot{C}H_2$$
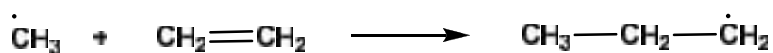
The newly formed free radical further adds on to another molecule of olefin.

$$\overset{\displaystyle\cdot}{CH_3CH_2CH_2} \quad + \quad CH_2{=\!=}CH_2 \quad\longrightarrow\quad CH_3CH_2CH_2CH_2\overset{\displaystyle\cdot}{CH_2}$$
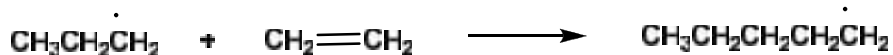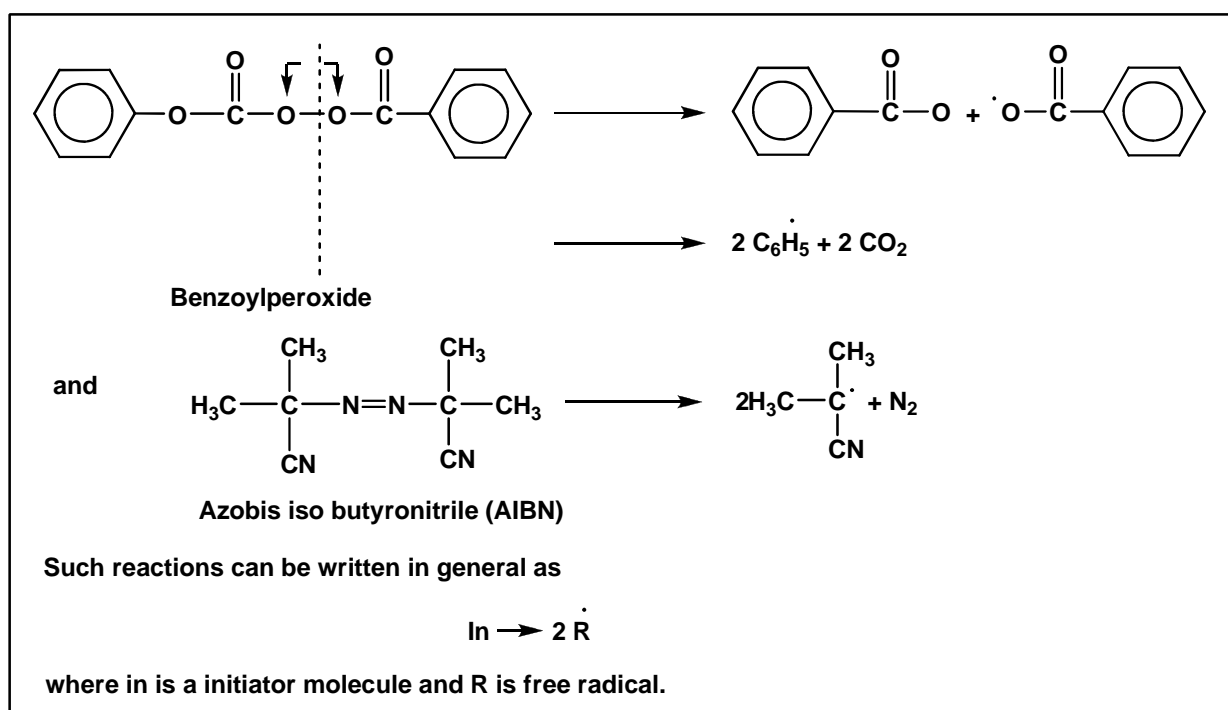
The reaction continues till the formed free radical couples with another free radical and termination of the reaction takes place.

The above reaction is used as the propagation step in the polymerization of ethylene.

Free-radical Mechanism of Polymerization

The free radical mechanism of polymerization take place and three steps viz initiation, propagation and termination.

Benzoylperoxide

and

Azobis iso butyronitrile (AIBN)

Such reactions can be written in general as

$$In \longrightarrow 2\overset{\displaystyle\cdot}{R}$$

where in is a initiator molecule and R is free radical.

Chain initiation

It involves two steps viz. decomposition of the initiator

$$In \qquad 2R^{\cdot}$$
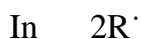
and the addition of the first vinyl monomer $\underset{\displaystyle SG}{CH_2{=\!=}CH}$ molecule to the free radical (R) and the formation of (I) as intermediate.

Where SG is substituent group

Chain propagation

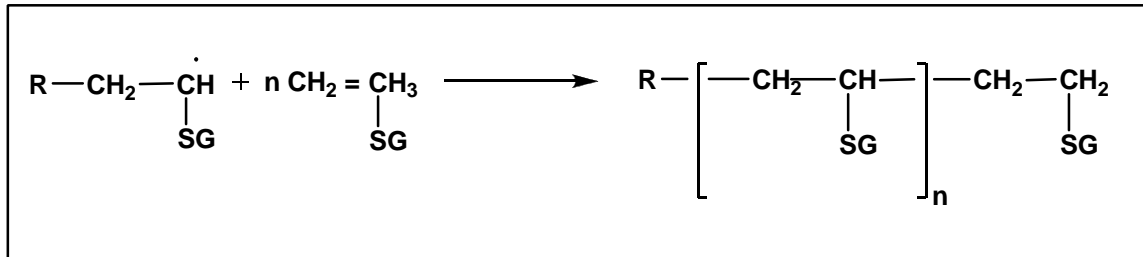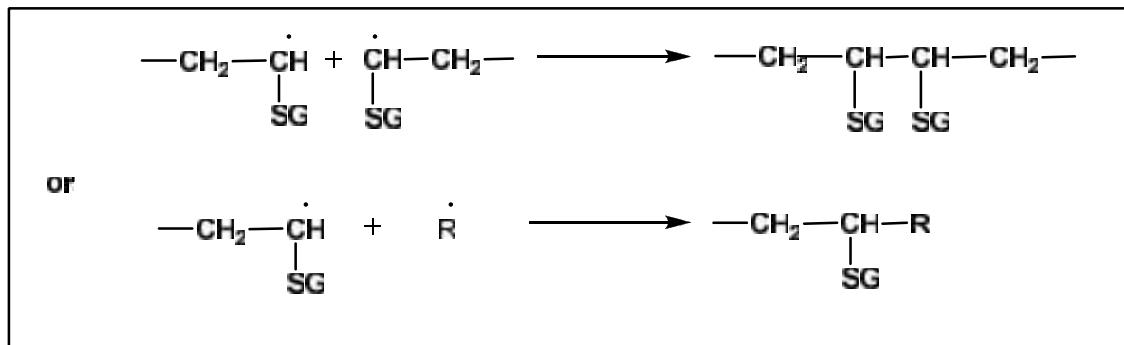It is accomplished by the addition of monomer molecules to (I) leading to the formation of macro-radicals. In general
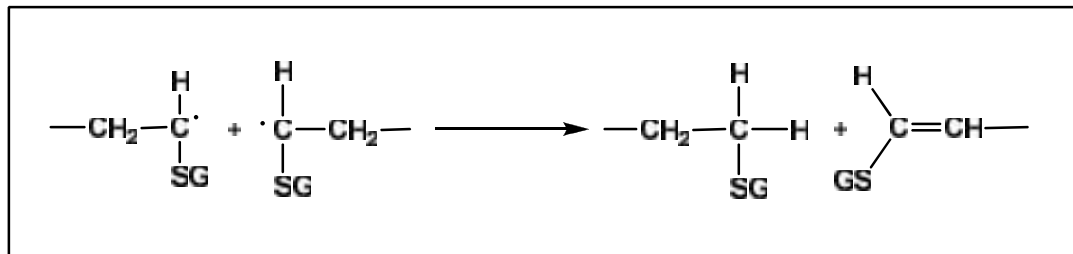

Chain termination

The growing polymer chain can be terminated by

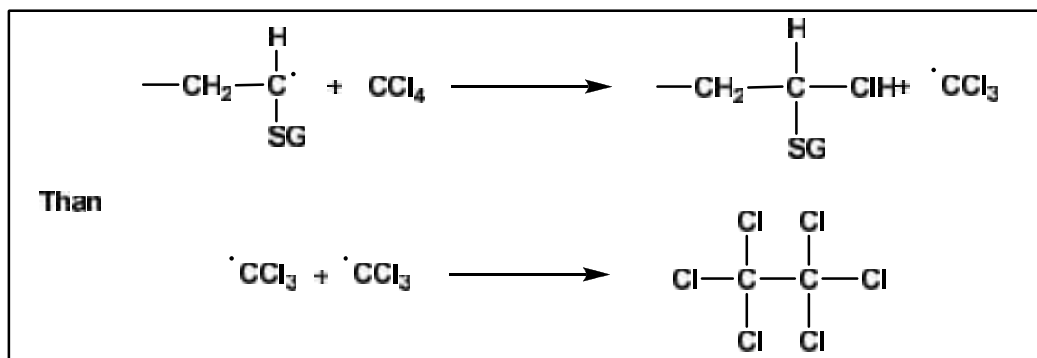(a) Recombination, which consists of combination of two radicals either

(b) Disproportionation: It involves the transfer of a hydrogen atom of one macro-radical to another to form two macromolecules, one of them with a double bond at its end
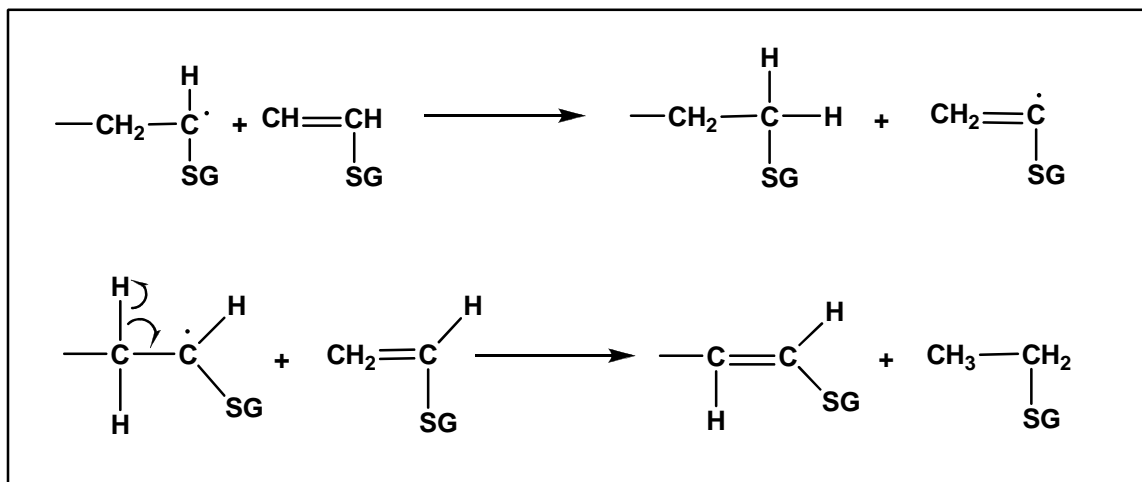
"At T   60°C, PMMA and vinyl acetate chains terminate mainly by disproportionation".

(c) Reaction with the solvent molecules (like carbon tetrachloride)

$$—CH_2—\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle SG}{|}}{C}}\cdot \;+\; CCl_4 \longrightarrow —CH_2—\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle SG}{|}}{C}}—ClH+\; \cdot CCl_3$$

Than

$$\cdot CCl_3 + \cdot CCl_3 \longrightarrow Cl—\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}—\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}—Cl$$

Chain transfer reactions in free radical polymerization. In these reactions, the original growing free radical chain is terminated by the reaction with the monomer molecule and a new chain is initiated.

$$—CH_2—\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle SG}{|}}{C}}\cdot \;+\; CH=CH \; (SG) \longrightarrow —CH_2—\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle SG}{|}}{C}}—H \;+\; CH_2=\overset{\cdot}{\underset{\underset{\displaystyle SG}{|}}{C}}$$

Chlorination of Methane

$$CH_4 \ + \ Cl_2 \ \xrightarrow{\text{UV light}} \ CH_3Cl \ + \ HCl$$

Methyl chloride

$$CH_3Cl \ + \ Cl_2 \ \xrightarrow{\text{UV light}} \ CH_2Cl_2 \ + \ HCl$$

Methylene chloride

$$CH_2Cl_2 \ + \ Cl_2 \ \xrightarrow{\text{UV light}} \ CHCl_3 \ + \ HCl$$

Chloroform

$$CHCl_3 \ + \ Cl_2 \ \xrightarrow{\text{UV light}} \ CCl_4 \ + \ HCl$$

Carbon tetrachloride
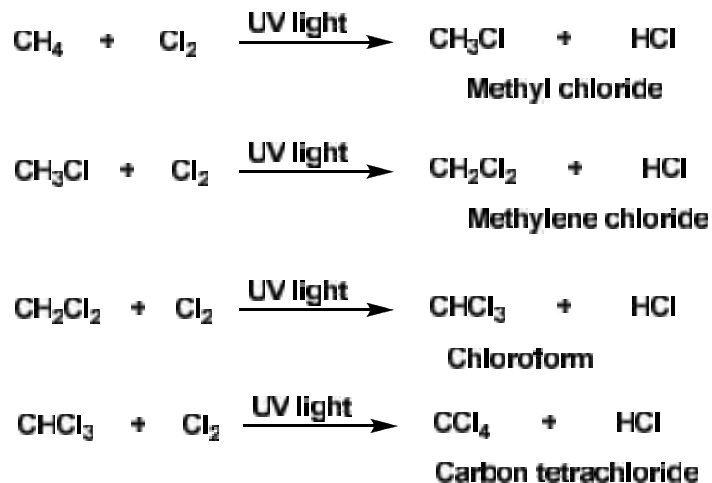
The above chlorination proceeds via the free radical mechanism. Various steps are given below:

Initiation

$$\dot{C}l_2 \ \xrightarrow{hv} \ 2\dot{C}l$$

Propagation

Methyl Free radical

$$Cl_2 \ + \ \dot{C}H_3 \ \longrightarrow \ CH_3Cl \ + \ \dot{C}l$$
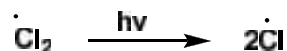
The reaction continues and finally CCl$_4$ is obtained as the final product.

Termination

$$\dot{C}l \ + \ \dot{C}l \ \longrightarrow \ Cl\text{---}Cl$$

$$\dot{C}l \ + \ \dot{C}H_3 \ \longrightarrow \ CH_3\text{---}Cl$$
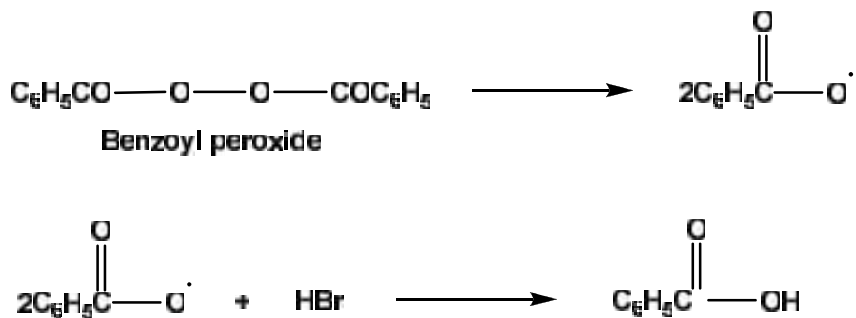
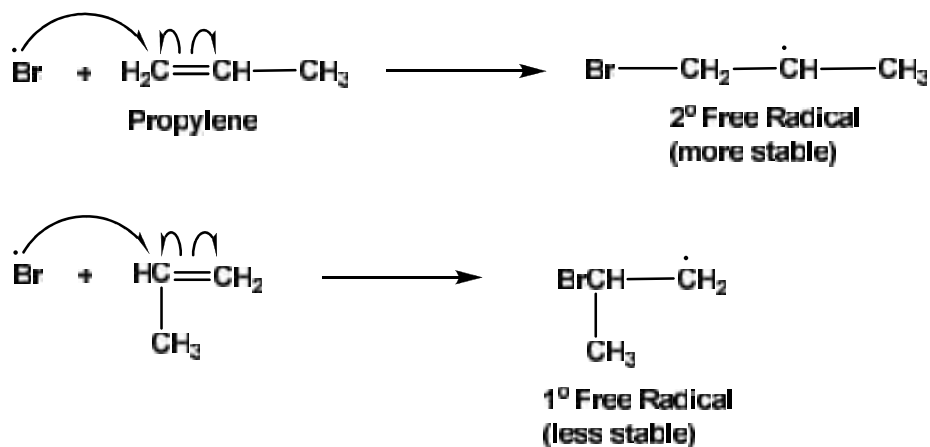$$\dot{C}H_3 \ + \ \dot{C}H_3 \ \longrightarrow \ CH_3\text{---}CH_3$$
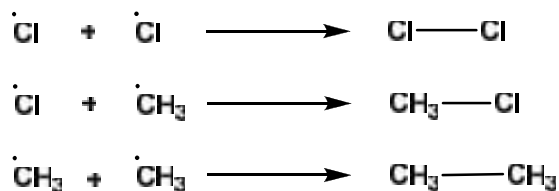
Reaction of Propene with HBr in presence of peroxide

Propene reacts with HBr in presence of peroxide and forms n-propyl bromide via free radical mechanism.

(i)   The peroxide on dissociation gives two alkoxy radicals, which attack HBr to form bromine free radical (Br·).

$$C_6H_5CO—O—O—COC_6H_5 \longrightarrow 2C_6H_5\overset{O}{\overset{\|}{C}}—O·$$

Benzoyl peroxide

$$2C_6H_5\overset{O}{\overset{\|}{C}}—O· + HBr \longrightarrow C_6H_5\overset{O}{\overset{\|}{C}}—OH$$

(ii)   The bromine free radical then attacks the alkene molecule giving two bromo alkyl free radicals (the 2° free radical and 1° free radical, the former is more stable then latter).

$$·Br + H_2C=CH—CH_3 \longrightarrow Br—CH_2—\overset{·}{C}H—CH_3$$

Propylene   2° Free Radical
                                         (more stable)

$$·Br + \underset{\overset{|}{CH_3}}{HC}=CH_2 \longrightarrow \underset{\overset{|}{CH_3}}{BrCH}—\overset{·}{C}H_2$$
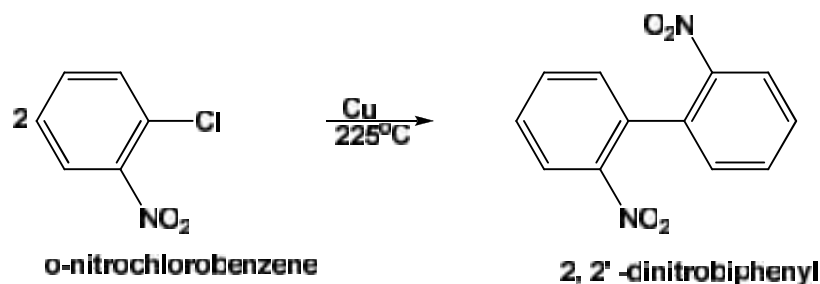
1° Free Radical
(less stable)

(iii)   The more stable free radical reacts with HBr forming anti Markownikoff product and another bromine radical, which propogates the chain reaction.
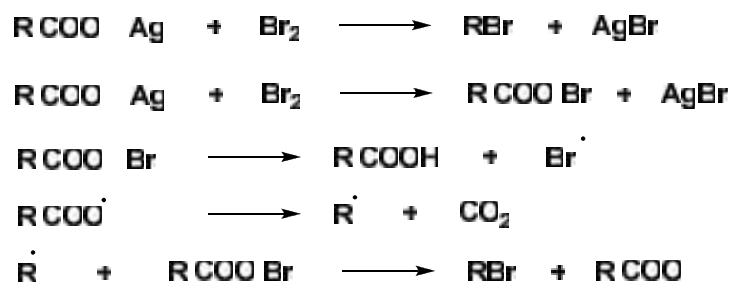
$$Br—CH_2—\overset{·}{C}H—CH_3 + H : Br \longrightarrow Br—CH_2CH_2CH_3 + ·Br$$

2° Free Radical   n-Propyl bromide
(more stable)
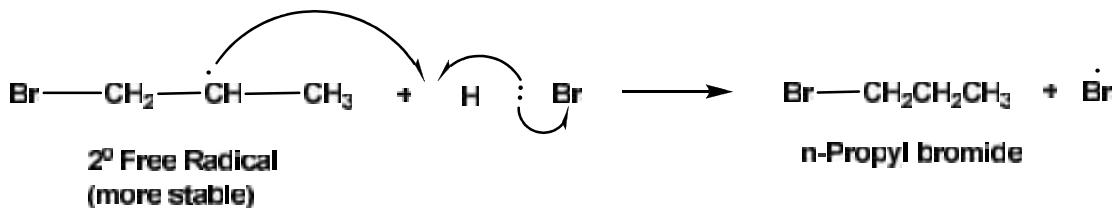
Kolbe electrolytic reaction (Dimerization of alkyl radicals)

$$2RCO_2^- \xrightarrow[\text{anode}]{-e^-} 2R\dot{C}O_2 \xrightarrow{-CO_2} 2\dot{R} \longrightarrow R\text{---}R$$
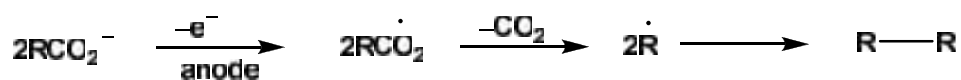
The Ullmann Reaction (Dimerization of aryl radicals)

o-nitrochlorobenzene

2, 2'-dinitrobiphenyl

Hunsdiecker Reaction (Decarboxylative bromination)

$$RCOO\ Ag + Br_2 \longrightarrow RBr + AgBr$$

$$RCOO\ Ag + Br_2 \longrightarrow RCOO\ Br + AgBr$$

$$RCOO\ Br \longrightarrow RCOOH + \dot{B}r$$

$$R\dot{C}OO \longrightarrow \dot{R} + CO_2$$

$$\dot{R} + RCOO\ Br \longrightarrow RBr + RCOO$$

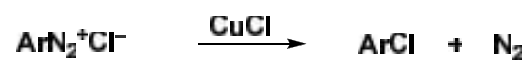## Gomberg Reaction

This reaction involves the synthesis of biaryls by radical reaction. When the acidic solution of a diazonium salt is made alkaline, the aryl portion of the diazonium salt couples with another aromatic ring and forms diphenyl.

Gomberg-Bachman reaction

$$C_6H_5N_2^+\ Cl^- \xrightarrow{OH^-} C_6H_5\text{---}N{=}N\text{---}OH \longrightarrow C_6\dot{H}_5 + N_2 + \dot{O}$$

$$C_6\dot{H}_5 + C_6H_5NO_2 + \dot{O}H \longrightarrow p\text{-}C_6H_5\text{---}C_6H_5NO_2 + H_2O$$

a free radical mechanism
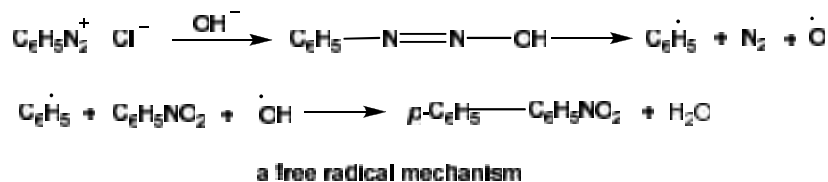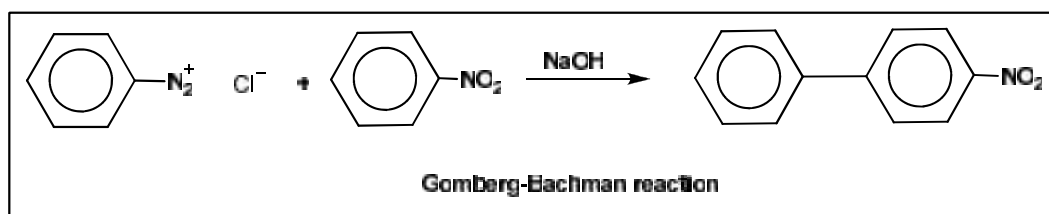
Sandmeyer Reaction

Sandmeyer reaction also take place via free radical mechanism. Decomposition of diazonium salts in presence Cu^+ ions. In this reaction the free radical, $Ar\cdot$, is formed as an intermediate.

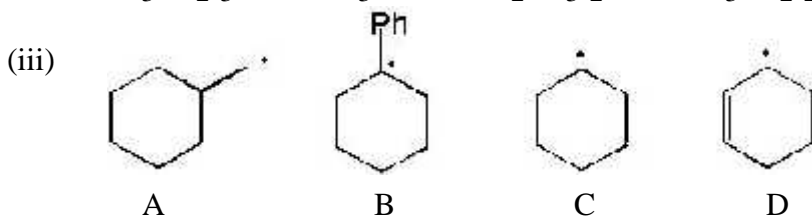$$ArN_2^+Cl^- \xrightarrow{\text{CuCl}} ArCl \ + \ N_2$$

Questions

(1) Arrange the following radicals in increasing order of stability.

(i) A. C_6H_5 H_2 B. $CH_2=CH–\overset{\cdot\cdot}{C}$ $_2$ C. $(C_6H_5)_2\overset{\odot}{CH}$

(ii) A. $(CH_3CH_2)_3C$ B. $CH_3CHCH(CH_2CH_3)_2$ C. $(CH_3CH_2)_2CHCH_2CH_2$

(iii)

   A   B   C   D

(2) Write the mechanism of following reactions:
   (a) Gombers reaction
   (b) sandmayer reaction
   (c) Halogenation of alkanes
   (d) Anti-Markovnikov addition of HBr
   (e) Free radical polymerization of alkenes.

(3) Propose a mechanism for each of the following reactions.

A. $(CH_3)_3CH + Br_2 \xrightarrow[\text{light}]{\text{light}} (CH_3)_3CBr + Br_2$

B. $n\ CF_2=CF_2 \xrightarrow{\text{peroxides}} -(CF_2CF_2)_n-$

C.

$+ Cl_2 \xrightarrow{\text{Heat}}$

D.

$+ Cl_2 \xrightarrow{\text{light}}$
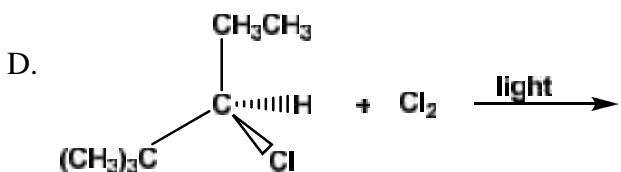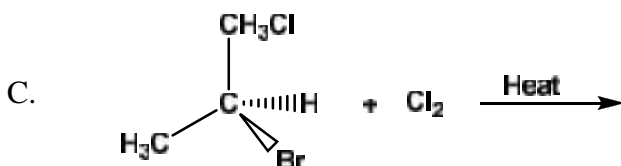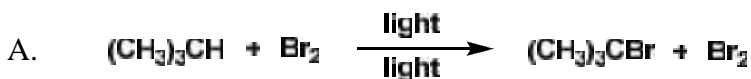
(4) Which of the following reactions proceeds by way of a free radical mechanism?

A. $CH_3CH=CH_2 + Br_2 \xrightarrow[\text{peroxides}]{CCl_4} CH_3CHBrCH_2Br$

B. $CH_3CH=CH_2 + HBr \longrightarrow CH_3CH_2CH_2Br$ heat

C. $(CH_3)_3CBr + KOH \longrightarrow (CH_3)_2C=CH_2 + KOH + H_2O$ heat

D. $CH_3CH_2Br + KOH \longrightarrow CH_3CH_2OH + KBr$

CARBENE

Besides Carbocation ,Carbanion and Free radical ,there are other reactive intermediates which are produced during reaction.These are carbene (>C:) and nitrene(RN:).

Outlines:

1. Definition
2. Generation
3. Important Features
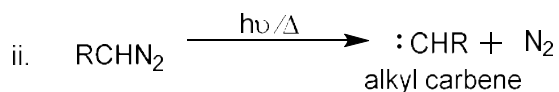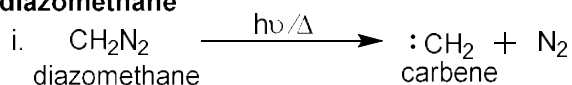4. Reactions and Synthetic Applications

Carbene(H_2C:):-

1 Definition

- First proposed in 1930s
- Existance was Established in 1959 by spectroscopic studies.
- Highly reactive.
- Short lived and neutral species.
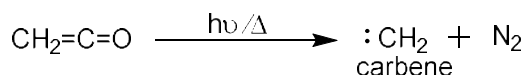- Strong electrophile(electron deficient species containing two odd electron)

2 Generation:

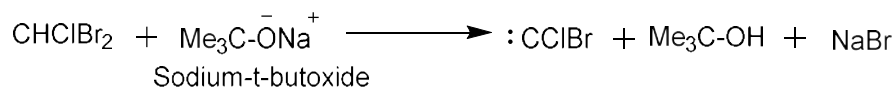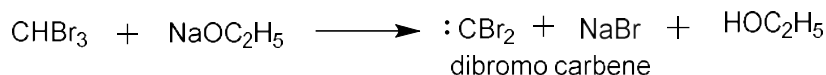**I. By photolysis or (pyrolysis of aliphatic diazo compounds)**
eg: diazomethane

i. CH_2N_2 $\xrightarrow{h\upsilon/\Delta}$ $:CH_2 + N_2$
diazomethane   carbene

ii. $RCHN_2$ $\xrightarrow{h\upsilon/\Delta}$ $:CHR + N_2$
           alkyl carbene

II. Photolysis or pyrolysis of ketone

$CH_2=C=O$ $\xrightarrow{h\upsilon/\Delta}$ $:CH_2 + N_2$
               carbene

III. Simmons-Smith Reactions

$CH_2I_2 + Zn/Cu$ couple $\xrightarrow{\Delta}$ $:CH_2 + ZnI_2$

IV. Reaction of Base on suitable polyhalogen compounds

$CHCl_3 + NaOH \longrightarrow :CHCl_2 + NaCl + H_2O$
                      dichloro carbene

$CHBr_3 + NaOC_2H_5 \longrightarrow :CBr_2 + NaBr + HOC_2H_5$
                      dibromo carbene

$CHClBr_2 + Me_3C\overset{-}{O}\overset{+}{Na} \longrightarrow :CClBr + Me_3C\text{-}OH + NaBr$
       Sodium-t-butoxide

Mechanism:

Acidic (due to e⁻ withdrawing groups
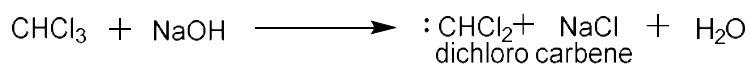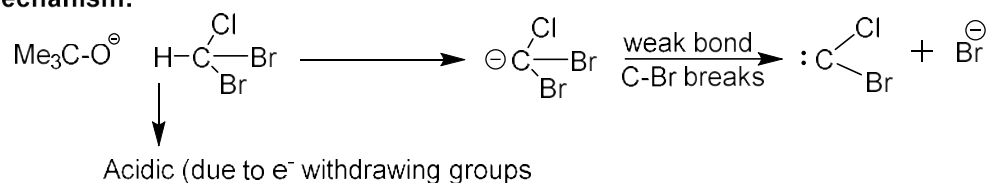
3   <u>Important Features</u>

Types of Carbene: They are of two types (i)Singlet and (ii)Triplet

I) Singlet Carbene:

- Both the electrons are present in different forms or different orbital(different Spin states)(if two electrons present in the same orbital are called lone pair electrons or non-bonding electron.
- But they are paired in sp^2 hybridized orbitals and behave as a paired electrons.
- Act both as nucleophile and electrophile.
- Produced by photolysis of CH_2N_2(diazomethane).
- Less stable form.

Spin State: Its spin state is one, so it is called Singlet.

Spin number of Carbene(S)=**(+1/2-1/2=0)**

$$\left[+1/2\Big\uparrow [:C]\Big\downarrow -1/2\right]$$
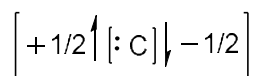
Spin state= (2S+1), (2x0+1)=1

S=Sum of Spin no. of all electrons.

Hybridization:

sp^2 hybridized orbitals in bond formation.

Bent Shape.

Bond angle(H-C-H) is 103^0.

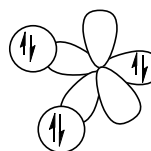Bond Length 112 pm (C-H).

C= $\underbrace{\boxed{\uparrow\downarrow}}_{\substack{2s}} \underbrace{\boxed{\uparrow}\,\boxed{\uparrow}\,\boxed{\ }}_{\substack{2p}}$

sp^2 hybridization
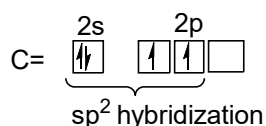
Three sp^2 hybrid orbital and one pure p-orbital

II) Triplet Carbene:

- Both electrons are present in different orbitals with same spin (electrons are not paired).
- Behave as radical(i.e. diradical).
- Produced by the photolysis of ketones($CH_2=C=O$).
- It is more stable than singlet carbine.

Spin State:

- Its spin state is three , therefore it is called triplet.
- Two unpaired electron in same spin.
- Spin number =(+1/2+1/2)= 1

$$\left[\begin{array}{c}+1/2\uparrow \cdot CH_2 \cdot \downarrow -1/2 \\ -1/2\downarrow \cdot CH_2 \cdot \uparrow +1/2\end{array}\right]$$
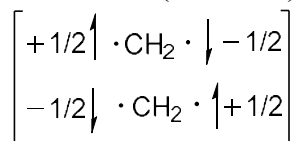
- Spin state(2S+1)=(2x1+1)=3

Hybridization:

- sp hybrid orbital in bend
- Linear shape.

- Bond angle H-C-H of 180^0 and bond length of 103 ppm (C-H).

C= [electron configuration diagram: 2s, 2p orbitals] sp hybridization

(two sp H.O. with two pure p-orbitols)

Triplet state is more stable than singlet state about 10 k.cal/mol.

They behave more like radicals (due to unpaired electrons) whereas singlet carbine can react both as a nucleophile and as electrophile.
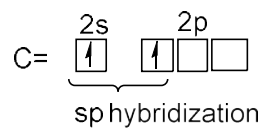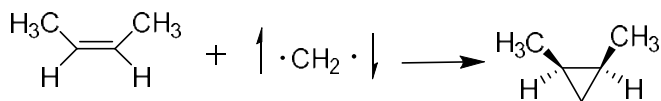
4 <u>Reactions and Synthetic Applications</u>:

Carbene undergo several types of organic reaction.

i) Addition to alkenes: Reaction of singlet carbene are stereospecific and stereoselective i.e. reaction of singlet carbene with alkene occurs in synadition(Specific manner) and gives one product(stereoselective).

Cis-1,2-dimethyl cyclo propane (III)
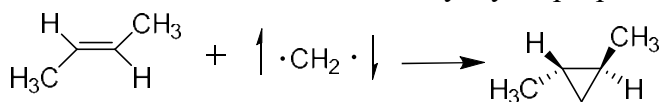
trans-1,2-dimethyl cyclo propane (IV)

But with triplet carbene, reaction are neither stereospecific nor stereoselective. For **e.g.**

Cis and/or Trans-but-2-ene $\xrightarrow[\quad \cdot CH_2 \cdot \quad]{\text{Triplet carbene}}$ Mixture of (III) and (IV)
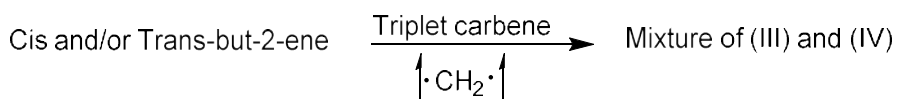
ii) Insertion Reaction: Carbene can be inserted into a C-H bond and reaction may be inter and intramolecular.

Inter molecular

$CH_3CH_2\ddot{C}H \longrightarrow H_3C-\overset{H}{\underset{}{C}}=CH_2 + $ [cyclopropane structure H_2C-CH_2 / C / H_2]

Intra molecular
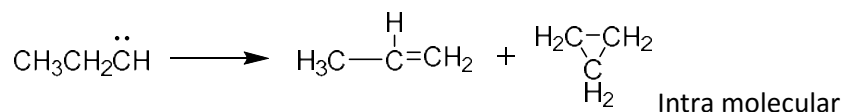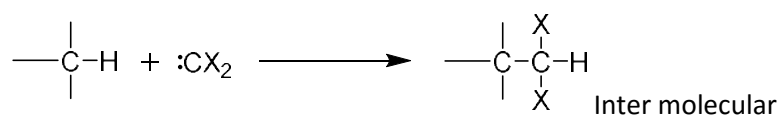
iii) Ring Expansion Reaction: Halogenated carbine formed by CHX_3/base adds to (C=C) bond, followed by ring expansion and gives product with one extra C atom in ring.
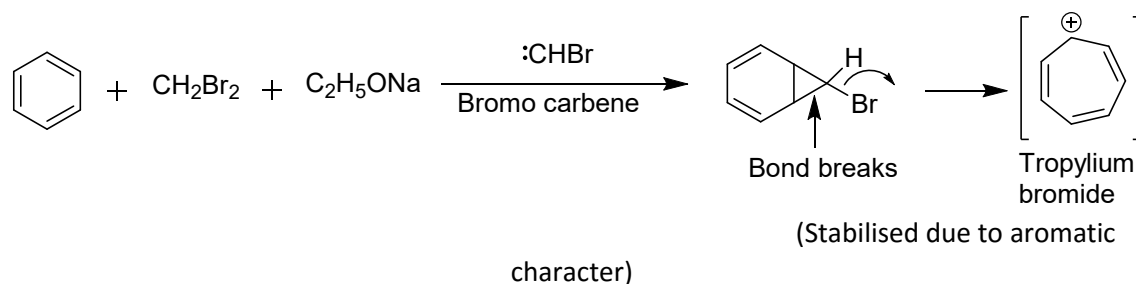
iv) Synthetic application of carbene:

Carbene are formed as reactive intermediate species in some important reactions such as:

a) **Reimer-Tieman Reaction:** Conversion of phenoxide to o-hydroxybenzaldehyde involves an electrophilic attack by dichlorocarbene.
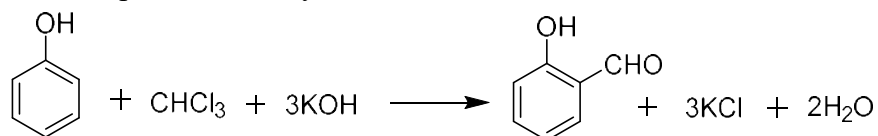
b) **Carbylamine reaction:**
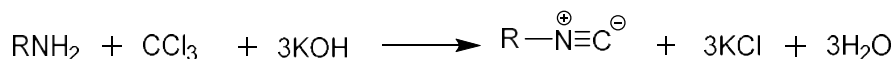
c) **Arndt Eistert and Wolf rearrangement:** Proceed by RCOCH:,acylecarbene.
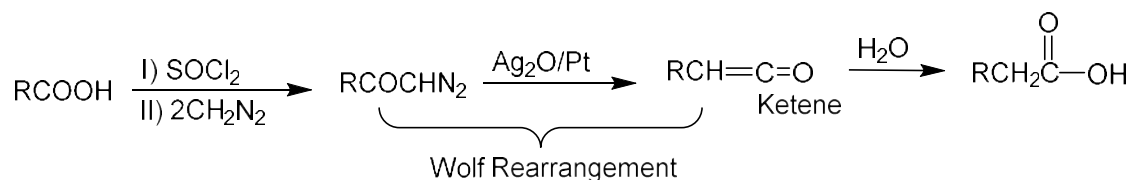
QUESTIONs

Q 1- What are singlet and triplet carbenes? Draw their structures. Why are the addition reactions of singlet carbenes on carbon-carbon double bonds stereospecific while such reactions of triple carbenes are not? Explain taking suitable example

Q-2: Give the mechanism of atleast two reactions which are proceed through carbine intermediate ?

Q-3: Complete the following reaction with mechanism-

+ CHCl$_3$ + 3KOH $\rightarrow$
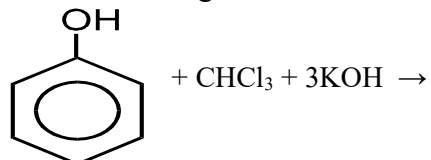
Q-4 Write the mechanism of the following conversion-

$$RNH_2 + CHCl_3 + 3KOH \longrightarrow RNC + 3KCl + 3H_2O$$
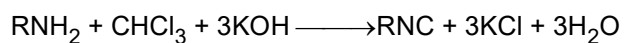
NITRENE

Outlines:

1. Definition
2. Generation
3. Reactions and Synthetic Applications

1 Definition

- It contains a nitrogen atom having a sextet of electrons and so it is electron deficient.
- Highly reactive and act as a strong nucleophile because there is need of two electrons to complete their octate .It is very difficult to form these species because they tend to polymerize to form (NH)n as soon as they are formed. Hence substituted nitrenes are used.
- Two Types of nitrenes: (i) Singlet and (ii) Triplet

2 Generation

(i) Thermal decomposition of azides or by α -elimination

(a)
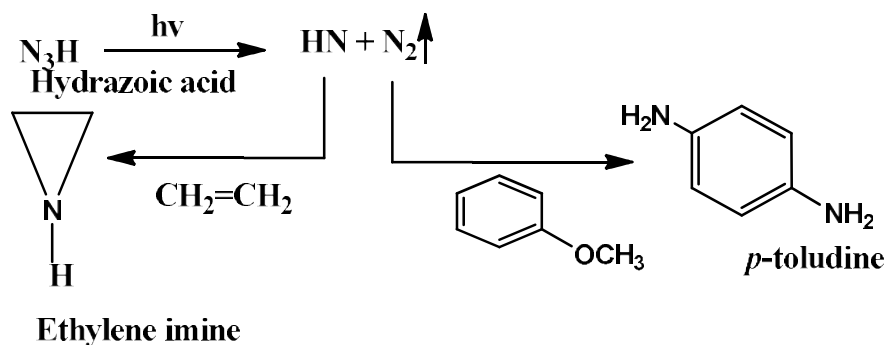
(b)
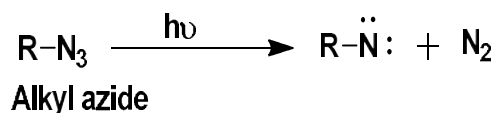
(ii) From Isocyanate

(iii) From acyl azide

R–C(=O)–N₃ →(hυ)→ R–C(=O)–N̈: + N₂

Acyl azide → Acyl nitrene + N₂

3 Reactions

i) Me–CH=CH₂ + H–N̈H₂ →

Propene imine

ii) Me–CH=CH–Me (cis) + H–N̈: →

cis-but-2-ene-N-alkyl imine

iii) (H, Me / Me, H alkene) + R–C(=O)–N̈: →

trans-but-2-ene-N-alkyl imine
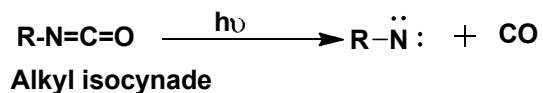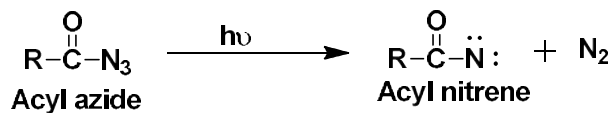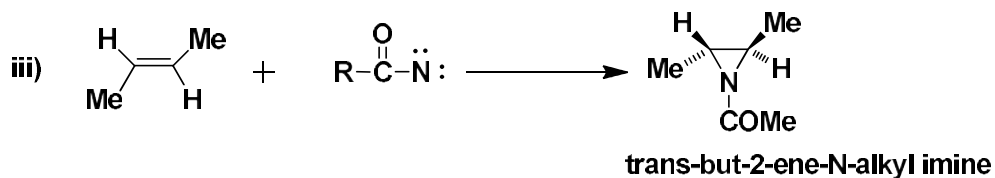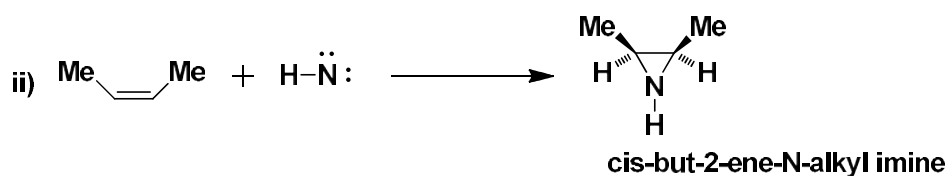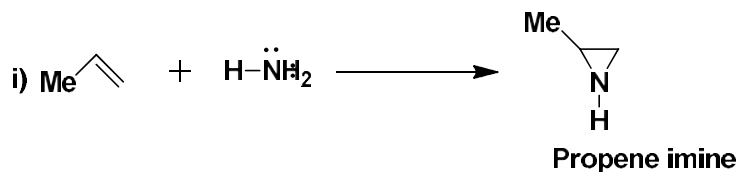
(iv) Insertion into C-H bond:

Me₂(Me)C–H(Me) + H₃C–C(=O)–N̈: → (Me)₃C–NH–C(=O)–Me

Acetyl nitrene → Acetyl-t-butylamine
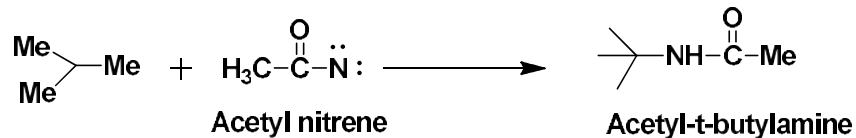
(v) Combination of two nitrene:

(biphenyl azide) →(hυ/Δ)→ [N̈: :N̈] → N̈=N̈

2,2-azodiphenyl
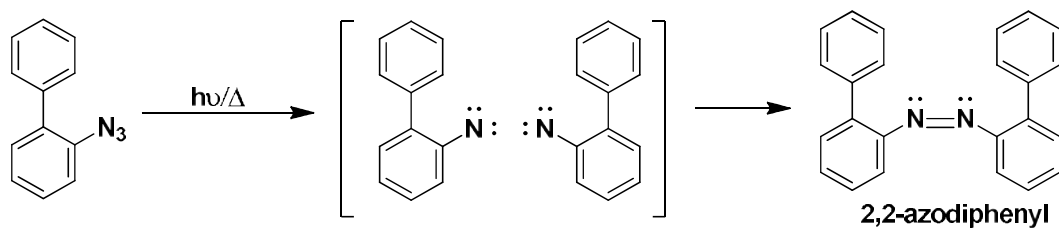
Synthetic Applications

Acyl nitrenes invoived in following reactions as intermediate

(i) Hofmann bromamide rearrangement reactions

$$R-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + KOH \longrightarrow \left[R-\overset{\overset{O}{\|}}{C}-\ddot{N}: \right] \longrightarrow R-N=C=O \xrightarrow{H_2O} R-NH_2 + CO$$
Alkyl isocynade

(ii) Lossen Rearrengement Reaction:

$$R-\overset{\overset{O}{\|}}{C}-NH-OH \xrightarrow{\overset{\ominus}{OH}} \left[R-\overset{\overset{O}{\|}}{C}-\ddot{N}: \right] \longrightarrow R-N=C=O \xrightarrow{H_2O} R-NH_2 + CO_2$$
Acyl nitrene   **Alkyl isocynade**

(iii) Curtius Rearrengement Reaction:

$$R-\overset{\overset{O}{\|}}{C}-N_3 \xrightarrow{\Delta} \left[R-\overset{\overset{O}{\|}}{C}-\ddot{N}: \right] \longrightarrow R-N=C=O \xrightarrow{H_2O} R-NH_2 + CO_2$$
Azide   **Acyl nitrene**   **Alkyl isocynade**
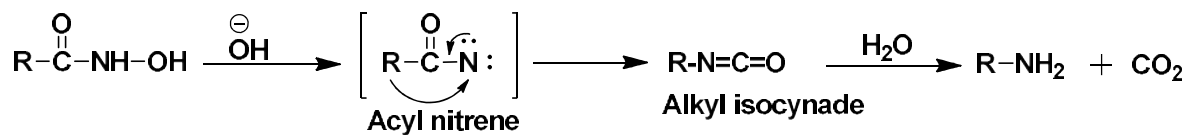
Questions

Q-1: What are the nitrenes? Write two methods of generation of nitrene.

Q-2: Discuss the mechanism of following reaction-
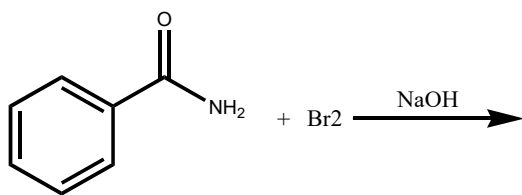
Q-3: Discuss the mechanism of following reaction

        1- Loosen rearrangement

        2- Curtius rearrangement

Q-4:   Complete the following reaction-

(cyclohexanone)   +   NH$_2$OH $\xrightarrow{\text{H+}}$ Intermediate $\xrightarrow{\text{H}_2\text{O}}$ Product
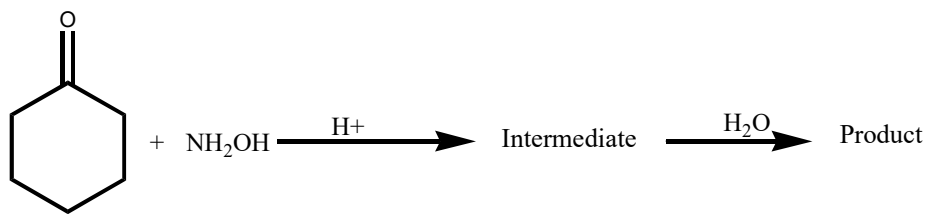
Ylides

Ylides are defined as compounds in which a positively charged hetero atom (e.g. N, P or S) is connected to a carbon carrying a negative charge. They are also referred as vicinial ionic (i.e., with positive and negative charges on adjacent atoms) intermediates. There are three main type of ylides: phosphorus, nitrogen and sulfur, although arsenic, selenium etc., ylides are also known. Phosphorus and sulfur ylides can be represented in two canonical forms but nitrogen ylides have only one structures. Phosphorus ylides are much more stable than nitrogen ylides. Sulfur ylides have a low stability. The ylides are represented as shown below:

Ylides

$$\overset{\ominus}{C}H_2 - \overset{+}{Z} \quad (Z = N, S, P)$$
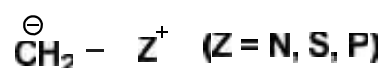
Preparation

By deprotonation of quaternary salts with suitable base.

$$(CH_3)_3 \overset{+}{N}CH_3\overset{-}{B}r \xrightarrow[\text{ether}]{C_6H_6Li} (CH_3)_3 \overset{+}{N}-\overset{-}{C}H_2 + LiBr$$

Tetramethylammonium bromide

a nitrogen ylide

$$(CH_3)_3 \overset{+}{P}CH_3\overset{-}{B}r \xrightarrow[\text{ether}]{C_6H_6Li} (CH_3)_3 \overset{+}{P}-\overset{-}{C}H_2 + LiBr$$

Tetramethylphosphonium bromide

a shosphorus ylide

$$(CH_3)_2 \overset{+}{S}CH_3\overset{-}{B}r \xrightarrow[\text{ether}]{C_6H_6Li} (CH_3)_2 \overset{+}{S}-\overset{-}{C}H_2 + LiBr$$

Tetramethylsulphonium bromide
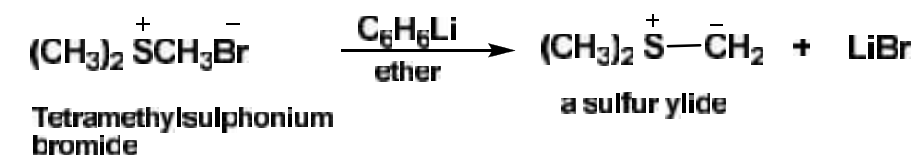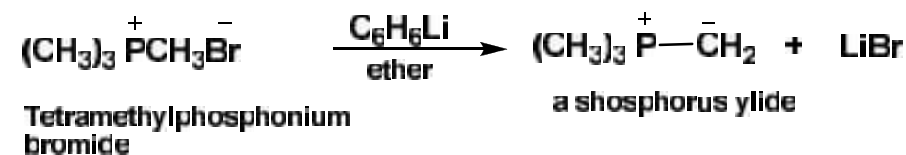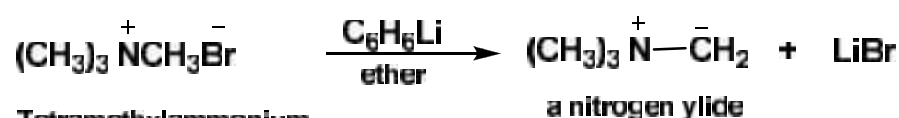
a sulfur ylide

Reactions of ylides

(a) Phosphorus ylides react with carbonyl compounds and to give alkenes (wittig reaction).

$$Ph_3 \overset{\oplus}{P}-\overset{-}{C}H_2 + O{=}C\,(R)_2 \longrightarrow Ph_3 P{-}CH_2 \longrightarrow Ph_3 P{=}O + CH_2{=}C(R)_2$$

$$O{-}C(R)_2$$
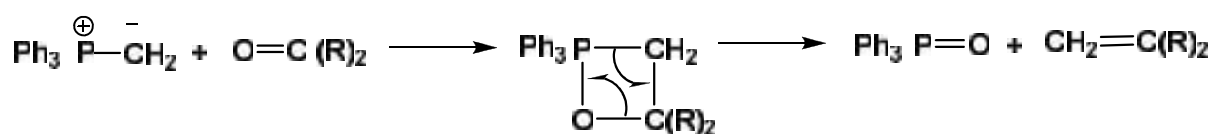
(b) Sulfur ylides react with carbonyl compounds and to give epoxide.

$(CH_3)_2 \overset{+}{S}-\overset{-}{C}H_2$ + $O{=}C (R)_2$ $\longrightarrow$ $(CH_3)_2 \overset{+}{S}-CH_2$ $\longrightarrow$ $CH_2-C(R)_2$ + $(CH_3)_2$

a sulfur ylide

$\overset{-}{O}-C(R)_2$

epoxide
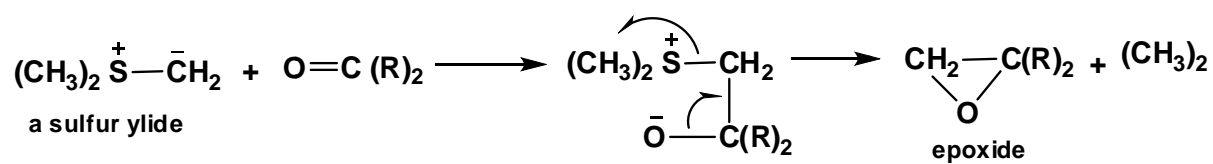
(c) Nitrogen ylides under go rearrangement reactions

a) Reaction with a carbonyl group

$R_3\overset{+}{N}-\overset{-}{C}H_2$ + $CH_3-\underset{O}{\overset{\|}{C}}-CH_3$ $\longrightarrow$ $\overset{H^+}{\longrightarrow}$ $R_3\overset{+}{N}-CH_2-\underset{OH}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3$

b) Stevens rearrangement

$H_3C-\underset{X^-}{\overset{+}{\underset{CH_2}{\overset{CH_3}{\underset{|}{\overset{|}{N}}}}}}-CH_3$ $\xrightarrow[\text{base}]{\text{strong}}$ $H_3C-\underset{X^-}{\overset{+}{\underset{CH_2^-}{\overset{CH_3}{\underset{|}{\overset{|}{N}}}}}}-CH_3$ $\longrightarrow$ $H_3C-\overset{CH_3}{\underset{|}{\overset{|}{N}}}-CH_2CH_3$

c) Sommelet rearrangement

$\xleftarrow[\text{transfer}]{H^+}$
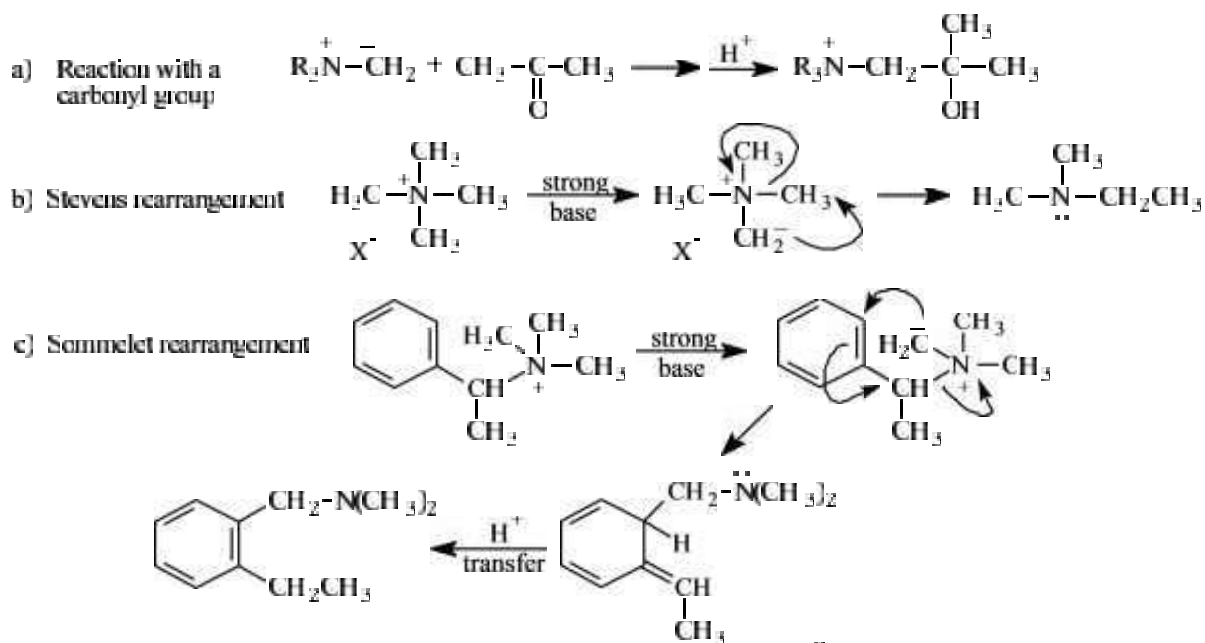
Diels-Alder Reactions

1. Definition
2. Important Mechanistic Features
3. Examples and Synthetic Applications

In general

The Diels-Alder reaction is an organic chemical reaction between a conjugated diene and a substituted alkene, commonly termed the dienophile, to form a substituted cyclohexene system. It was first described by Otto diels and Kurt Alder in 1928, for which work they were awarded the Nobel prize in Chemistry in 1850. The Diels-Alder reaction is particularly useful in synthetic organic chemistry as a reliable method for forming 6-membered systems with good control over region- and stereochemical properties.

General reaction

diene   +   dienophile   Cyclohexene
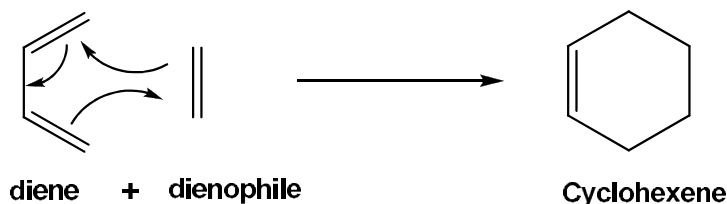
Mechanism
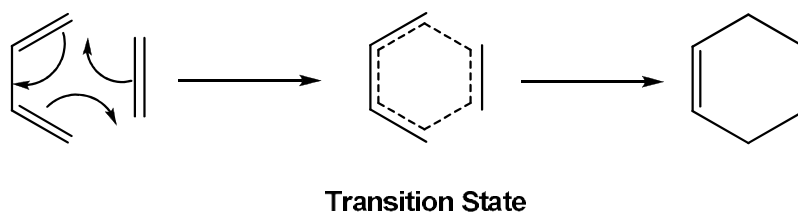
Transition State

Mechanistic features

Concerted mechanism. [4+2] cycloaddition pericyclic reaction a concerted reaction that proceeds through a cyclic transition state.

Only the s-cis conformation of the diene can react.

diene   dienophile   transition state   new σ bond
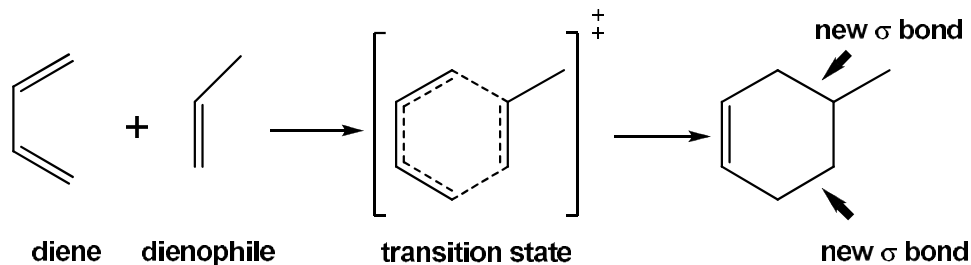
What makes a reactive dienophile?

The most reactive dienophiles have an electron-withdrawing group (EWG) directly attached to the double bond.

Typical EWGs

$C=C$ with EWG

$C=O$

$-C\equiv N$

Electron withdrawing group

$CH_2=CH-CH=CH_2$ + $CH_2=CH-CCH_3$ (with $=O$) $\xrightarrow{\Delta}$ cyclohexene with CCH_3 (C=O) substituent

conjugated diene   dienophile

$CH_2=CH-CCH_3$ (with $=O$) $\longleftrightarrow$ $\overset{+}{C}H_2-CH=CCH_3$ (with O^-)

resonance contributors of the dienophile

$\overset{\delta+}{CH_2}$---CH----CCH_3 (with $\overset{\delta-}{O}$)

resonance hybrid

a 1,4-addition reaction to 1,3-butadiene

Example

$CH_2{=}CHCH{=}CH_2$ + $CH_2{=}CH{-}\overset{\displaystyle O}{\overset{\|}{C}}H$

100° C

(100%)

Example

$CH_2{=}CHCH{=}CH_2$ + $CH_2{=}CH{-}\overset{\displaystyle O}{\overset{\|}{C}}H$

100° C

via:

(100%)

Acetylenic Dienophile

$CH_2{=}CHCH{=}CH_2$ + $CH_3CH_2O\overset{\displaystyle O}{\overset{\|}{C}}C{\equiv}C\overset{\displaystyle O}{\overset{\|}{C}}OCH_2CH_3$

100° C

98%
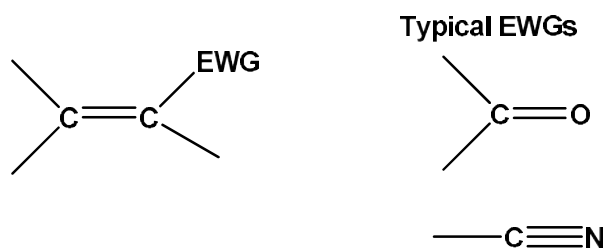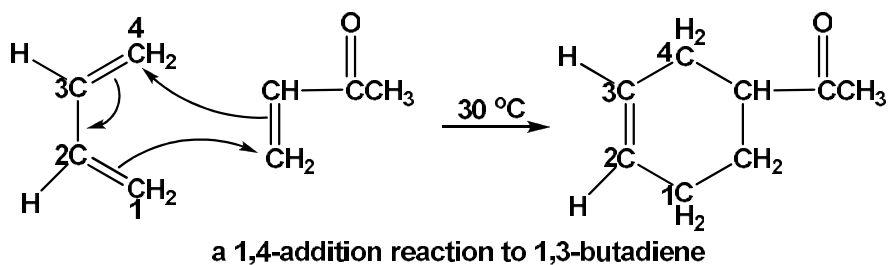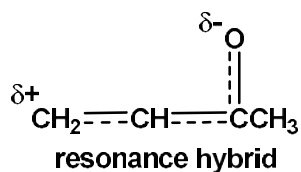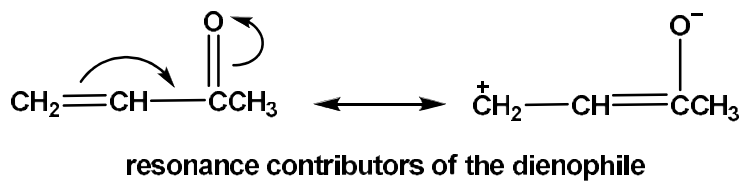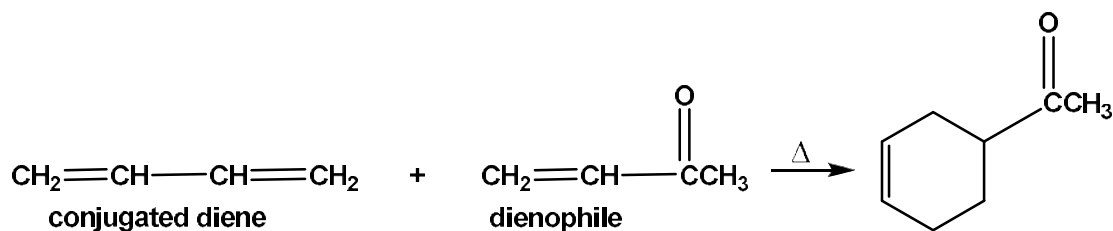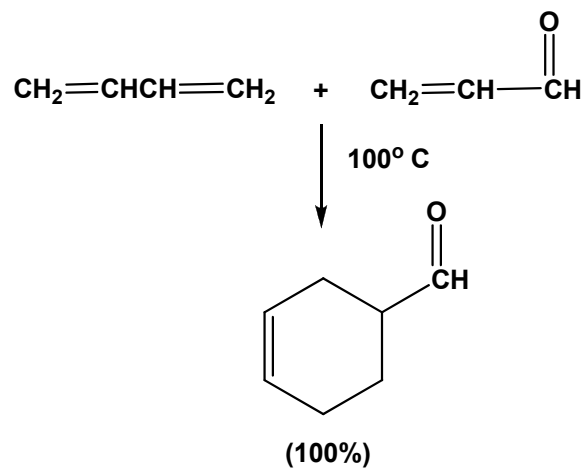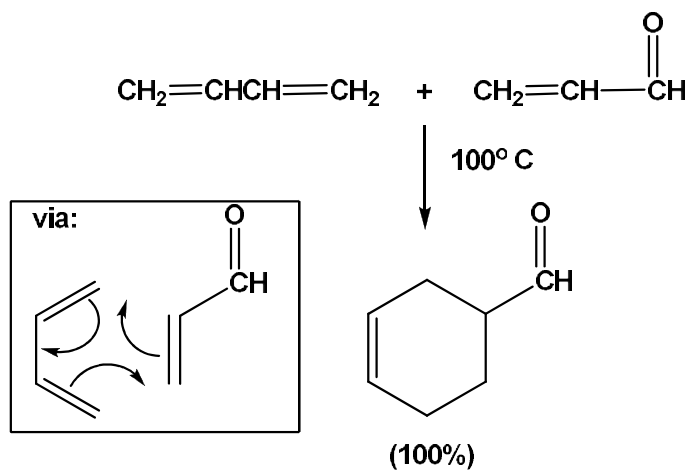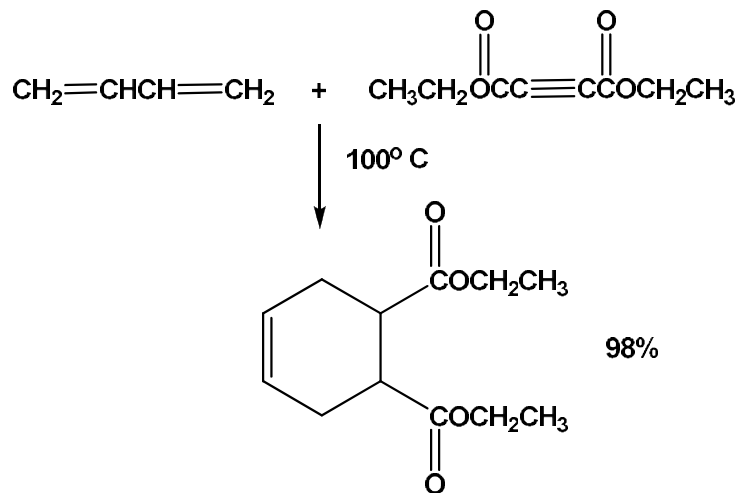
Diels-Alder Reaction

Stereospecific syn addition

cis-trans relationship of substituents of alkene is retained in the product.

The most reactive dienophiles have an electron-withdrawing group (EWG) directly attached to the double bond.

The most reactive dienes have an electron-donating (releasing) group (ERG) directly attached to the double bond. Eg. -OR (ether)

Cis → Cis
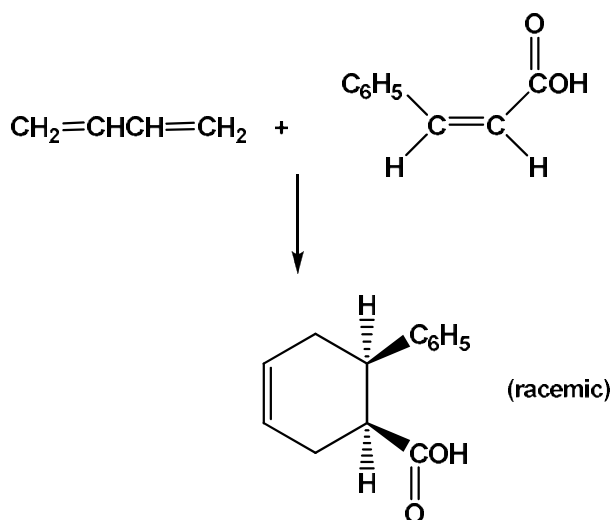
Only the s-cis conformation of the diene can participate in a Diels–Alder reaction

Only product. But, is it enantiomeric?

Applications

Diels-Alder reaction has been used as a important step in the synthesis of various natural products such as polycyclic hydrocarbons, α-terpineol, camphene, antharidine etc.
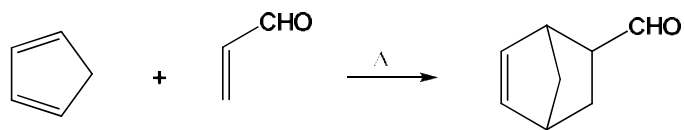
Acraldehyde
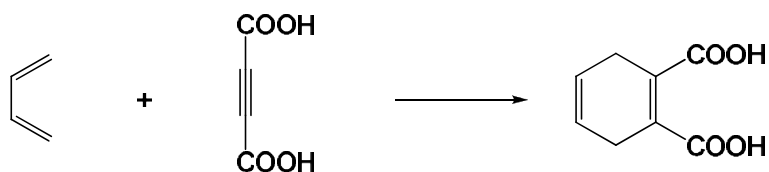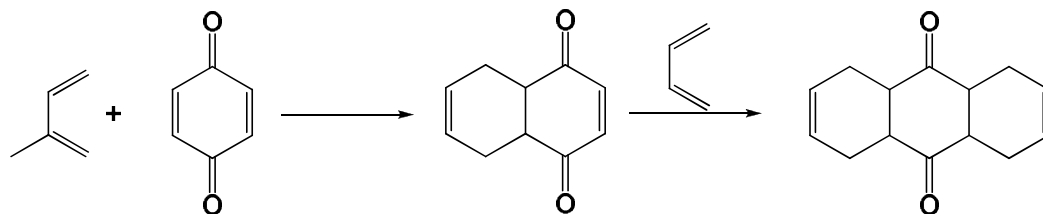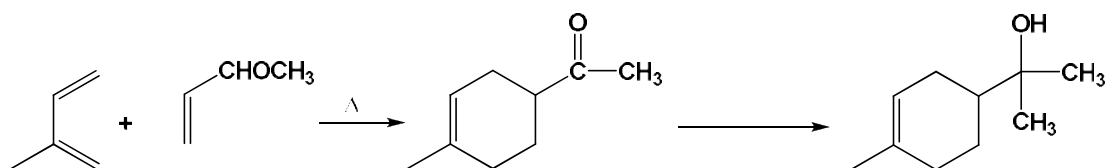
Questions

Rank the compounds below in order of increasing rate of the Diels-Alder reaction.

1   **2**   **3**
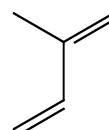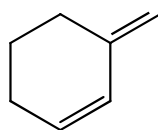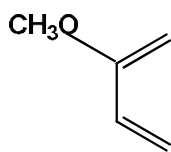
A) 1 < 2 < 3   B) 3 < 1< 2   C) 3 < 2 < 1   **D) 2 < 3 < 1**

Trans → Trans

$CH_2=CHCH=CH_2$ +

Only product
(racemic)
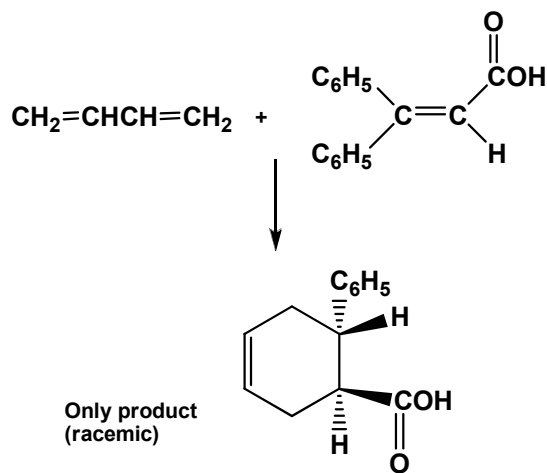
Question

What is the product of the Diels-Alder reaction that occurs between the reactions shown here?

NC

heat

CN

(A)   (B)   (C)   (D)
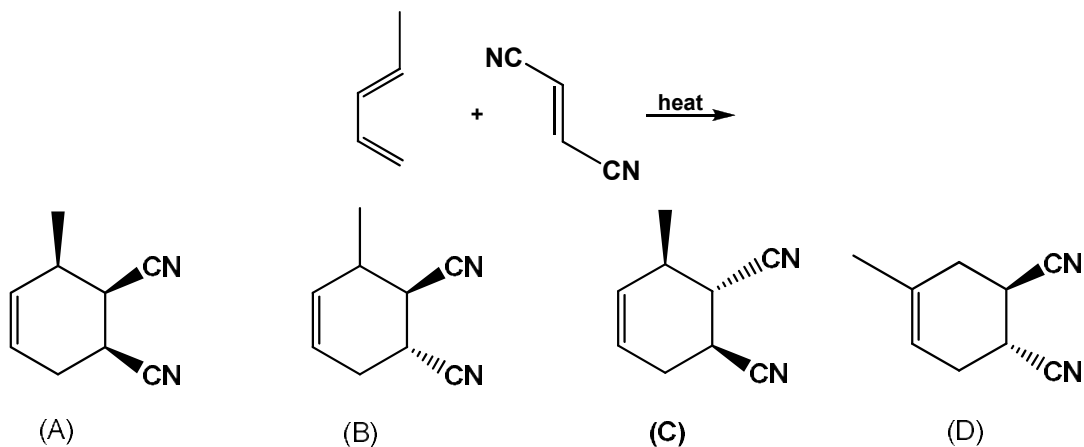
Stereospecific, concerted, syn addition:

cis dienophile → cis product

trans dienophile → trans product
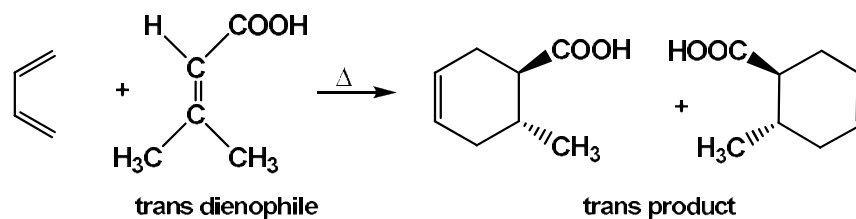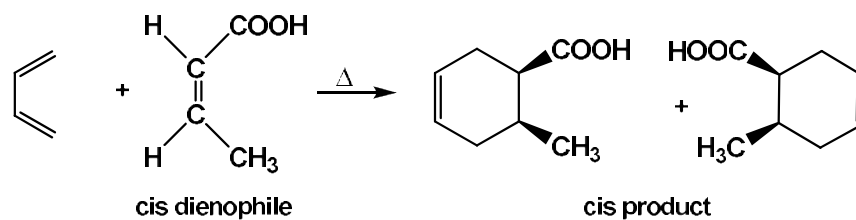
Question

Select the correct starting materials to make the compound at the right through the Diels-Alder reaction.

A)

B)

C)

D)
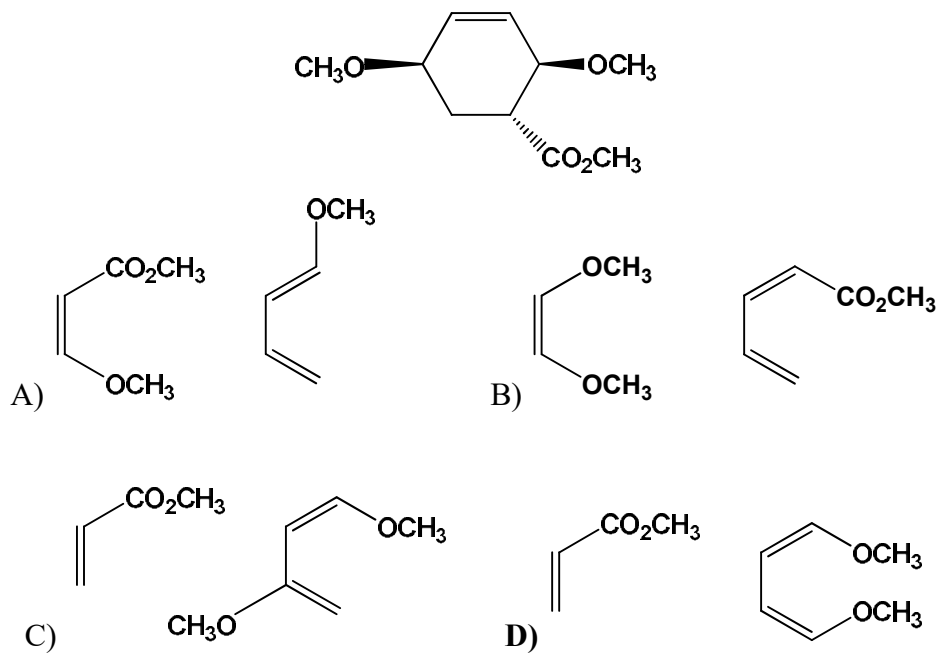
Module on Thermodynamics

Pre-Test

1) What is the difference between a state function and path function in Thermodynamics? Give examples.

2) What does the Internal Energy of a system represent? Does it have any relation with temperature?

3) State Hess' Law of constant summation.

4) The enthalpies of all elements in their standard states are (i) unity (ii) zero (iii) <0 (iv) different for each element

5) In a process 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process?

6) The equilibrium constant for a reaction is 10. What will be the value of $\Delta G°$? $R = 8.315 JK^{-1}mol^{-1}$, $T = 300K$

7) Find ΔS when 1.00 mol of water vapor initially at 200°C and 1.00 bar undergoes a reversible cyclic process for which $q = -145J$

8) The entropy of a system increases continuously in a spontaneous, irreversible process: (i) true for all systems (ii) false for all systems?

Thermodynamics and Equilibrium

Learning Objectives: *Defining the scope of Thermodynamics in Chemistry. Understanding of the basic concepts, the Ist and IInd Laws of Thermodynamics and their Applications. Introduction of state functions U (Internal Energy) & H (Enthalpy), heat capacities C_v and C_P under the Ist Law of Thermodynamics. Introduction of Entropy S under the IInd Law to define spontaneity of a process. Introduction of the state functions A & G to determine conditions of Material Equilibrium.*

Thermodynamics is a macroscopic science that studies the interrelationships of the various equilibrium properties of a system and the changes in equilibrium properties in processes. We shall be studying *equilibrium* thermodynamics, which deals with systems in equilibrium.

Any study of Thermodynamics should start with basic definitions: system & surrounding. It should talk about the different types of systems: isolated, closed, open. Under properties of the system one needs to mention about **_Extensive_** and **_Intensive_** properties (all thermodynamic state functions U, H, S, A, G plus V (volume) are extensive, while pressure, temperature, density, refractive index etc. are intensive). Further one needs to mention about State of a System, Change in State, Path, Cycle, Process [**Refer to G. W. Castellan, chapter "Energy and the First law of Thermodynamics"**].

The equilibrium concept can be divided into the following three kinds of equilibrium. For mechanical equilibrium, no unbalanced forces act on or within the system; For material equilibrium, no net chemical reactions are occurring in the system, nor is there any net transfer of matter from one part of the system to another or between the system and its surroundings; the concentrations of the chemical species in the various parts of the system are constant in time. For thermal equilibrium between a system and its surroundings, there must be no change in the properties of the system or surroundings when they are separated by a thermally conducting wall. For thermodynamic equilibrium, all three kinds of equilibrium must be present [**Refer to I. N. Levine chapter "Thermodynamics"**].

Ist Law of Thermodynamics

Work & Heat

Heat and **_work_** are defined only in terms of processes. Before and after the process of energy transfer between system and surroundings, heat and work do not exist. Heat is an energy transfer between system and surroundings due to a temperature difference. Work is an energy transfer between system and surroundings due to macroscopic force acting through a distance. Heat and work are forms of energy transfer rather than forms of energy. [**Refer to Levine**]

Under the Ist Law of Thermodynamics only $P-V$ work is considered. The work done in a volume change is called $P-V$ work. Processes are **_Reversible_** or **_Irreversible_** in Thermodynamics. A reversible process is one where the system is always infinitesimally close to equilibrium, and an infinitesimal change in conditions can reverse the process to restore both system and surroundings to their initial states.
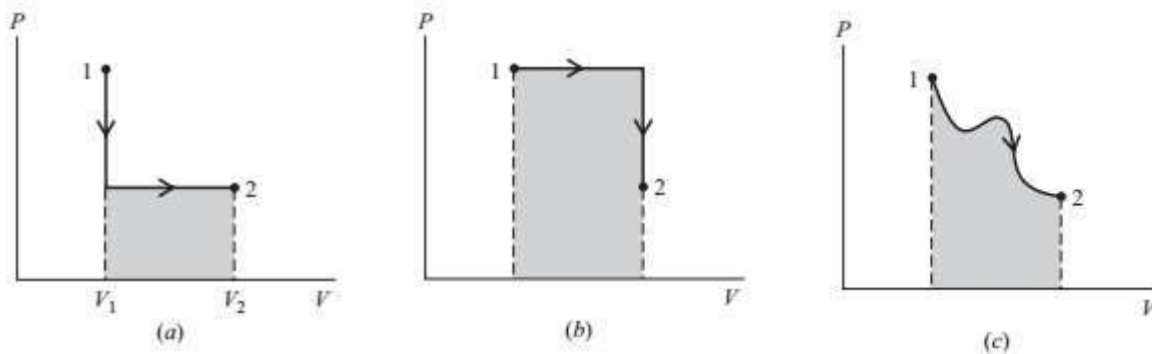
The work w done on the system in a reversible process (the heavy lines) equals minus the shaded area under the P-versus-V curve. The work depends on the process used to go from state 1 to state 2. **_The work done in the process (area under the curve) is different for the three different processes._**

The mathematical form of the Ist Law of Thermodynamics may be written in the form:

$\Delta U = q + w$ - where ΔU is the energy change undergone by the system in the process, q is the heat flow into the system during the process, and w is the work done on the system during the process.

For an infinitesimal process, $dU = \delta q + \delta w$ where dU is the infinitesimal change in system energy in a process with infinitesimal heat δq flowing into the system and infinitesimal work δw done on the system. The statement of the Ist Law says that "In an isolated system, energy can neither be created nor destroyed".

Attention is drawn to the fact that the differential of a state function represents an exact differential and is written with a "d", whereas the differentials of path functions q and w are inexact and are represented with a "δ". An exact differential integrates to a finite difference; $\int_{1}^{2} dU = U_2 - U_1$ **_An inexact differential integrates to a total quantity,_** $\int_{1}^{2} \delta q = q$ **_which depends on the path of integration._**

The cyclic integral of an exact differential is zero for any cycle, $\oint dU = \Delta U = 0$. **_The cyclic integral of an inexact differential is usually not zero._**[Refer to G. W. Castellan]

CHANGES IN STATE AT CONSTANT VOLUME

If the volume of a system is constant in the change in state, then d V = 0, and the first law equation

becomes $dU = \delta q_V$ Since $U = f(V,T)$, $\therefore dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$. At constant volume this

yields $\delta q_V = \left(\frac{\partial U}{\partial T}\right)_V dT$. Dividing by dT we obtain $C_V \equiv \frac{\delta q_V}{dT} = \left(\frac{\partial U}{\partial T}\right)_V$, the heat capacity of the system

at constant volume. Further, we obtain $dU = C_v dT$ (infinitesimal change), which on integrating gives

$$\Delta U = \int_{T_1}^{T_2} C_V dT = q_V$$
(finite change). Hence heat becomes a state function for a process carried out at constant

volume.

CHANGES IN STATE AT CONSTANT PRESSURE

In chemical systems most often processes are carried out at constant pressure rather than constant volume. There is no straightforward relation where the Internal Energy U may be expressed as a simple function of pressure. Hence another state function has to be introduced to circumvent this problem. For a change in state at constant pressure the first-law statement $\Delta U = q + w$ gives

$$U_2 - U_1 = q + w = q - \int_{V_1}^{V_2} PdV = q_P - P\int_{V_1}^{V_2} dV = q_P - P(V_2 - V_1)$$

$q_P = U_2 + PV_2 - U_1 - PV_1 = (U_2 + PV_2) - (U_1 + PV_1) = H_2 - H_1$, $\Delta H = q_P$ where the state function

$H \equiv U + PV$ is called the Enthalpy of the system. Hence, in constant pressure processes heat again

becomes a state function. For an infinitesimal change in state the following equations may be written:

$dH = \delta q_P$ Since $H = f(P,T)$, $\therefore dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$. At constant pressure this yields

$\delta q_P = \left(\frac{\partial H}{\partial T}\right)_P dT$. Dividing by dT we obtain $C_P \equiv \frac{\delta q_P}{dT} = \left(\frac{\partial H}{\partial T}\right)_P$, the heat capacity of the system at

constant pressure. Further, we obtain $dH = C_P dT$ (infinitesimal change), which on integrating gives

$$\Delta H = \int_{T_1}^{T_2} C_P dT = q_P$$
(finite change).

Reversible Isothermal Process in a Perfect Gas

Consider the special case of a reversible isothermal (constant-T) process in a perfect gas. (the system is assumed closed.) For a fixed amount of a perfect gas, U depends only on T. Therefore $\Delta U = 0$ for an isothermal change of state in a perfect gas. This also follows from $dU = C_V dT$ for a perfect gas. The first law $\Delta U = q + w$ becomes $0 = q + w$ and $q = -w$. Integration of $dw_{rev} = -PdV$ and use of $PV = nRT$ give

$$w = -\int_1^2 PdV = -\int_1^2 \frac{nRT}{V} dV = -nRT \int_1^2 \frac{1}{V} dV = -nRT(\ln V_2 - \ln V_1)$$

$$w = -q = nRT \ln \frac{V_1}{V_2} = nRT \ln \frac{P_2}{P_1}$$

Example 1: Calculation of q, w and ΔU

A cylinder fitted with a frictionless piston contains 3.00 mol of He gas at $P = 1.00$ atm and is in a large constant-temperature bath at 400 K. The pressure is reversibly increased to 5.00 atm. Find w, q and ΔU for this process.

It is an excellent approximation to consider the helium as a perfect gas. Since T is constant, U is zero.

$$w = (3.00 mol)(8.314 Jmol^{-1}K^{-1})(400K) \ln(5.00/1.00) = (9980 J) \ln 5.00$$

$$w = (9980 J)(1.609) = 1.61 \times 10^4 J$$

Also, $q = -w = -1.61 \times 10^4 J$. Of course, w (the work done on the gas) is positive for the compression. The heat q is negative because heat must flow from the gas to the surrounding constant-temperature bath to maintain the gas at 400 K as it is compressed.

Example 2: **The sign convention in thermodynamics**

If an electric motor produced 15 kJ of energy each second as mechanical work and lost 2 kJ as heat to the surroundings, then the change in the internal energy of the motor each second is

$$\Delta U = -2kJ - 15kJ = -17kJ$$

Suppose that, when a spring was wound, 100 kJ of work was done on it but 15 kJ escaped to the surroundings as heat. The change in internal energy of the spring is

$$\Delta U = +100kJ - 15kJ = +85kJ$$

Example 3: Work of adiabatic expansion

Consider the adiabatic, reversible expansion of 0.020 mol Ar, initially at 25°C, from 0.50 dm3 to 1.00 dm3. Using the formula $VT^c = const.$, where $c = C_{V,m} / R$, the work can be calculated. The molar heat capacity of argon at constant volume is $12.48 JK^{-1}mol^{-1}$, so c = 1.501. Therefore,

$$T_f = (298K)\left(\frac{0.50dm^3}{1.00dm^3}\right)^{\frac{1}{1.501}} = 188K$$

It follows that $\Delta T = -110K$, $w = \Delta U = C_V \Delta T$ ($q = 0$ for adiabatic process)

$$\therefore w = \{(0.020mol) \times (12.48 JK^{-1}mol^{-1})\} \times (-110K) = -27J$$. Note that temperature change is independent of the amount of gas but the work is not.

<div align="center">

2nd Law of Thermodynamics

</div>

The concept of Carnot cycle will not be used in this approach. Entropy to be introduced as the criterion for spontaneity.

Spontaneous Processes Some things happen naturally; some things don't. A gas expands to fill the available volume, a hot body cools to the temperature of its surroundings, under the right conditions iron rusts, but objects spontaneously do not unrust and a chemical reaction runs in one direction rather than

another. Some aspect of the world determines the spontaneous direction of change, the direction of change that does not require work to be done to bring it about.

A gas can be confined to a smaller volume, an object can be cooled by using a refrigerator, and some reactions can be driven in reverse (as in the electrolysis of water). However, none of these processes is spontaneous; each one must be brought about by doing work.

Thermodynamics is silent on the rate at which a spontaneous change in fact occurs, and some spontaneous processes (such as the conversion of diamond to graphite) may be so slow that the tendency is never realized in practice whereas others (such as the expansion of a gas into a vacuum) are almost instantaneous.

The recognition of two classes of process, spontaneous and non-spontaneous, is summarized by the Second Law of thermodynamics. This law may be expressed in a variety of equivalent ways. One statement was formulated by Kelvin: **No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.**

What determines the direction of spontaneous change? It is not the total energy of the isolated system. The First Law of thermodynamics states that energy is conserved in any process, and we cannot disregard that law now and say that everything tends towards a state of lower energy: the total energy of an isolated system is constant.

Is it perhaps the energy of the system that tends towards a minimum? Two arguments show that this cannot be so. First, a perfect gas expands spontaneously into a vacuum, yet its internal energy remains constant as it does so. Secondly, if the energy of a system does happen to decrease during a spontaneous change, the energy of its surroundings must increase by the same amount (by the First Law). The increase in energy of the surroundings is just as spontaneous a process as the decrease in energy of the system. When a change occurs, the total energy of an isolated system remains constant but it is parcelled out in different ways. Can it be, therefore, that the direction of change is related to the distribution of energy? We shall see that this idea is the key, and that spontaneous changes are always accompanied by a dispersal of energy, an increase in disorder. [**Refer to P. Atkins, Physical Chemistry**]

Not only do systems evolve spontaneously in a direction that lowers their energy but that they also seek to increase their disorder. What are the requirements to characterize this disorder? We want to put this idea on a quantitative basis. We also want this property to be a property to be a state function. It has

been shown mathematically that though δq_{rev} is an inexact differential, multiplying it by the integrating

factor $\frac{1}{T}$ converts it to an exact differential (beyond the scope of this treatment). In Thermodynamic

terms this means that $\frac{\delta q_{rev}}{T}$ represents the differential of a state function. We can write $dS = \frac{\delta q_{rev}}{T}$,

where the state function S is called the entropy. Because entropy is a state function $\Delta S = 0$ for a cyclic

process; i.e. mathematically $\oint dS = \oint \frac{\delta q_{rev}}{T} = 0$

The question arises – how to determine the role played by entropy in governing the direction of any spontaneous process? To be able to focus on the entropy alone, we will consider an infinitesimal spontaneous change in an isolated system. ***Isolated system is chosen because the energy remains constant in it so that the effect of entropy can be studied separately.*** Because the energy remains constant, the driving force for any spontaneous process in an isolated system must be due to an increase in entropy, which can be expressed mathematically by $dS > 0$ If the system is isolated how is the entropy of the system increasing. The only possible answer is – **It must be created within the system itself. Unlike energy, entropy is not necessarily conserved; it increases whenever a spontaneous process takes place.** The entropy of an isolated system will continue to increase until no more spontaneous processes occur, in which case the system will be in equilibrium.
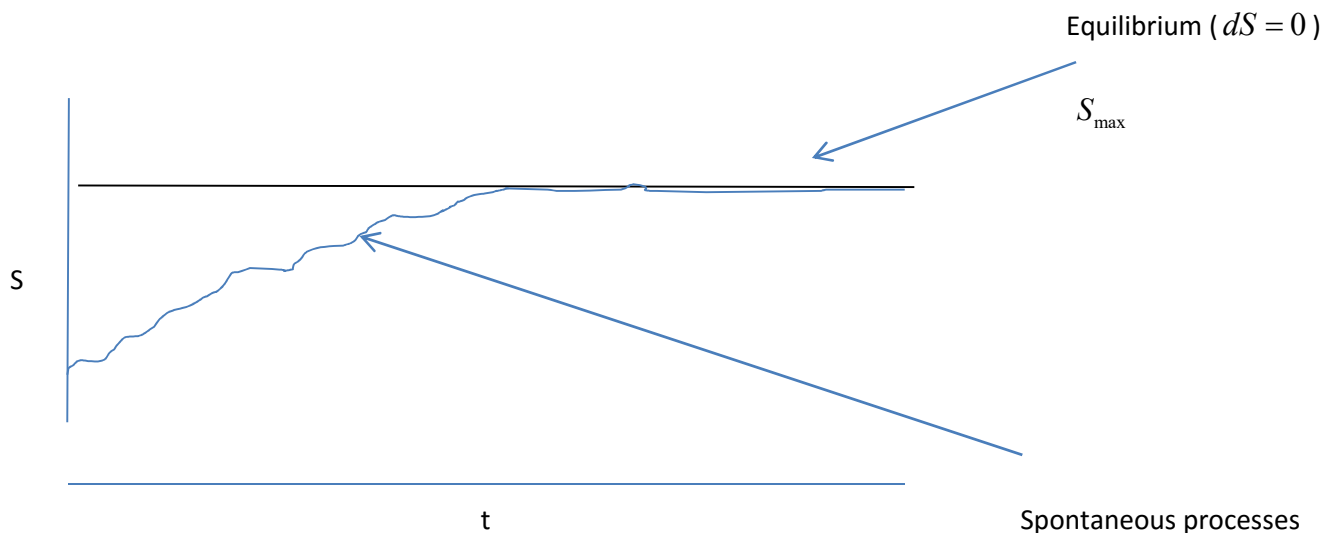
$$dS > 0 \qquad \text{(spontaneous process in an isolated system)}$$

$$dS = 0 \qquad \text{(reversible process/equilibrium in an isolated system).}$$

For other types of systems, energy as heat can flow in or out of the system and it is convenient to view dS in any infinitesimal process as consisting of two parts. One part of dS is the entropy created by the irreversible process itself, and the other part is the entropy due to the energy as heat exchanged between the system and its surroundings.

dS_{prod} - created by the irreversible process, always positive

dS_{exch} - exchange of energy as heat with the surroundings, given by $\delta q / T$, can be positive ,negative, zero.

For any process $dS = dS_{prod} + dS_{exch} = dS_{prod} + \delta q / T$.

For a reversible process, $\delta q = \delta q_{rev}, dS_{prod} = 0$, so $dS = {\delta q_{rev}}/{T}$.

For an irreversible or spontaneous process, $dS_{prod} > 0, dS_{exch} = {\delta q_{irrev}}/{T}$, so $dS > {\delta q_{irrev}}/{T}$. The last two equations can be combined as $dS \geq {\delta q}/{T}$, or $\Delta S \geq \int {\delta q}/{T}$ - **Clausius Inequality**.

[**Refer to Mcquarrie & Simon – Physical Chemistry a Molecular Approach**]

Example: Entropy changes in the ideal gas

Starting with the combined I & II Law, $TdS = dU + PdV$ and rewriting it as $dU = C_v dT + PdV$ we further obtain $dS = {C_v}/{T} dT + {P}/{T} dV$. For an ideal gas, replacing $p = nRT / V$ the equation becomes

$dS = {C_v}/{T} dT + {nR}/{V} dV$. For a finite change in state integrating this relation we get

$\Delta S = \int_{T_1}^{T_2} {C_v}/{T} dT + nR \int_{V_1}^{V_2} {dV}/{V}$. Considering C_v being a constant we finally obtain $\Delta S = C_v \ln(\frac{T_2}{T_1}) + nR \ln(\frac{V_2}{V_1})$

For pressure-temperature relationship we can use $dH = C_p dT$ and replacing $V = nRT / P$ and using similar logic as above we finally obtain $\Delta S = C_p \ln(\frac{T_2}{T_1}) - nR \ln(\frac{P_2}{P_1})$

Example 4: ΔS **for heating at constant** P

The specific heat capacity c_P of water is nearly constant at $1.00cal(g^\circ C)$ in the temperature range 25°C to 75°C at 1 atm . (a) Find ΔS when 100 g of water is reversibly heated from 25°C to 50°C at 1 atm. (b) Without doing the calculation, state whether ΔS for heating 100 g of water from 50°C to 75°C at 1 atm will be greater than, equal to, or less than ΔS for the 25°C to 50°C heating.

(a) The system's heat capacity is $C_P = mc_P = (100g)[1.00cal(g^\circ C) = 100cal/K$ (A temperature change of one degree Celsius equals a change of one kelvin)

For the heating process, with C_P constant gives $\Delta S = \int_{T_1}^{T_2} \delta q_{rev} / T = \int_{T_1}^{T_2} C_P / T \, dT = C_P \ln \dfrac{T_2}{T_1}$

$= (100cal/K)\ln\dfrac{323K}{298K} = 8.06cal/K = 33.7J/K$

(b) Since C_P is constant, the reversible heat required for each of the processes with $\Delta T = 25^\circ C$ is the same. For the 50°C to 75°C change, each infinitesimal element of heat dq_{rev} flows in at a higher temperature than for the 25°C to 50°C change. Because of the $1/T$ factor in $dS = dq_{rev}/T$, each dq_{rev} produces a smaller increase in entropy for the higher-temperature process, and ΔS is smaller for the 50°C to 75°C heating. The higher the temperature, the smaller the entropy change produced by a given amount of reversible heat.

Example 5:

One mole of an ideal gas, $C_P = 5/2R$, initially at 20 °C and 1 atm pressure, is transformed to 50 °C and 8 atm pressure. Calculate ΔS .

Using the equation $\Delta S = C_P \ln(\dfrac{T_2}{T_1}) - nR \ln(\dfrac{P_2}{P_1})$,

$\Delta S = \dfrac{5}{2} R \ln\dfrac{323.15K}{293.15K} - R\ln\dfrac{8atm}{1atm} = \dfrac{5}{2} R(0.0974) - 2.079R = -1.836R = -1.836(8.314J/Kmol) = -15.26J/Kmol$

Example 6:

Let *n* moles of a perfect gas undergo an adiabatic free expansion into a vacuum (the Joule experiment). (*a*) Express ΔS in terms of the initial and final temperatures and volumes. (*b*) Calculate ΔS_m if $V_2 = 2V_1$.

(a) The initial state is T_1, V_1, and the final state is T_1, V_2, where $V_2 > V_1$. T is constant because $\left(\partial T \big/ \partial V\right)_U$ is zero for a perfect gas. Although the process is adiabatic $(q = 0)$, ΔS is not zero because the process is irreversible. We know that $\Delta s = nR \ln \dfrac{V_2}{V_1}$, since the temperature integral is zero when $T_2 = T_1$.

(b) If the original container and the evacuated container are of equal volume, then $V_2 = 2V_1$ and $\Delta S = nR \ln 2$. We have

$$\Delta S / n = \Delta S_m = R \ln 2 = [8.314 J(molK)](0.693) = 5.76 J / (molK)$$

Equilibrium

Consider an isolated system that is not at material equilibrium. The spontaneous chemical reactions or transport of matter between phases that are occurring in this system are irreversible processes that increase the entropy. These processes continue until the system's entropy is maximized. Once S is maximized, any further processes can only decrease S, which would violate the second law. The criterion for equilibrium in an isolated system is maximization of the system's entropy S .

When we deal with material equilibrium in a closed system, the system is ordinarily not isolated. Instead, it can exchange heat and work with its surroundings. Under these conditions, we can take the system itself plus the surroundings with which it interacts to constitute an isolated system, and the **condition for material equilibrium in the system is then maximization of the total entropy of the system plus its surroundings:** $S_{syst} + S_{surr}$ is a maximum at equilibrium.

The above statement is perfectly valid for material equilibrium, but the question arises – is it convenient to always consider the changes in thermodynamic properties of the surroundings as well? The answer is a clear "No". Can we not devise a criterion for material equilibrium that refers to properties of the system only? Since S_{syst} is a maximum at equilibrium only for an isolated system, consideration of the

entropy of the system does not furnish us with an equilibrium criterion. We must look for another system state function to find the equilibrium criterion. [Refer to Levine].

The condition of reversibility/equilibrium according to the second law of thermodynamics may be written as
$$TdS = \delta q_{rev}$$

and for irreversible change as per Clausius Inequality as
$$TdS > \delta q.$$

The two relations can be combined into
$$TdS \geq \delta q.$$

By using the first law in the form
$$\delta q = dU + \delta w,$$

the combined Ist and IInd Law of Thermodynamics can be written as
$$TdS \geq dU + \delta w,$$

or
$$-dU - \delta w + TdS \geq 0.$$

While considering equilibrium we have to go beyond only P-V work and include all kinds of work. Here
$$\delta w = PdV + \delta w_a,$$

where the subscript "a" stands for "additional" work. Finally,
$$-dU - PdV - \delta w_a + TdS \geq 0.$$

This relation expresses the condition of equilibrium (=) and of spontaneity (>) for a transformation in terms of changes in properties of the system $dU, dV, dS,$ and the amount of work δw or δw_a associated with the transformation.

Transformations at Constant Temperature

If a system undergoes an isothermal change in state, then
$$TdS = d(TS),$$

and the earlier relation can be written as
$$-dU + d(TS) \geq \delta w,$$

or
$$-d(U - TS) \geq \delta w.$$

The combination of variables in brackets is given a special symbol "A".

By definition,
$$A \equiv U - TS.$$

Being a combination of other functions of the state, A is a function of the state of the system; A is called the Helmholtz energy of the system.

The earlier relation reduces to the form
$$-dA \geq \delta w,$$

or by integrating
$$-\Delta A \geq w.$$

The significance of A is given by the above relation; the work produced in an isothermal transformation is less than or equal to the decrease in the Helmholtz energy. The equality sign applies to the reversible

transformation, so the maximum work obtainable in an isothermal change in state is equal to the decrease in the Helmholtz energy. This maximum work includes all the kinds of work produced in the transformation.

Transformations at Constant Temperature and under Constant Pressure

Since P is a constant $$PdV = d(PV).$$

The temperature is constant, so $$TdS = d(TS).$$

The earlier relation becomes $$-[dU + d(PV) - d(TS)] \geq \delta w_a$$

Or $$-d(U + PV - TS) \geq \delta w_a.$$

The combination of variables in brackets is given a special symbol "G".

By definition, $$G \equiv U + PV - TS = H - TS = A + PV.$$

Being a composite of properties of the state of a system G is a property of the state; G is called the **Gibbs energy** of the system. More commonly, G is called the **free energy** of the system. Substituting in the last equation $$-dG \geq \delta w_a,$$

or by integrating $$-\Delta G \geq w_a.$$

Fixing our attention on the equality sign we have $$-\Delta G = w_{a,rev}$$

which reveals an important property of the Gibbs energy; the decrease in Gibbs energy $-\Delta G$ associated with a change in state at constant T and P is equal to the maximum work $w_{a,rev}$ over and above expansion work, which is obtainable in the transformation. A practical example of w_a is the work done by an electrochemical cell.

The conditions for equilibrium may be formulated thus: *In a closed system the material equilibrium condition at constant T and V is the minimization of the Helmholtz energy A, and at constant T and P material-equilibrium condition is the minimization of the Gibbs energy G.*

$dA = 0$ at equilibrium, constant T, V ; $dG = 0$ at equilibrium, constant T, P
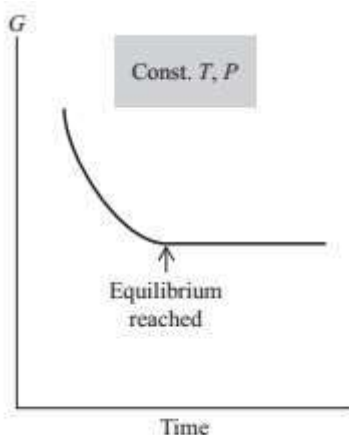
Thus, the state function G continually decreases during material changes at constant T and P until equilibrium is reached.

ΔG also gives a criterion for spontaneity of a process at constant temperature and pressure.

If ΔG is negative (<0), the process is spontaneous

If ΔG is positive (>0), the process is non-spontaneous

If $\Delta G = 0$, the process is at equilibrium.

Some unsolved problems

1. Consider the following cycle using 1 mol of a diatomic ideal gas initially at 298 K and 1.00 atm.

i) Isothermal expansion to twice its volume with $P_{ext} = 0.50$ atm.

ii) Reversible isothermal compression from 0.50 atm to 1.00 atm.

a) Calculate Δq for each step and for the cycle

b) Calculate q/T for each step and for the cycle

c) Calculate ΔS for each step and for the cycle

d) Comment on the similarity or difference between the answers in parts b and c. That is, what is the point of this problem in your own words?

2.a)   Calculate the change in entropy for the system when 100.0 g of water at 80.0 °C is poured into 100.0 g of water at 10.0 °C in an insulated vessel. You can assume the vessel does not itself absorb any heat in this process.

b)   Why is $\Delta S°_{vap,m} \gg \Delta S°_{fus,m}$ for a given substance?

3.   Use the data in tables in the back of your book to calculate $\Delta G°$ at 298 K for the following reaction from $\Delta G_f°$ values at 298K and also from $\Delta S°$ and $\Delta H°$ values at 298K. Is this reaction (from the reactants in their standard states to the products in their standard states) spontaneous at this temperature?

$$N_2 \, (g) + 3 \, H_2 \, (g) \rightarrow 2 \, NH_3 \, (g)$$
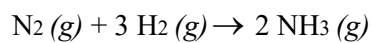
ELECTROCHEMISTRY

What is Electrochemistry?

Electrochemistry is the study of the interchange of chemical energy and electrical energy. The process of conversion of chemical energy into electrical energy is called electrochemical reaction and the reverse process is called electrolytic reaction or electrolysis. A device that produces electrical energy from a chemical reaction is called an electrochemical cell and devices that undergo chemical reaction with the aid of electricity are called electrolytic cells.

SINGLE ELECTRODE POTENTIAL

An electrochemical cell consists of two half-cells. With an open-circuit, the metal electrode in each half-cell transfers its ions into solution. Thus an individual electrode develops a potential with respect to the solution. The potential of a single electrode in a half-cell is called the **Single electrode potential.** Thus in Daniel cell in which the electrodes are not connected externally, the anode Zn/Zn^{2+} develops a negative charge and the cathode Cu/Cu^{2+}, a positive charge. The amount of the charge produced on an individual electrode determines its single electrode potential.

The single electrode potential of a half-cell depends on : (a) concentration of ions in solution ; (b) tendency to form ions ; and (c) temperature.

Standard emf of a cell

The emf generated by an electrochemical cell is given by the symbol E. It can be measured with the help of a potentiometer. The value of emf varies with the concentration of the reactants and products in the cell solutions and the temperature of the cell. When the emf of a cell is determined under standard conditions, it is called the standard emf. The standard conditions are : (a) 1 M solutions of reactants and products ; and (b) temperature of $25°$ C. Thus standard emf may be defined as the emf of a cell with 1 M solutions of reactants and products in solution measured at $25°$ C. Standard emf of a cell is represented by the symbol E°. For gases 1 atm. pressure is a standard condition instead of concentration. For Zn-Cu voltaic cell, the standard emf, E° is 1.10V.

$$Zn \mid Zn^{2+}_{(aq, 1M)} \quad \parallel Cu^{2+}_{(aq, 1M)} \mid Cu \qquad E° = 1.10 \text{ V}$$
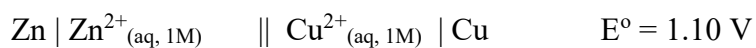
Determination of emf of a half-cell

By a single electrode potential, we also mean the emf of an isolated half-cell or its half-reaction. The emf of a cell that is made of two half-cells can be determined by connecting them to a voltmeter. However, there is no way of measuring the emf of a single half-cell directly. The emf of the newly constructed cell, E is determined with a voltmeter. The emf of the unknown half-cell E° can then be calculated from the expression

$$E_{measured} = E_R - E_L$$

$$= E_{reduction} - E_{oxidation}$$

$$= E_{cathode} - E_{anode}$$

If the standard half-cell (SHE) acts as anode, the equation becomes

$$E_R = E_{measured} \qquad (E_L = 0)$$

On the other hand, if standard half-cell is cathode, the equation takes the form

$$E_L = -E_{measured} \qquad (E_R = 0)$$

The standard hydrogen half-cell or Standard Hydrogen Electrode (SHE), is selected for coupling with the unknown half-cell. It consists of a platinum electrode immersed in a 1 M solution of H^+ ions maintained at 25 °C. Hydrogen gas at one atmosphere enters the glass hood and bubbles over the platinum electrode. The hydrogen gas at the platinum electrode passes into solution, forming H^+ ions and electrons.

The emf of the standard hydrogen electrode is arbitrarily assigned the value of zero volts. So, SHE can be used as a standard for other electrodes.
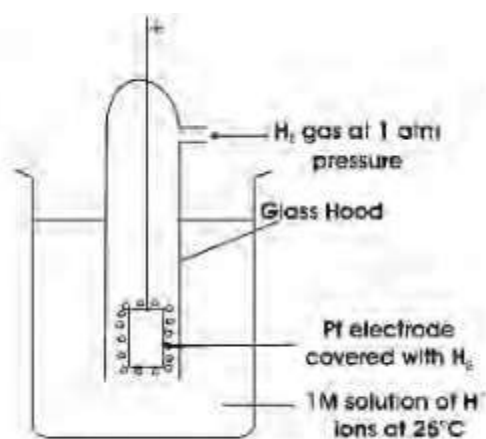
Fig.   ' The standard hydrogen electrode

The half-cell whose potential is desired, is combined with the hydrogen electrode and the emf of the complete cell determined with a voltmeter. The emf of the cell is the emf of the half-cell.

For example, it is desired to determine the emf of the zinc electrode, $Zn \mid Zn^{2+}$. It is connected with the SHE. The complete electrochemical cell may be represented as :

$$Zn \mid Zn^{2+} \parallel H^+ \mid H_2 \text{ (1 atm), Pt}$$
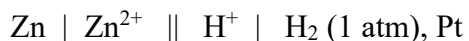
The emf of the cell has been found to be -0.76 V which is the emf the zinc half-cell. Similarly, the emf of the copper electrode, $Cu^{2+} \mid Cu$ can be determined by pairing it with the SHE when the electrochemical cell can be represented as :

Pt, H_2 (1 atm) | H_+ || Cu^{2+} | Cu

The emf of this cell has been determined to be 0.34 V which is the emf of the copper half-cell.

$$E^o_{cell} = E^o_{Cu/Cu^{2+}} - E^0_{SHE}$$

$$=0.34 - Zero$$

$$=0.34 \text{ V}$$

The two situations are explained as follows :

When it is placed on the right-hand side of the zinc electrode, the hydrogen electrode reaction is

$$2H^+ + 2e^- \ ---->\ H_2$$
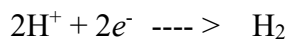
The electrons flow to the SHE and it acts as the cathode.

When the SHE is placed on the left hand side, the electrode reaction is

$$H_2 \ -- -- --> 2H^+ + 2e^-$$
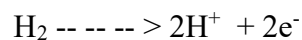
The electrons flow to the copper electrode and the hydrogen electrode

as the anode. Evidently, the SHE can act both as anode and cathode and, therefore can be used to determine the emf of any other half-cell electrode (or single electrode).

According to IUPAC convention, the standard reduction potentials alone are the standard potentials. The values of the standard potentials at 25°C (298 K) for some common Reduction Half-reactions are listed in Table below which is known as Electrochemical series.

Standard Reduction Potentials at 25ºC (298K)

Electrochemical Series

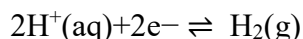| Electrode	Electrode Reaction	Electrode Potential ($E°/V$)
Li	$Li^+ + e^- \longrightarrow Li$	-3.05
K	$K^+ + e^- \longrightarrow K$	-2.93
Ba	$Ba^{2+} + 2e^- \longrightarrow Ba$	-2.90
Sr	$Sr^{2+} + 2e^- \longrightarrow Sr$	-2.89
Ca	$Ca^{2+} + 2e^- \longrightarrow Ca$	-2.87
Na	$Na^+ + e^- \longrightarrow Na$	-2.71
Mg	$Mg^{2+} + 2e^- \longrightarrow Mg$	-2.37
Al	$Al^{3+} + 3e^- \longrightarrow Al$	-1.66
Mn	$Mn^{2+} + 2e^- \longrightarrow Mn$	-1.18
Zn	$Zn^{2+} + 2e^- \longrightarrow Zn$	-0.76
Cr	$Cr^{3+} + 3e^- \longrightarrow Cr$	-0.74
Fe	$Fe^{2+} + 2e^- \longrightarrow Fe$	-0.44
Cd	$Cd^{2+} + 2e^- \longrightarrow Cd$	-0.40
Co	$Co^{2+} + 2e^- \longrightarrow Co$	-0.27
Ni	$Ni^{2+} + 2e^- \longrightarrow Ni$	-0.25
Sn	$Sn^{2+} + 2e^- \longrightarrow Sn$	-0.14
Pb	$Pb^{2+} + 2e^- \longrightarrow Pb$	-0.12
H_2	$2H^+ + 2e^- \longrightarrow H_2$	0.00
Cu	$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.34
I_2	$I_2 + 2e^- \longrightarrow 2I^-$	+0.54
Hg	$Hg^{2+} + 2e^- \longrightarrow Hg$	+0.89
Ag	$Ag^+ + e^- \longrightarrow Ag$	+0.80
Br_2	$Br_2 + 2e^- \longrightarrow 2Br^-$	+1.08
Pt	$Pt^{2+} + 2e^- \longrightarrow Pt$	+1.20
Cl_2	$Cl_2 + 2e^- \longrightarrow 2Cl^-$	+1.36
Au	$Au^{3+} + 3e^- \longrightarrow Au$	+1.50
F	$F_2 + 2e^- \longrightarrow 2F^-$	+2.87

Increasing Reduction Potential

Reference Electrodes

It should be clear by now that at least two electrodes are necessary to make a potential measurement. In potentiometry, those two electrodes are generally called the *indicator* electrode and the *reference* electrode. The indicator electrode possesses some characteristic that allows it to selectively respond to changes in the activity of the analyte being measured. For the measured potential to have meaning in this context, the reference electrode must be constructed so that its composition is fixed and its response is stable over time, with observed changes in measured potential due solely to changes in analyte concentration.

The standard reduction potential, or E^0, allows to predict the ease with which a half-cell reaction occurs relative to other half-reactions. Values of E^0 are most often reported as the potential measured in an electrochemical cell for which the *standard hydrogen electrode* is used as a reference.

The *standard hydrogen electrode*, or SHE, is composed of an inert solid like platinum on which hydrogen gas is adsorbed, immersed in a solution containing hydrogen ions at unit activity. The half-cell reaction for the SHE is given by

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$$

and the half-cell potential arbitrarily assigned a value of zero ($E^0 = 0.000$ V).

Practical application of the SHE is limited by the difficulty in preparing and maintaining the electrode, primarily due to the requirement for H_2 (g) in the half-cell. Most potentiometric methods employ one of two other common reference half-cells – the *saturated calomel electrode* (SCE) or the *silver-silver chloride electrode* (Ag/AgCl).

1. Saturated Calomel Electrode (SCE)

The SCE is a half cell composed of *mercurous chloride (Hg_2Cl_2, calomel)* in contact with a mercury pool. These components are either layered under a saturated solution of potassium chloride (KCl) or within a fritted compartment surrounded by the saturated KCl solution (called

a double-junction arrangement). A platinum wire is generally used to allow contact to the external circuit. The half reaction is described by

$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-(sat'd)$$
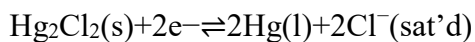
with an E^0 value of +0.244 V. A common arrangement for the SCE is shown below, left side. In this arrangement, a paste is prepared of the calomel and solution that is saturated with KCl.
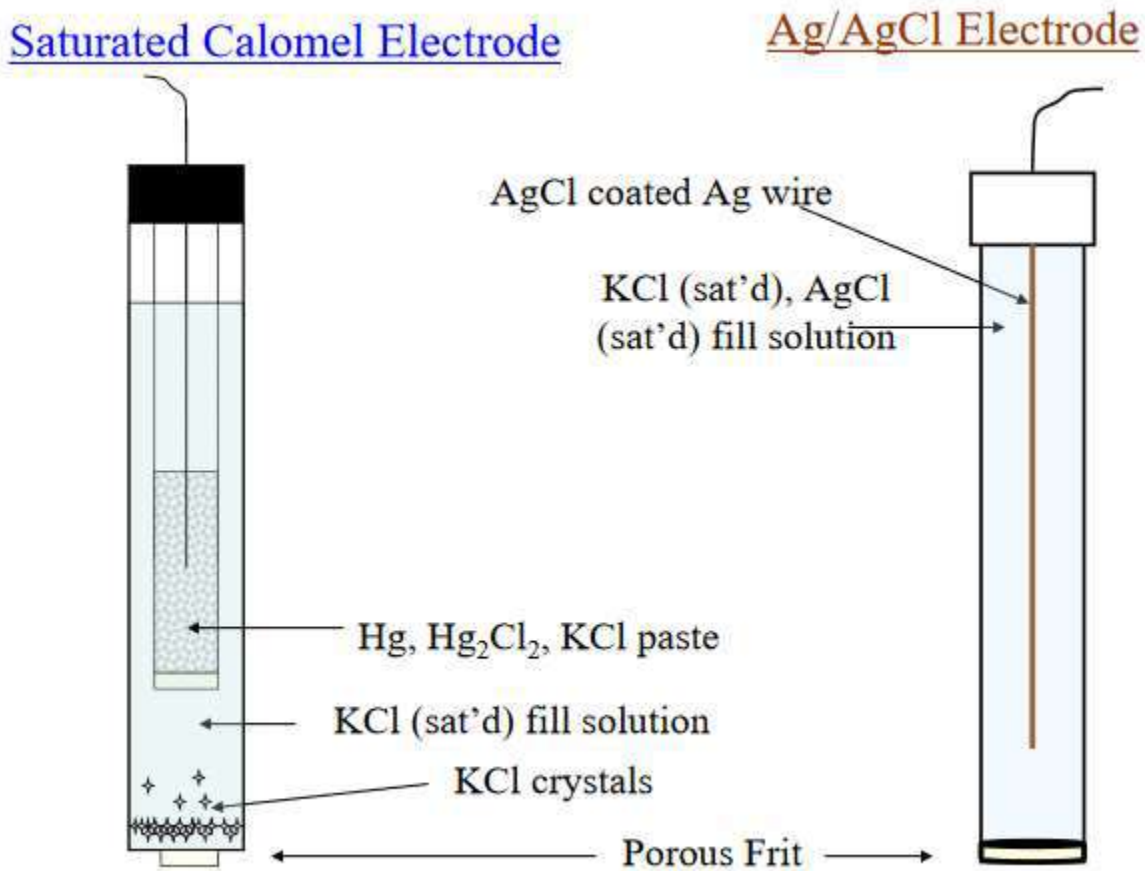
The solution over the paste is also saturated with KCl, with some solid KCl crystals present. Contact to the measurement cell is made through a porous glass frit or fiber which allows the movement of ions, but not the bulk solution. In many electrodes designed for potentiometry, the reference half cell is contained within the body of the sensing electrode. This arrangement is referred to as a "combination" electrode.

2. Silver/Silver Chloride (Ag/AgCl)

The silver/silver chloride reference electrode is composed of a silver wire, sometimes coated with a layer of solid silver chloride, immersed in a solution that is saturated with potassium chloride and silver chloride. The pertinent half reaction is

$$AgCl(s)+e- \Leftrightarrow Ag(s)+Cl^- (sat'd)$$

with a value for E^0 of +0.222 V. The actual potential of the half-cell prepared in this way is +0.197 V vs SHE, which arises because in addition to KCl, AgCl also contributes to the chloride activity, which is not exactly unity. A schematic of the Ag/AgCl reference electrode is shown at right in the previous figure.

Both the SCE and the Ag/AgCl reference electrodes offer stable half-cell potentials that do not change over time or with temperature. In addition, the loss of electrolyte to evaporation does not change the saturated nature of the solution, nor the potential. One must be aware that the contact junctions of the half cells by nature slowly leak fill solution into the external solution in which they are found. As such, there are instances where measurements of certain ions, like chloride, might be affected by the ions introduced to the measurement solution by leakage. The doublejunction design prevents this problem by placing a second solution between the reference half cell and the measurement solution.

Predicting Cell EMF

The standard emf E°, of a cell is the standard reduction potential of right-hand electrode (cathode) minus the standard reduction potential of the left-hand electrode (anode). That is,

$$E^o_{cell} = E^o_{right} - E^o_{left}$$

$$= Cathode\ potential - Anode\ potential$$

Let us predict the emf of the cell

$$Zn_{(s)}\ |\ Zn^{2+}_{(aq)}\ ||\ Ag^+_{(aq)}\ |\ Ag$$
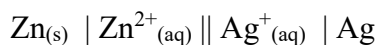
by using the Eo values from the table.

$E^\circ_{cell} = E^\circ_R - E^\circ_L = 0.80 - (- 0.763)$

$$= 0.80 + 0.763 = 1.563 \text{ V}$$

Predicting Feasibility of Reaction

The feasibility of a redox reaction can be predicted with the help of the electrochemical series. The net emf of the cell reaction, E_{cell}, can be calculated from the expression

$E^\circ \text{ cell} = E^\circ_{cathode} - E^\circ_{anode}$

In general, if $E^\circ cell = +$ ve, the reaction is feasible. If E° cell $= $ -ve, the reaction is not feasible.

Example 1 : Predict whether the reaction

$$2Ag_{(s)} + Zn^{2+}_{(aq)} \longrightarrow 2Ag^+_{(aq)} + Zn_{(s)}$$

is feasible or not.

Solution : The cell half reactions are

Anode : $2Ag_{(s)} \longrightarrow 2Ag^+_{(aq)} + 2e^-$ $E^\circ = 0.80$ V

Cathode : $Zn^{2+}_{(aq)} + 2e^- \longrightarrow Zn_{(s)}$ $E^\circ = -0.763$ V

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$E^\circ_{cell} = -0.763 \text{ V} - 0.80 \text{ V}$$

$$= -1.563 \text{ V}$$

Since E°_{cell} is negative, the given reaction is not feasible.

Example 2 : Determine the feasibility of the reaction

$$2Al_{(s)} + 3Sn^{4+}_{(aq)} \longrightarrow 2Al^{3+} + 3Sn^{2+}_{(aq)}$$

Solution : The given reaction consists of the following half reactions

Anode : $2Al_{(g)} \longrightarrow 2Al^{3+} + 6e^-$

Cathode : $3Sn^{4+} + 6e^- \longrightarrow 3Sn^{2+}$ $E^\circ = -1.66$ V
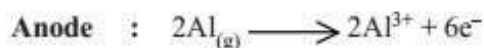
$$E^\circ_{cell} = 0.15 - (- 1.66)$$ $E^\circ = + 0.15$ V

$$= 1.81 \text{ V}$$

Since E°_{cell} is positive, the reaction is feasible.

Galvanic Cell

A galvanic cell is an important electrochemical cell. It is named after Luigi Galvani an Italian physicist. It is also called Voltaic cell, after an Italian physicist, Alessandro Volta. A galvanic cell generally consists of two different metal rods called electrodes. Each electrode is immersed in a solution containing its own ions and these form a half cell. Each half cell is connected by a salt bridge, or separated by a porous membrane. The solutions in which the electrodes are immersed are called electrolytes.

The chemical reaction that takes place in a galvanic cell is the redox reaction. One electrode acts as anode in which oxidation takes place and the other acts as the cathode in which reduction takes place. The best example of a galvanic cell is the Daniell cell.

Daniell cell

The Daniell cell was invented by a British chemist, John Frederic Daniell. In the Daniell cell, copper and zinc electrodes are immersed in a solution of copper (II) sulfate ($CuSO_4$ (aq)) and zinc (II) sulfate ($ZnSO_4$ (aq)) respectively. The two half cells are connected through a salt bridge. Here zinc acts as anode and copper acts as cathode.
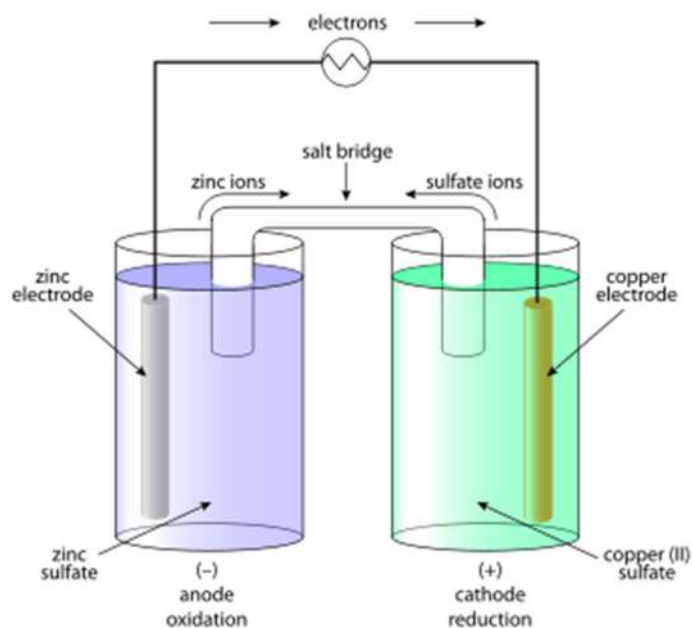
At the anode, zinc undergoes oxidation to form zinc ions and electrons. The zinc ions pass into the solution. If the two electrodes are connected using an external wire, the electrons produced by the oxidation of zinc travel through the wire and enter into the copper cathode, where they reduce the copper ions present in the solution and form copper atoms that are deposited on the cathode.
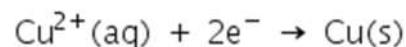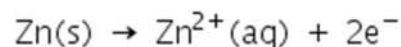
The anodic reaction is represented as:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$
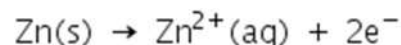
The cathodic reaction is represented as:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$
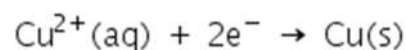
Total cell reaction is the sum of the two half cell reactions:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

- - - - - - - - - - - - - - - - - -
$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$
- - - - - - - - - - - - - - - - - -

Charge Transport within the Cell

For the cell to operate, not only must there be an external electrical circuit between the two electrodes, but the two electrolytes (the solutions) must be in contact. The need for this can be understood by considering what would happen if the two solutions were physically separated. Positive charge (in the form of Zn^{2+}) is added to the electrolyte in the left compartment, and removed (as Cu^{2+}) from the right side, causing the solution in contact with the zinc to acquire a net positive charge, while a net negative charge would build up in the solution on the copper side of the cell. These violations of *electroneutrality* would make it more difficult (require more work) to introduce additional Zn^{2+} ions into the positively-charged electrolyte or for electrons to flow into right compartment where they are needed to reduce the Cu^{2+} ions, thus effectively stopping the reaction after only a chemically insignificant amount has taken place.
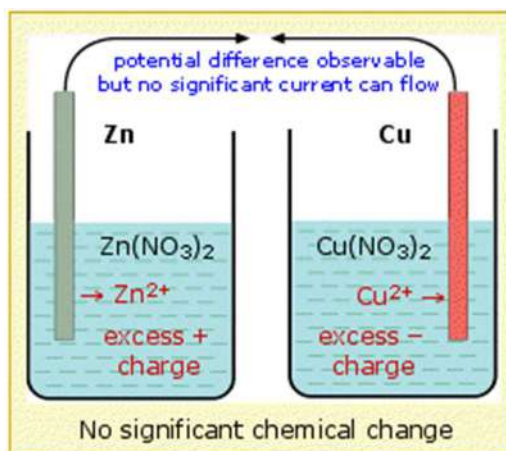
In order to sustain the cell reaction, the charge carried by the electrons through the external circuit must be accompanied by a compensating transport of ions between the two cells. This means that we must provide a path for ions to move directly from one cell to the other. This ionic transport involves not only the electroactive species Cu^{2+} and Zn^{2+}, but also the *counterions*, which in this example are nitrate, NO_3^-. Thus an excess of Cu^{2+} in the left compartment could be alleviated by the drift of these ions into the right side, or equally well by diffusion of nitrate ions to the left. More detailed studies reveal that both processes occur, and that the relative amounts of charge carried through the solution by positive and negative ions depends on their relative *mobilities*, which express the velocity with which the ions are able to make their way through the solution. Since negative ions tend to be larger than positive ions, the latter tend to have higher mobilities and carry the larger fraction of charge.

In the simplest cells, the barrier between the two solutions can be a porous membrane, but for precise measurements, a more complicated arrangement, known as a *salt bridge*, is used. The salt bridge consists of an intermediate compartment filled with a concentrated solution of KCl and fitted with porous barriers at each end. The purpose of the salt bridge is to minimize the natural potential difference, known as the *junction potential*, that develops when any two phases are in contact. This potential difference would combine with the two half-cell potentials so as introduce a degree of uncertainty into any measurement of the cell potential. With the salt bridge, we have two liquid junction potentials instead of one, but they tend to cancel each other out.

What is a Salt Bridge?

The salt bridge is usually an inverted U-tube filled with a concentrated solution of an inert electrolyte. The inert electrolyte is neither involved in any chemical change, nor does it react with the solutions in the two half cells. Generally salts like, KCl, KNO_3, NH_4NO_3 are used as the electrolyte.

How is a Salt Bridge made?

To prepare salt bridge, agar-agar or gelatin is mixed with a hot concentrated solution of electrolyte and is filled in the U-tube. On cooling, the solution sets in the form of a gel inside the U-tube and thus prevents the inter mixing of the fluids. The two ends of the U-tube are then plugged with cotton wool to minimise diffusion.

Significance of Salt Bridge

- Its main function is to prevent the potential difference that arise between the two solutions when they are in contact with each other. This potential difference is called the liquid junction potential.
- It completes the electrical circuit by connecting the electrolytes in the two half cells.
- It prevents the diffusion of solutions from one half cell to the other.
- It maintains the electrical neutrality of the solutions in the two half cells.

How is the electrical neutrality of the solutions in the two half cells maintained using a salt bridge?

In the anodic half cell, there will be accumulation of positive charge when the positive ions that are formed pass into the solution. To maintain the electrical neutrality, salt bridge provides negative ions.

For example, in Daniell cell, zinc oxidizes at the anode and passes into the solutions as Zn^{2+} ions, so there will be accumulation of positive charge in the solution. To maintain the electrical neutrality of the solution, the salt bridge provides negative ions (may be NO_{3^-} or Cl^-).
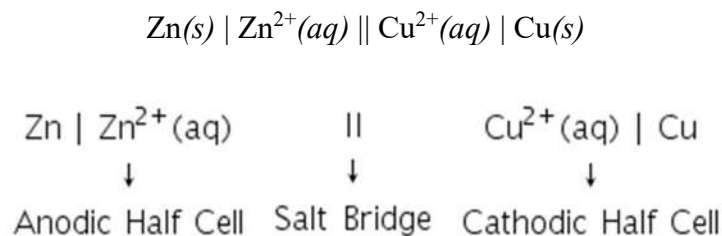
In the cathodic half cell, there will be accumulation of negative ions formed due to the reduction of positive ions. To maintain the electrical neutrality, salt bridge provides postive ions.

For example, in Daniell cell, Cu^{2+} ions from the $CuSO_4$ solution is reduced by the electron formed by the oxidation of zinc, and deposited on the copper cathode. As a result, the concentration Cu^{2+} ions decreases in the solution and that of SO_4^{2-} ions (sulphate ions) increases. So there will be an accumulation of negatively charged sulphate ions around the cathode. To maintain the electrical neutrality, salt bridge provides positive ions (may be, K^+ or NH_4+).

Cell description conventions

In order to make it easier to describe a given electrochemical cell, a special symbolic notation has been adopted. In this notation the cell we described above would be

$$Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$$

$$Zn \mid Zn^{2+}(aq) \qquad \parallel \qquad Cu^{2+}(aq) \mid Cu$$

$$\downarrow \qquad\qquad \downarrow \qquad\qquad \downarrow$$

Anodic Half Cell   Salt Bridge   Cathodic Half Cell

There are several other conventions relating to cell notation and nomenclature that you are expected to know:

- The **anode** is where oxidation occurs, and the **cathode** is the site of reduction. In an actual cell, the identity of the electrodes depends on the direction in which the net cell reaction is occurring.

- If electrons flow from the left electrode to the right electrode (as depicted in the above cell notation) when the cell operates in its spontaneous direction, the potential of the right electrode will be higher than that of the left, and the cell potential will be positive.

- "Conventional current flow" is from positive to negative, which is opposite to the direction of the electron flow. This means that if the electrons are flowing from the left electrode to the right, a galvanometer placed in the external circuit would indicate a current flow from right to left.

Nernst Equation

Electrochemistry deals with cell potential as well as energy of chemical reactions. The energy of a chemical system drives the charges to move, and the driving force give rise to the cell potential of a system called galvanic cell. The energy aspect is also related to the chemical equilibrium. All these relationships are tied together in the concept of **Nearnst equation**.

Walther H. Nernst (1864-1941) received the Nobel prize in 1920 "**in recognition of his work in thermochemistry**". His contribution to chemical thermodynamics led to the well known equation correlating chemical energy and the electric potential of a galvanic cell or battery.

Electric Work and Gibb's Free Energy

Energy takes many forms: mechanical work (potential and kinetic energy), heat, radiation (photons), chemical energy, nuclear energy (mass), and electric energy. A summary is given regarding the evaluation of electric energy, as this is related to electrochemistry.

Electric Work

Energy drives all changes including chemical reactions. In a redox reaction, the energy released in a reaction due to movement of charged particles give rise to a **potential difference**. The maximum potential differenc is called the **electromotive force,** (EMF), E and the maximum electric work W is the product of charge q in Coulomb (C), and the potential $\Box E$ in Volt (= J / C) or EMF.

$W = q \ \Box E$ C J/C (units)

Note that the EMF ΔE is determined by the nature of the reactants and electrolytes, not by the size of the cell or amounts of material in it. The amount of reactants is proportional to the charge and available energy of the galvanic cell.

Gibb's Free Energy

The **Gibb's free energy** ΔG is the negative value of maximum electric work,

$$\Delta G = -W$$
$$= -q \, \Delta E$$

A redox reaction equation represents definite amounts of reactants in the formation of also definite amounts of products. The number (n) of electrons in such a reaction equation, is related to the amount of charge trnasferred when the reaction is completed. Since each mole of electron has a charge of 96485 C (known as the Faraday's constant, F),
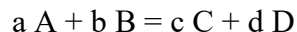
$$q = n \, F$$

and,

$$\Delta G = -n \, F \, \Delta E$$

At standard conditions,

$$\Delta G° = -n \, F \, \Delta E°$$

The General Nernst Equation

The general Nernst equation correlates the Gibb's Free Energy ΔG and the EMF of a chemical system known as the galvanic cell. For the reaction

$$a \, A + b \, B = c \, C + d \, D$$

and

$$Q = \frac{[C]^c \, [D]^d}{[A]^a \, [B]^b}$$

It has been shown that

$$\Delta G = \Delta G° + R\,T \ln Q$$

and

$$\Delta G = -\,n\,F\Delta E.$$

Therefore

$$-\,n\,F\,\Delta E = -\,n\,F\,\Delta E° + R\,T \ln Q$$

where *R, T, Q* and *F* are the gas constant (8.314 J mol^{-1} K^{-1}), temperature (in K), reaction quotient, and Faraday constant (96485 C) respectively. Thus, we have

$$\Delta E = \Delta E° - \frac{R\,T}{n\,F} \ln \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

This is known as the **Nernst equation**. The equation allows us to calculate the cell potential of any galvanic cell for any concentrations. Some examples are given in the next section to illustrate its application.

It is interesting to note the relationship between equilibrium and the Gibb's free energy at this point. When a system is at **equilibrium**, $\Delta E = 0$, and $Q_{eq} = K$. Therefore, we have,

$$\Delta E° = \frac{R\,T}{n\,F} \ln \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}, \quad \text{(for equilibrium concentrations)}$$

Thus, the equilibrium constant and $\Delta E°$ are related.

The Nernst Equation at 298 K

At any specific temperature, the Nernst equation derived above can be reduced into a simple form. For example, at the standard condition of 298 K (25°), the Nernst equation becomes

$$\Delta E = \Delta E° - \frac{0.0592\ \text{V}}{} \log \frac{[C]^c\,[D]^d}{}$$

$$\frac{n}{} \qquad [A]^a \, [B]^b$$

Please note that log is the logrithm function based 10, and ln, the natural logrithm function.

Determination of the emf of a cell : The Nernst Equation

Nernst equation relates the equilibrium potential of an half cell with the standard electrode potential, temperature, activity and reaction quotients of the reacting species. It is named after the German physical chemist Walther Nernst.

$$M^{n+} + ne^- \rightarrow Mn(s)$$

Nernst showed that for the electrode reaction; , the electrode potential at any concentration measured with respect to SHE can be represented as:

$$E_{(M^{n+}|M)} = E^0{}_{(M^{n+}|M)} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

Where, $E_{(M^{n+}|M)}$ is the electrode potential of the half cell, $E^0{}_{(M^{n+}|M)}$ is the standard electrode potential, $[M]$ is the concentration of the metal, $[M^{n+}]$ is the concentration of the metal ion, R is the universal gas constant (8.314 J/K/mole), T is the temperature in kelvin, n is the number of electron involved in the reaction, and F is the Faradays constant (96500 C/mole).

But the concentration of the solid M is taken as unity and substituting the values of R, F and T=298 K (Room Temperature), the above equation reduces to:

$$E_{cell} = E^0{}_{cell} - \frac{0.059}{n} \log \frac{1}{[M^{n+}]}$$

Calculation of emf of Daniell Cell

In Daniell cell, the electrode potentials of the half cells are written as:

$$E_{(Cu^{2+}|Cu)} = E^0_{(Cu^{2+}|Cu)} - \frac{RT}{nF}\ln\frac{1}{[Cu^{2+}]}$$

$$E_{(Zn^{2+}|Zn)} = E^0_{(Zn^{2+}|Zn)} - \frac{RT}{nF}\ln\frac{1}{[Zn^{2+}]}$$

$$E_{cell} = E_{(Cu^{2+}|Cu)} - E_{(Zn^{2+}|Zn)}$$

$$E_{cell} = E^0_{(Cu^{2+}|Cu)} - \frac{RT}{nF}\ln\frac{1}{[Cu^{2+}]} - E^0_{(Zn^{2+}|Zn)} - \frac{RT}{nF}\ln\frac{1}{[Zn^{2+}]}$$

$$= \{E^0_{(Cu^{2+}|Cu)} - E^0_{(Zn^{2+}|Zn)}\} - \frac{RT}{nF}\{\ln\frac{1}{[Cu^{2+}]} - \ln\frac{1}{[Zn^{2+}]}\}$$

$$E_{cell} = E^0_{cell} - \frac{RT}{nF}\ln\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

At 298 K, $E_{cell} = E^0_{cell} - \frac{0.059}{2}\ln\frac{[Zn^{2+}]}{[Cu^{2+}]}$

So Nernst equation is generally represented as:

$$E_{cell} = E^0_{cell} - \frac{Rt}{nF}\ln\frac{a_{Red}}{a_{Ox}}$$

Where, a_{Red} is the activity (Concentration) of reduced species, and a_{Ox} is the activity (Concentration) of oxidised species.

So the electrode potential of an electrochemical depends on the standard electrode potential, temperature, no. of electrons involved in the chemical reaction and the concentration of the reacting species.

Learning Outcomes

- Students understand the terms, electrochemical cell, electrolytic cell, Daniell cell, salt bridge, EMF.
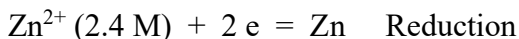
- Students acquire the skill to construct a Daniell cell.

- Students understand the significance of salt bridge.

- Students acquire the skill to calculate the electrode potential of a half cell and full cell using the Nernst equation.

- Students acquire the skill to measure the EMF of a cell by viewing animation & simulator.

- Students understand how the electrode potential of a given cell varies with the concentration of electrolytes in the anodic and cathodic half cell.

Example 1

Calculate the EMF of the cell

$Zn(s) \mid Zn^{2+}$ (0.024 M) $\parallel Zn^{2+}$ (2.4 M) $\mid Zn(s)$

Solution

Zn^{2+} (2.4 M) $+ 2$ e $=$ Zn   Reduction

Zn $=$ Zn^{2+} (0.024 M) $+ 2$ e   Oxidation

Zn^{2+} (2.4 M) $=$ Zn^{2+} (0.024 M), $\square E° = 0.00$ - - Net reaction

Using the Nernst equation:

$$\square E = 0.00 - \frac{0.0592}{2} \log \frac{(0.024)}{(2.4)}$$
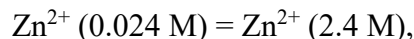
$$= (-0.296)(-2.0)$$

$$= 0.0592 \text{ V}$$

Discussion

Understandably, the Zn^{2+} ions try to move from the concentrated half cell to a dilute solution. That driving force gives rise to 0.0592 V. From here, you can also calculate the energy of dilution.

If you write the equation in the reverse direction,

$$Zn^{2+} (0.024 \text{ M}) = Zn^{2+} (2.4 \text{ M}),$$

its voltage will be -0.0592 V. At equilibrium concentrations in the two half cells will have to be equal, in which case the voltage will be zero.
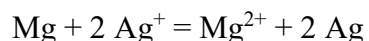
Example 2

Show that the voltage of an electric cell is unaffected by multiplying the reaction equation by a positive number.
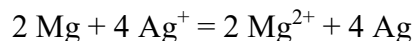
Solution

Assume that you have the cell

$$Mg \mid Mg^{2+} \parallel Ag^{+} \mid Ag$$
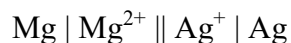
and the reaction is:

$$Mg + 2\ Ag^{+} = Mg^{2+} + 2\ Ag$$

Using the Nernst equation

$$\Box E = \Box E^{\circ} - \frac{0.0592}{2} \log \frac{[Mg^{2+}]}{[Ag^{+}]^{2}}$$

If you multiply the equation of reaction by 2, you will have

$$2\ Mg + 4\ Ag^{+} = 2\ Mg^{2+} + 4\ Ag$$

Note that there are 4 electrons involved in this equation, and $n = 4$ in the Nernst equation:

$$\Box E = \Box E^{\circ} - \frac{0.0592}{} \log \frac{[Mg^{2+}]^{2}}{}$$

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$$\frac{4 \quad [Ag^+]^4}{}$$
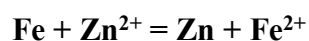
which can be simplified as

$$\Box E = \Box E° - \frac{0.0592}{2} \log \frac{[Mg^{2+}]}{[Ag^+]^2}$$

Thus, the cell potential $\Box E$ is not affected.

Example 3

The standard cell potential d$E°$ for the reaction

$$Fe + Zn^{2+} = Zn + Fe^{2+}$$

is -0.353 V. If a piece of iron is placed in a 1 M Zn^{2+} solution, what is the equilibrium concentration of Fe^{2+}?

Solution

The equilibrium constant K may be calculated using

$$K = 10^{(n \Box E°)/0.0592}$$
$$= 10^{-11.93}$$
$$= 1.2 \times 10^{-12}$$
$$= [Fe^{2+}]/[Zn^{2+}].$$

Since $[Zn^{2+}] = 1$ M, it is evident that

$$[Fe^{2+}] = 1.2E\text{-}12 \text{ M}.$$

Example 4

From the standard cell potentials, calculate the solubility product for the following reaction:

$$AgCl = Ag^+ + Cl^-$$
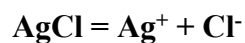
Solution

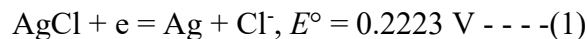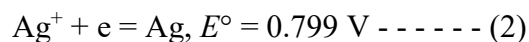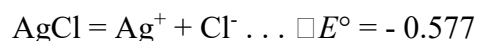There are Ag⁺ and AgCl involved in the reaction, and from the table of standard reduction potentials, you will find:

$$AgCl + e = Ag + Cl^-, E° = 0.2223 \text{ V} ----(1)$$

Since this equation does not contain the species Ag⁺, you need,

$$Ag^+ + e = Ag, E° = 0.799 \text{ V} ------(2)$$

Subtracting (2) from (1) leads to,

$$AgCl = Ag^+ + Cl^- \ldots \Box E° = -0.577$$

Let K_{sp} be the solubility product, and employ the Nernst equation,

$$\log K_{sp} = (-0.577) / (0.0592) = -9.75$$
$$K_{sp} = 10^{-9.75} = 1.8\text{x}10^{-10}$$

This is the value that you have been using in past tutorials. Now, you know that K_{sp} is not always measured from its solubility.

Confidence Building Questions

- **In the lead storage battery,**

  Pb | PbSO₄ | H₂SO₄ | PbSO₄, PbO₂ | Pb
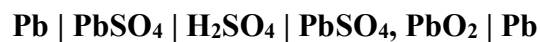
  would the voltage change if you changed the concentration of H₂SO₄? (yes/no)

  Answer ... Yes!
  Hint...
  The net cell reaction is

  $$Pb + PbO_2 + 2 \text{ } HSO_4^- + 2 \text{ } H^+ \Box \text{ } 2 \text{ } PbSO_4 + 2 \text{ } H_2O$$

and the Nernst equation

$$\Box E = \Box E° - (0.0592/2)\log\{1/\{[HSO_4^-]^2[H^+]^2\}\}.$$

- **Choose the correct Nernst equation for the cell**

    Zn(s) | Zn^{2+} || Cu^{2+} | Cu(s).

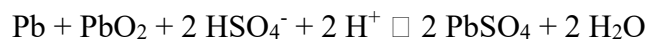   A. $\Box E = \Box E° - 0.0296 \log([Zn^{2+}] / [Cu^{2+}])$
    B. $\Box E = \Box E° - 0.0296 \log([Cu^{2+}] / [Zn^{2+}])$
    C. $\Box E = \Box E° - 0.0296 \log(Zn / Cu)$
    D. $\Box E = \Box E° - 0.0296 \log(Cu / Zn)$

Answer ... A

Hint...

The cell as written has

Reduction on the Right: $Cu^{2+} + 2\ e = Cu$

oxidation on the left: $Zn = Zn^{2+} + 2\ e$

Net reaction of cell is $Zn\ (s) + Cu^{2+} = Cu\ (s) + Zn^{2+}$
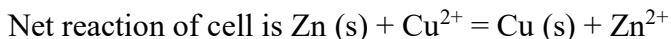
- **The standard cell potential $\Box E°$ is 1.100 V for the cell,**

    Zn(s) | Zn^{2+} || Cu^{2+} | Cu(s).

    If [Zn^{2+}] = 0.01 M, and [Cu^{2+}] = 1.0 M, what is $\Box E$ or EMF?

Answer ... 1.159 V

Hint...

A likely wrong result is 1.041 V.

The term that modifies $\Box E$ is $-(0.059/n)\log\{[Zn^{2+}]/[Cu^{2+}]\}$ (n = 2 in this case).

Understandably, if the concentration of Zn^{2+} is low, there is more tendency for the reaction,

$$Zn = Zn^{2+} + 2\ e.$$
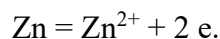
- **The logarithm of the equilibrium constant, log K, of the net cell reaction of the cell**

$$\textbf{Zn(s) | Zn}^{2+} \textbf{|| Cu}^{2+} \textbf{| Cu(s)} \ldots \square E^{\circ} = \textbf{1.100 V}$$

is

A. 1.100 / 0.0291
B. -1.10 / 0.0291
C. 0.0291 / 1.100
D. -0.0291 / 1.100
E. 1.100 / 0.0592

Answer ... A

Hint...

Use the Nernst equation in the form

$$0 = 1.100 - 0.0296 \log ([Zn^{2+}] / [Cu^{2+}])$$

The Nernst equation is useful for the determination of equilibrium constants.

****

Pretest for Module
on
Chemical Kinetics

1. Which order of reaction obeys the expression $t_{1/2} \propto 1/[A]$?
   a) First   **b)** Second   c) Zero   d) Third

2. A first order reaction completes 60 % in 20 minutes. The time required for the completion of 90 % of reaction is
   a) 30 min   b) 60 min   c) 40 min   **d)** 50 min

3. The unit of zero order of reaction is
   a) $L\ mol^{-2}\ s^{-1}$ b) s^{-1}
   c) $mol\ L^{-1}\ s^{-1}$ d) $L\ mol^{-1}\ s^{-1}$

4. The half life for the acid-catalysed hydrolysis of sucrose to form glucose and fructose, which is first order overall, is 3.20 h at 25°C. What is the rate constant for the reaction at this temperature?
   a) $6.02 \times 10^{-5}\ s^{-1}$ b) $0.217\ s^{-1}$
   c) $2.61 \times 10^{-5}\ s^{-1}$ d) $0.24 \times 10^{-15}\ s^{-1}$

5. Which of the following statements about the kinetics of the reaction
   $H_2(g) + Br_2(g) \rightarrow 2HBr\ (g)$ is definitely true?
   a) The reaction is first order with respect to bromine, Br_2.
   b) The reaction is first order with respect to bromine, Br_2.
   c) The reaction is second order overall.
   d) It is not possible to predict the kinetics of the reaction from the stoichiometry.

6. The graph between ln k vs. 1/T is a straight line. The slope of the line is
   a) $-E_a/2.303\ R$ b) $-2.303R/\ E_a$ c) $2.303R/\ E_a$ d) $E_a/2.303\ R$

7. For a first order reaction when log k was plotted against 1/T Straight line with a slope of -6000 was obtained. What will the activation energy of the reaction?

   a) 27.48 kcal   b) 10.4 kcal   c) 120 Kcal   d) none of the above

8. The role of a catalyst is to change
   a) Equilibrium constant   b) Enthalpy of reaction
   c) Activation energy of reaction   d) none of the above

9. Which of the following does not affect the rate of reaction?
   a) Amount of reactant taken   b) Physical state of reactant
   c) Size of the vessel   **d)** Enthalpy of reaction

10. Activation energy of a reaction can be determined by

a) By determining the rate constant at two different temperature

b) By determining the probability of collision

c) By measuring equilibrium constant

d) none of the above

Module

Chemical Kinetics

Lecture 1

Outline of the module

This module presents some of the phenomenological concepts of chemical kinetics. It may be treated as complementary to thermodynamics for studying the chemical reactions as thermodynamics does not provide any information about the rate at which and the extent at which any reaction will occur. Thermodynamic principles tell only about the feasibility of a chemical reaction whereas chemical kinetics concerns with the measurement of rate of reactions occurring under given experimental conditions. The study of these subjects also provides valuable information about the factors which affects the rate of reaction as well as about the mechanistic aspects of the reaction. Students will learn that the time-dependence of the reactant and product concentrations during a chemical reaction can be described by differential equations known as rate law. A rate law serves to define a rate constant, which is one of the most important parameters used to describe the dynamics of chemical reaction.

Rate of reaction: Let us consider the general reaction

aA + bB→cC+ dD
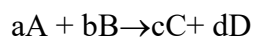
The stoichiometric coefficients a, b, c and d signify that for the disappearance of a moles of A and b moles of B at any instant, c moles of C and d moles of D will appear. **The rate may,**

therefore, be defined as the rate of disappearance of A or B per mole, which in turn, is equal to the rate of appearance of C or D per mole.

$$\text{Rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

Note that the rate of disappearance or rate of appearance of different reactants and products may be the same or different depending on the stoichiometry of the equation, but the rate of disappearance or rate of appearance per mole of any reactant or product will always be same as it represents the rate of the reaction.

As the rate of a reaction decreases gradually with the progress of the reaction, $-\frac{1}{a}\frac{d[A]}{dt}$ ....etc represent **instantaneous rate** of the reaction at time t, because these involve concentration changes over an infinitesimally short time interval, dt, but if it is written as $-\frac{1}{a}\frac{\Delta[A]}{\Delta t}$, it represent **average rate** over a finite time interval, Δt. Both average and instantaneous rate of reaction decreases with time.

The reaction rate is also proportional to the product of concentrations of the reactants, each raised to some power. Accordingly,

$$\text{Rate } \alpha \ [A]^m[B]^n$$

Or $\qquad\qquad$ $\text{Rate} = k \ [A]^m[B]^n$

Therefore, the differential rate law may have the form

$$\text{Rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt} \quad = k \ [A]^m[B]^n$$

The exponent's m and n are known as partial order of reaction with respect to A and B respectively, (m + n) represents the overall order of reaction and k is a proportionality constant called rate constant. It is defined as the rate of a reaction when the concentration of each reactant is equal to unity. Each reaction is characterized by its own rate constant Thus, rate law is the expression in which reaction rate is related with molar concentration of reactants with each term raised to some power at a fixed temperature, which may or may not be same as stoichiometric coefficient of reacting species in a balanced chemical equation. The rate law with its rate

constant and order of various reacting species must be determined from the measurement of reaction rates and cannot be deduced from reaction stoichiometry of the balanced –reaction equation.

The order of a reaction can be 0, 1, 2,3 and even a fraction. The units of k depend on the overall order of the reaction. The value of k does not depend on concentration of either reactants or product. It depends on temperature and catalyst used in the reaction. Each reaction is characterized by its own reaction rate constant

Units of rate constant

Reaction	Order	Units of rate constant
Zero order reaction	0	$mol.L^{-1}sec^{-1}$
First order reaction	1	sec^{-1}
Second order reaction	2	$mol^{-1}.L.sec^{-1}$

Example 1. The reaction

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

NO_2 is formed at the rate of 0.0072 mol/litre-second at some time (i) what is the rate of change of $[O_2]$

(ii) Calculate the rate of change of $[N_2O_5]$ at this time, and (iii) write the differential rate law for the reaction.

Example 2. In a reaction $H_2 + I_2 \rightarrow 2 HI$, The rate of disappearance of $[I_2]$ was found to be $1.0x\ 10^6$ mol/L/s, what would be the corresponding rate of appearance of HI.

**Example 3** For a reaction $2A + 3B \rightarrow C + 4D$, the following expression

$$[\ \log - \frac{d[A]}{dt}\ = \log + \frac{d[D]}{dt} + X\ ]\ \text{is valid, then find out the value of X}$$

Lecture 2

Concept of Molecularity and Order in Elementary and Complex Reactions

There are very few reactions that take place in one step. A reaction that occurs in one step is called an elementary reaction. In such an elementary reaction the total number of molecules taking part in the reaction is termed as molecularity of the reaction. When the complete reaction consists of more than one step then it is known as a complex reaction. Molecularity helps in understanding the mechanism of a reaction. In case of a complex reaction, molecularity as such has no significance. Each elementary reaction involved in the complex reaction has its own molecularity. Therefore, as such, molecularity is only a theoretical concept for a complex reaction. In a complex reaction the overall kinetics of the reaction can be determined on the basis of slowest elementary reaction. The order can change with the conditions, such as pressure, temperature, concentration etc., whereas molecularity is invariant for a chemical equation. For example – decomposition of NH_3 on tungsten is a zero order reaction whereas on hot quartz it is first order reaction. Order may or may not be equal to the molecularity but in an elementary reaction they are generally the same. Molecularity must always be an integer and can never be zero whereas order can be an integer, a fractional quantity, zero or even negative. We illustrate the above concepts through the following examples.
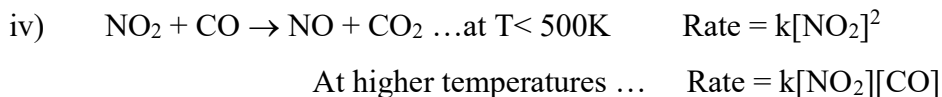
i) $2N_2O_5 \rightarrow 4NO_2 + O_2$ ………   Rate $= k[N_2O_5]$
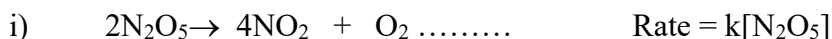
This is an example of a bimolecular reaction but the kinetics of the reaction is first order.

ii) $H_2 + I_2 \rightarrow 2HI$ …….   Rate $= k[H_2][I_2]$

Example of a second order reaction.

iii) $2SO_2 + O_2 \xrightarrow{NO} 2SO_3$ …..   Rate $= k[NO]^2[O_2]$
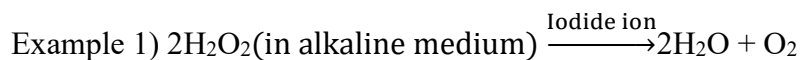
The above reaction is an example of a third order reaction. In this reaction the rate does not depend on the concentration of the main substrate, that is, SO_2.

iv) $NO_2 + CO \rightarrow NO + CO_2$ …at T< 500K   Rate $= k[NO_2]^2$

At higher temperatures …   Rate $= k[NO_2][CO]$

Solved problems

Example 1) $2H_2O_2$(in alkaline medium) $\xrightarrow{\text{Iodide ion}}$ $2H_2O + O_2$

Show the mechanism that leads to rate $= k[H_2O_2][I^-]$.

Solution

Experimental evidence suggests that this reaction takes place in following two steps.

   i) $H_2O_2 + I^- \rightarrow H_2O + IO^-$

    ii) $H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$

The first step is slow and therefore the rate determining step.

Integrated Rate Law

Differential rate law equations involve infinitesimally small quantities like d[A], d[B], dt etc. These cannot be measured practically. Hence, the differential rate law equations are integrated to obtain equations involving measurable quantities, so that the rate of the reaction, rate constant can be determined. Note that the rate law expression relates the rate and the concentration, while integrated rate expression relates time and concentration.

1) **Zero order reaction**: The rate of such reactions is proportional to zero power of the concentration of the reactant.

    Example: $2NH_3$ (g) $\rightarrow N_2$ (g) $+3H_2$ (g)
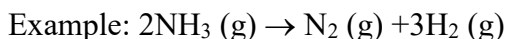
    Rate $= k[NH_3]^0 = k$

    Example: Thermal decomposition of HI on gold surface is another example of zero order reaction.

In zero order reactions the rate constant (k) is equal to the rate of reaction at all concentrations.

2) **First order reactions**: The rate of such reactions is proportional to first power of the concentration of the reactant.

    Hydrogenation of ethane is an example of first order reaction.

    C_2H_4 (g) $+ H_2$ (g) $\rightarrow C_2H_6$ (g)
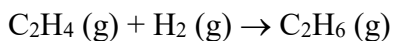
    Rate $= k[C_2H_4][H_2]^0 = k[C_2H_4]$

The rate expression is obtained by integrating the respective differential rate expression. For reactant A $\rightarrow$ Product

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]$$

On integration, the following expression is obtained, $[A] = [A]_0 \exp(-kt)$

This equation can also be written in the form

$$t = \frac{2.303}{k} \, log \, \frac{[A]_0}{[A]}$$

Slope of the linear fit to the graph between $log \, \frac{[A]_0}{[A]}$ versus time can be used to calculate the value
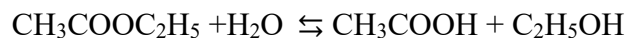
of the rate constant of the reaction.

The length of time required for half of the reactant to disappear is called the half-life of the reaction and is written as $t_{1/2}$. Equation $\ln [A]/[A]_0 = -kt$ can be used to derive a relationship between the rate constant k and half-life of the reaction. At time $t = t_{1/2}$ the concentration of A $=[A]_0/2$. On substitution of these values in above equation we have $\ln \frac{1}{2} = -kt_{1/2}$.

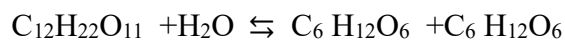$$\text{Therefore, } t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

$T_{1/2}$ of first order reaction is independent of initial concentration of reactant.

There are reactions in which more than one species is involved, but the order of the reaction is one. Such reactions are known as *pseudo-unimolecular reaction* and they involve either solvent molecule in excess or a catalyst as one of the reacting species. Examles of such type of reaction are:
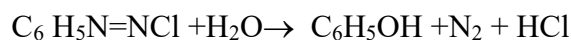
(i) Acid hydrolysis of an ester

$$H^+$$

$$CH_3COOC_2H_5 + H_2O \leftrightharpoons CH_3COOH + C_2H_5OH$$

(ii) Inversion of cane sugar H^+

$$C_{12}H_{22}O_{11} + H_2O \leftrightharpoons C_6 H_{12}O_6 + C_6 H_{12}O_6$$

cane sugar   Glucose   Fructose

(iii) Decomposition of benzene diazonium chloride

$$C_6 H_5N=NCl + H_2O \rightarrow C_6H_5OH + N_2 + HCl$$

Solved Problems

1) The reaction $N_2O_5 \rightarrow 2NO_2 + 1/2O_2$, the initial concentration of N_2O_5 was 1.24×10^{-2} mol.L^{-1} at 318K. The concentration of N_2O_5 after 60 minutes was found to be 0.20×10^{-2} mol.L^{-1}. Calculate the rate constant of the reaction.

Solution: Using $k = \frac{2.303}{t} \, log \, \frac{[A]_0}{[A]} = \frac{2.303}{60} \, log \, \frac{1.24 \times 10^{-2} \, \text{mol.L}^{-1}}{0.20 \times 10^{-2} \, \text{mol.L}^{-1}} = 0.0304 \text{min}^{-1}$

2) The rate law for the reaction described by N_2O_2 (g) $\rightarrow$ 2NO (g) is first order in the concentration of N_2O_2 (g) . Derive an expression for the time dependent behavior of [NO], the product concentration.

Solution: The rate of formation of NO is given by the rate law

$$\text{Rate} = \frac{1}{2}\frac{d[NO]}{dt} = k\,[N_2O_2]$$

Since the rate law for the disappearance of N_2O_2 is first order, so the above rate law can be rewritten as

$$\frac{d[NO]}{dt} = 2k\,[N_2O_2]_0\,e^{-kt}$$

Separating the time and concentration variables gives us

$$d[NO] = 2k\,[N_2O_2]_0\,e^{-kt}\,dt$$

Integrating [NO] from $[NO]_0 = 0$ to [NO] and time variable from 0 to t gives us

$$[NO] = 2\,[N_2O_2]_0(1- e^{-kt})$$

Example 1) The reaction $2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$ obeys the rate law, $r = k[N_2O_5]$, where $k = 0.0084\ sec^{-1}$. If 2.5 moles of N_2O_5 were taken in a 5L flask, how many moles of N_2O_4 would remain after 60 sec.

Lecture 3

2) **Second order reactions:** For the second order reactions, we have two distinct cases. In the first case, both the reactants are identical. This is shown in equation

$$A + A \rightarrow \text{Product, or}$$

$$2A \rightarrow \text{Product}$$

The rate of such reactions is proportional to second power of the concentration of the reactant.

$$\text{The rate law} \quad -\frac{d[A]}{dt} = k\,[A]^2$$

An expression for [A] can be derived by separating the concentration and time variables and then integrating the resulting expression assuming that the initial concentration of A at time t=0 and at time t is [A], we get

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

A plot of 1/[A] *vs.*t will yield a straight line of slope k and intercept $1/[A]_0$

The half-life of second order reaction can be determined by setting $t = t_{1/2}$ and $[A] = [A]_0/2$

$$t_{1/2} = 1/k[A]_0$$

Notice that the half-life of second order reaction depends on the initial concentration of the reactant. This relation is different from that found for a first-order reaction, for which the half-life is independent of concentration.

Now consider the reaction when both reactants are not identical, the reaction is

$$A + B \rightarrow Product$$
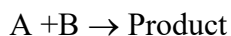
The rate of such reactions is

$$- \frac{d[A]}{dt} = \frac{d[B]}{dt} = k\,[A][B]$$

The extent of the progress of the reaction may be measured by using a variable x which measures the extent of progress of the reaction

$$x = [A]_0 - [A]_t = [B]_0 - [B]_t$$

Here $[A]_0$ and $[B]_0$ are the initial concentrations of A and B and their concentrations at time t are $[A]_t$ and $[B]_t$ respectively.
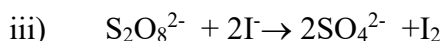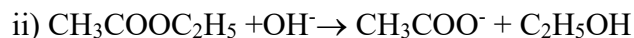
The resulting integrated rate equation may be written as

$$kt = \frac{1}{[A]_0 - [B]_0} \ln \frac{[A][B]_0}{[B][A]_0}$$

To obtain rate constant k, we need to plot the logarithm of the product in parenthesis of above equation against time. If $[A]_0 = [B]_0$ this equation is indeterminate. In this case, since $[A]_t = [B]_t$,

the equation $\qquad\qquad \frac{1}{[A]} = \frac{1}{[A]_0} + kt$; or $\frac{1}{[B]} = \frac{1}{[B]_0} + kt$ can be used to obtain k.

Example i) $NOBr\ (g) \rightarrow NO\ (g) + 1/2Br_2\ (g)$

is found to obey the rate law $r = \frac{d[NO]}{dt} = k\,[NOBr]^2$

ii) $CH_3COOC_2H_5 + OH^- \rightarrow CH_3COO^- + C_2H_5OH$

iii) $\quad S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$

Problem
The rate law for the reaction, $2Cl_2O \rightarrow 2Cl_2 + O_2$ at 200oC is found to be: rate $= k\,[Cl_2O]^2$
(a) How would the rate change if [Cl2O] is reduced to one-third of its original value?
(b) How should the [Cl2O] be changed in order to double the rate?
(c) How would the rate change if [Cl2O] is raised to threefold of its original value?

 Solution   a) Rate equation for the reaction,

$r = k [Cl_2O]^2$

Let the new rate be r'; so

$r' = k[(Cl_2 O)/3]^2 = 1/9 r$

(b) In order to have the rate $= 2r$, let the concentration of Cl_2O be x.

So $2r = kx^2$ .... (i)

We know that $r = k[Cl_2O]^2$ .... (ii)

Dividing Eq. (i) by (ii),

$2r/r = (kx^2)/(k[Cl_2O]_2)$

or $2 = x^2/[Cl_2O]_2$

or $x^2 = 2[Cl_2O]_2$

or $x = \sqrt{\sqrt{2}} [Cl_2 O]$

(d) New rate $= k[3Cl_2O]^2 = 9k[Cl_2O]^2 = 9r$

Lecture 4

As we have seen that rate law for an elementary reaction can be deduced from the reaction stoichiometry. However, for complex reactions that does not occur by a single step. One of the major goals of chemical kinetics is to determine the mechanism or sequence of elementary reactions, by which a complex reaction occurs. Here we will discuss the appropriate approximations used to derive the correct rate law for complex reaction from the proposed mechanism. Many reactions involve reaction intermediate, and overall kinetic process can be written as

$$Reactant \rightarrow intermediate \rightarrow Product$$

For Example, consider the reaction

$$NO_2 + CO \rightarrow NO + CO_2$$
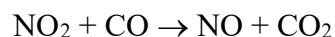
This reaction does not occur in a single step but proceeds by the following two-step process:

$$NO_2 + NO_2 \xrightarrow{k1} NO_3 + NO \qquad\qquad slow$$

$$NO_2 + CO \xrightarrow{k2} NO_2 + CO_2 \qquad\qquad \text{fast}$$
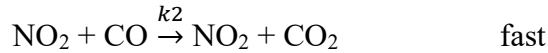
If the reaction is occurring in more than one step, then exact rate law can be derived with help of two types of approximations:

    i)   Rate limiting approximations: Rate limiting approximations used if it is known that out of two steps which step is slowest step. So for the above reaction the overall kinetics of the reaction is governed by step 1 as it is the slowest step or rate determining step. Therefore, rate law of reaction may be written as

$$r = \frac{d[NO]}{dt} = k_1\,[NO_2]^2$$

    ii)   Steady-state approximations: Steady-state approximations always applied with respect to the intermediate. Steady-state approximation assumes that rate of formation of an intermediate during the course of reaction is essentially equals to rate of its destruction so as to keep a constant concentration of intermediate throughout the reaction. We have seen that multistep reaction usually involves one or more intermediate species that do not appear in overall equation. Since these intermediates are very reactive and they do not accumulate to any *significant extent during the reaction.* *i. e. [I}<<[R] and [I}<<[P].*

Intermediate concentration [I] start from zero, rise to a maximum and then falls to zero. This concept of approximation can be used in consecutive irreversible first-order reactions.

Consider two consecutive irreversible first-order reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$
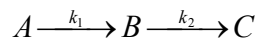
$$r_1 = k_1[A] \qquad\qquad r_2 = k_2[B]$$

$$\left(\frac{d[B]}{dt}\right)_1 = r_1 = k_1[A] \qquad\qquad \left(\frac{d[B]}{dt}\right)_2 = -r_2 = -k_2[B]$$

$$\frac{d[B]}{dt} = \left(\frac{d[B]}{dt}\right)_1 + \left(\frac{d[B]}{dt}\right)_2 = k_1[A] - k_2[B]$$

$$\left(\frac{d[A]}{dt}\right) = -k_1[A] \qquad \left(\frac{d[B]}{dt}\right) = k_1[A] - k_2[B] \qquad \left(\frac{d[C]}{dt}\right) = k_2[B]$$

Let only A be present in the system at $t = 0$

Then $[A]_0 \neq 0$; $[B]_0 = 0$ and $[C]_0 = 0$

$$d[A]/dt = -k_A[A]$$

On integration we obtain $[A] = [A]_o e^{-k_1 t}$

$$\left(\frac{d[B]}{dt}\right) = k_1 [A]_o e^{-k_1 t} - k_2 [B] \quad \text{on integration} \qquad [B] = \frac{k_1 [A]_o}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t})$$

Since, matter must be conserved therefore $[A] + [B] + [C] = [A]_o$

$$[C] = [A]_o \left(1 - \frac{k_2}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t}\right)$$

Suppose that in an industrial batch process a substance A produces the desired product B which goes to decay to a worthless product C, each stage of the reaction being first-order. At what time will product B be present in greatest concentration?

The time dependence of [B]

$$[B]_{max} = \frac{k_1 [A]_o}{k_2 - k_1}(e^{-k_1 t_{max}} - e^{-k_2 t_{max}})$$

A maximum should occur at $\dfrac{d[B]}{dt} = 0$

$$\frac{d[B]}{dt} = \frac{-k_1 [A]_o}{k_2 - k_1}(k_1 e^{-k_1 t} - k_2 e^{-k_2 t}) = 0$$

Since $[A]_o \neq 0$, $k_1 \neq 0$, hence $k_1 e^{-k_1 t} - k_2 e^{-k_2 t} = 0$

$$t_m = \frac{\ln k_2 - \ln k_1}{k_2 - k_1}$$

$$[B]_{max} = [A]_o \left(\frac{k_1}{k_2}\right)^{\frac{k_2}{k_1 - k_2}}$$

References:
1. Physical Chemistry by P. W. Atkins
2. Physical Chemistry by Ira N. Levine
3. Physical Chemistry by G. W. Castellan
4. Elements of Physical Chemistry by K. L. Kapoor

Assignment Problems

1. Which order of reaction obeys the expression $t_{1/2} \propto 1/[A]$?
   b) First   b) Second   c) Zero   d) Third

2. A first order reaction completes 60 % in 20 minutes. The time required for the completion of 90 % of reaction is
   b) 30 min   b) 60 min   c) 40 min   d) 50 min

3. Collision theory of reaction rates is most successful for
   a) All types of reactions   b) Reactions in solution
   c) Bi-molecular gaseous reactions   d) Termolecular reactions

4. Hydrolysis of ethyl acetate reaction in acidic medium follows
   a) First order kinetics   b) Second order kinetics
   c) Zero order kinetics   d) None of the above

5. What will be the unit of rate constant for n^{th} order of reaction?
   a) $(mol/L)^n \, s^{-1}$ b) $(mol/L \, s^{-1})^{n-1}$
   c) $(L \, mol^{-1} \, s^{-1})^{n-1}$ d) $(L \, mol^{-1})^{n-1} \, s^{-1}$

6. The inversion of cane sugar represented by
   a) First order kinetics   b) Second order kinetics
   c) Zero order kinetics   d) None of the above

7. Saponification of ethyl acetate follows :
   a) First order kinetics   b) Second order kinetics
   c) Zero order kinetics   d) None of the above

8. The unit of zero order of reaction is
   a) $L \, mol^{-2} \, s^{-1}$ b) s^{-1}
   c) $mol \, L^{-1} \, s^{-1}$ d) $L \, mol^{-1} \, s^{-1}$

9. The reaction rate becomes 2 times for every 10^0 C rise in temperature. How many times rate of reaction will be increased when temperature is increased from 30 to $80\ ^0$ C ?

   a)   16   b) 64   c) 32   d) 128

10. Half-life of radioactive ^{14} C is 5760 years. In how many years 200 mg of ^{14} C will be reduced to 25 mg?
    a) 17280   b) 5760   c) 23040   d) 1120

11. The half life of first order reaction $NH_2NO_2 \rightarrow N_2O + H_2O$ is 2.2 hours at 15^0 C. What will be time required for decomposition of 12.4 g of NH_2NO_2 if it was taken initially 1 mol.
    a)   4.34 hrs   b) 9.1 hrs   c) 0.7 hrs   d) 2.4 hrs

12. The half life for the acid-catalysed hydrolysis of sucrose to form glucose and fructose, which is first order overall, is 3.20 h at 25°C. What is the rate constant for the reaction at this temperature?

  a) $6.02 \times 10^{-5} \text{ s}^{-1}$ b) 0.217 s^{-1}

  c) $2.61 \times 10^{-5} \text{ s}^{-1}$ d) $0.24 \times 10^{-15} \text{ s}^{-1}$

13. Which of the following statements about the kinetics of the reaction

    $H_2(g) + Br_2(g) \rightarrow 2HBr \text{ (g)}$ is definitely true?

      a) The reaction is first order with respect to bromine, Br_2.

      b) The reaction is first order with respect to bromine, Br_2.

      c) The reaction is second order overall.

      d) **It** is not possible to predict the kinetics of the reaction from the stoichiometry.

14. The graph between ln k vs. 1/T is a straight line. The slope of the line is

      b) $-E_a/2.303 \text{ R}$ b) $-2.303R/ E_a$ c) $2.303R/ E_a$ d) $E_a/2.303 \text{ R}$

15. For the gas phase decomposition of ozone $2O_3 \rightarrow 3O_2$ the predicted order of reaction is

    a) 1   b) 1.5   c) 0   d) -1.5

16. For a first order reaction when log k was plotted against 1/T Straight line with a slope of - 6000 was obtained. What will the activation energy of the reaction?

    a) 27.48 kcal   b) 10.4 kcal   c) 120 Kcal   d) none of the above

17. The role of a catalyst is to change

  a) Equilibrium constant   b) Enthalpy of reaction

  c) Activation energy of reaction   d) none of the above

18. Which of the following does not affect the rate of reaction?

  a) Amount of reactant taken   b) Physical state of reactant

  c) Size of the vessel   d) Enthalpy of reaction

19. Activation energy of a reaction can be determined by

  a) By determining the rate constant at two different temperature

  b) By determining the probability of collision

  c) By measuring equilibrium constant

  d) none of the above

20. The given reaction $2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$ is an example of

    a) First order kinetics   b) Second order kinetics

    c) Zero order kinetics   d) Third order kinetics

Answer key
1. b
2. d
3. c
4. a
5. d
6. a
7. b
8. c
9. c
10. a
11. c
12. a
13. d
14. a
15. a
16. a
17. c
18. d
19. a
20. d