Spoon Feeding Electrochemistry

Simplified Knowledge Management Classes Bangalore

My name is Subhashish Chattopadhyay. I have been teaching for IIT-JEE, Various International Exams (such as IMO [International Mathematics Olympiad], IPhO [International Physics Olympiad], IChO [International Chemistry Olympiad]), IGCSE (IB), CBSE, I.Sc, Indian State Board exams such as WB-Board, Karnataka PU-II etc since 1989. As I write this book in 2016, it is my 25 th year of teaching. I was a Visiting Professor to BARC Mankhurd, Chembur, Mumbai, Homi Bhabha Centre for Science Education (HBCSE) Physics Olympics camp BARC Campus.

I am Life Member of …

- **IAPT (Indian Association of Physics Teachers)**
- **IPA (Indian Physics Association)**
- **AMTI (Association of Mathematics Teachers of India)**
- **National Human Rights Association**
- **Men's Rights Movement (India and International)**
- **MGTOW Movement (India and International)**

And also of

IACT (Indian Association of Chemistry Teachers)

The selection for National Camp (for Official Science Olympiads - Physics, Chemistry, Biology, Astronomy) happens in the following steps ….

1) **NSEP** (National Standard Exam in Physics) and **NSEC** (National Standard Exam in Chemistry) held around 24 rth November. Approx 35,000 students appear for these exams every year. The exam fees is Rs 100 each. Since 1998 the IIT JEE toppers have been topping these exams and they get to know their rank / performance ahead of others.

2) **INPhO** (Indian National Physics Olympiad) and **INChO** (Indian National Chemistry Olympiad). Around 300 students in each subject are allowed to take these exams. Students coming from outside cities are paid fair from the Govt of India.

3) The Top 35 students of each subject are invited at HBCSE (Homi Bhabha Center for Science Education) Mankhurd, near Chembur, BARC, Mumbai. After a 2-3 weeks camp the top 5 are selected to represent India. The flight tickets and many other expenses are taken care by Govt of India.

Since last 50 years there has been no dearth of "Good Books". Those who are interested in studies have been always doing well. This e-Book does not intend to replace any standard text book. These topics are very old and already standardized.

There are 3 kinds of Text Books

- The thin Books - Good students who want more details are not happy with these. Average students who need more examples are not happy with these. Most students who want to “Cram” quickly and pass somehow find the thin books “good” as they have to read less !!

- **The Thick Books - Most students do not like these, as they want to read as less as possible. Average students are “busy” with many other things and have no time to read all these.**

- The Average sized Books - Good students do not get all details in any one book. Most bad students do not want to read books of “this much thickness“ also !!

We know there can be no shoe that’s fits in all.

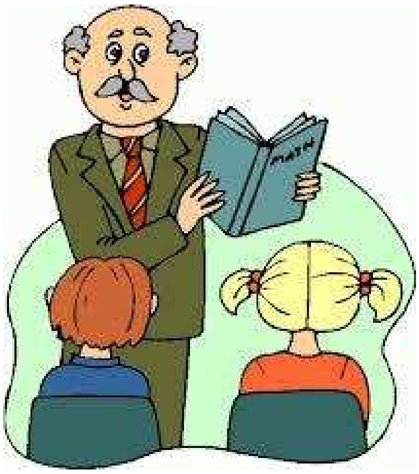
Printed books are not e-Books! Can’t be downloaded and kept in hard-disc for reading “later” ………

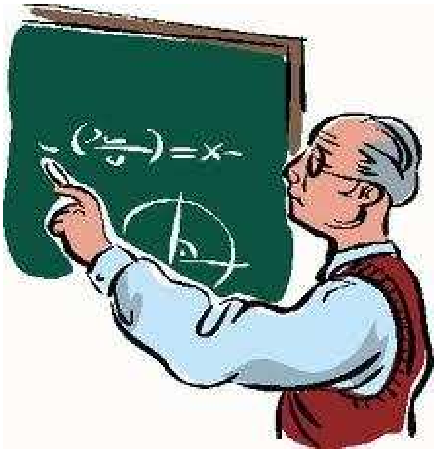
So if you read this book later, you will get all kinds of examples in a single place. This becomes a very good “Reference Material”. I sincerely wish that all find this “very useful”.

Students who do not practice lots of problems, do not do well. The rules of “doing well” had never changed …. Will never change !

In this e-Book I am trying to solve this problem. Those students who practice can learn.

No one can help those who are not studying, or practicing.





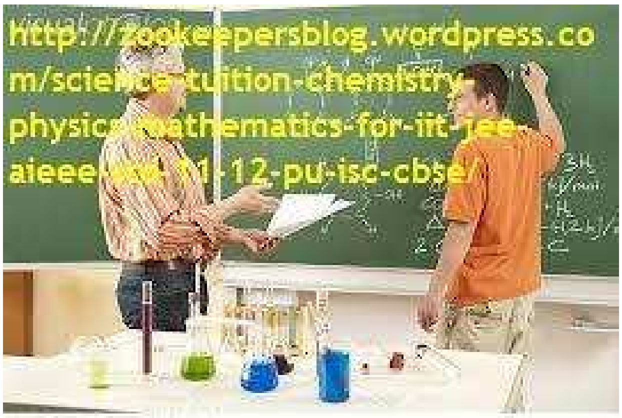
Learn more at http://skmclasses.weebly.com/iit-jee-home-tuitions-bangalore.html

Twitter - https://twitter.com/ZookeeperPhy

Facebook - https://www.facebook.com/IIT.JEE.by.Prof.Subhashish/

Blog - http://skmclasses.kinja.com

Blog - http://skmclasses.blog.com



A very polite request :

I wish these e-Books are read only by Boys and Men. Girls and Women, better read something else; learn from somewhere else.

Preface

We all know that in the species “Homo Sapiens “, males are bigger than females. The reasons are explained in standard 10, or 11 (high school) Biology texts. This shapes or size, influences all of our culture. Before we recall / understand the reasons once again, let us see some random examples of the influence

Random - 1

If there is a Road rage, then who all fight ? (generally ?). Imagine two cars driven by adult drivers. Each car has a woman of similar age as that of the Man. The cars “ touch “ or “ some issue happens”. Who all comes out and fights ? Who all are most probable to drive the cars ?

(Men are eager to fight, eager to rule, eager for war. Men want to drive. Men want to win)

Random - 2

Heavy metal music artists are all Men. Metallica, Black Sabbath, Motley Crue, Megadeth, Motorhead, AC/DC, Deep Purple, Slayer, Guns & Roses, Led Zeppelin, Aerosmith ….. the list can be in thousands. All these are grown-up Boys, known as Men.

(Men strive for perfection. Men are eager to excel. Men work hard. Men want to win.)

Random - 3

Apart from Marie Curie, only one more woman got Nobel Prize in Physics. (Maria Goeppert Mayer - 1963). So, … almost all are men.

(Men want to excel. Men strive for perfection. Men want to win. Men work hard. Men do better than women.)

Random - 4

The best Tabla Players are all Men.

(Men want to excel. Men strive for perfection. Men want to win. Men work hard. Men do better than women.)

Random - 5

History is all about, which Kings ruled. Kings, their men, and Soldiers went for wars. History is all about wars, fights, and killings by men.

Boys start fighting from school days. Girls do not fight like this

(Men are eager to fight, eager to rule, eager for war. Men want to drive. Men want to win.)

Random - 6

The highest award in Mathematics, the " Fields Medal " is around since decades. Till date only one woman could get that. (Maryam Mirzakhani - 2014). So, … almost all are men.

(Men want to excel. Men strive for perfection. Men want to win. Men work hard. Men do better than women.)

Random - 7

Actor is a gender neutral word. Could the movie like “ Top Gun “ be made with Female actors ? The best pilots, astronauts, Fighters are all Men.

Random - 8

In my childhood had seen a movie named “ The Tower in Inferno “. In the movie when the tall tower is in fire, women were being saved first, as only one lift was working….

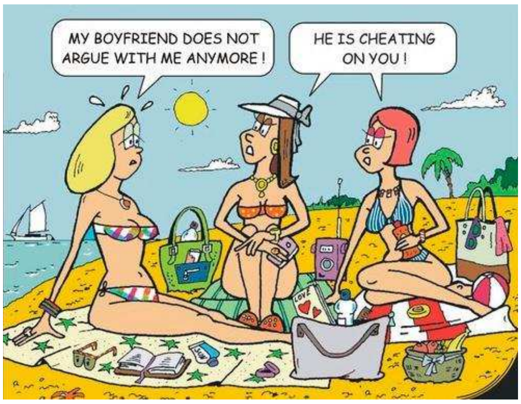
Many decades later another movie is made. A box office hit. “ The Titanic “. In this also …. As the ship is sinking women are being saved. **Men are disposable**. Men may get their turn later…

Movies are not training programs. Movies do not teach people what to do, or not to do. Movies only reflect the prevalent culture. Men are disposable, is the culture in the society. Knowingly, unknowingly, the culture is depicted in Movies, Theaters, Stories, Poems, Rituals, etc. I or you can’t write a story, or make a movie in which after a minor car accident the Male passengers keep seating in the back seat, while the both the women drivers come out of the car and start fighting very bitterly on the road. There has been no story in this world, or no movie made, where after an accident or calamity, Men are being helped for safety first, and women are told to wait.

Random - 9

Artists generally follow the prevalent culture of the Society. In paintings, sculptures, stories, poems, movies, cartoon, Caricatures, knowingly / unknowingly, “ the prevalent Reality “ is depicted. The opposite will not go well with people. If deliberately “ the opposite “ is shown then it may only become a special art, considered as a special mockery.

पत्नी (सल्टू से) : मुझे
नई साड़ी ला दो प्लीज।
सल्टू : पर तुम्हारी
दो-दो अलमारियां साड़ियों से ही तो भरी है।
पत्नी - वह सारी तो
पूरे मोहल्ले वालों ने
देख रखी है।
सल्टू - तो साड़ी लेने
के बजाए मोहल्ला
बदल लेते हैं।



Random - 10

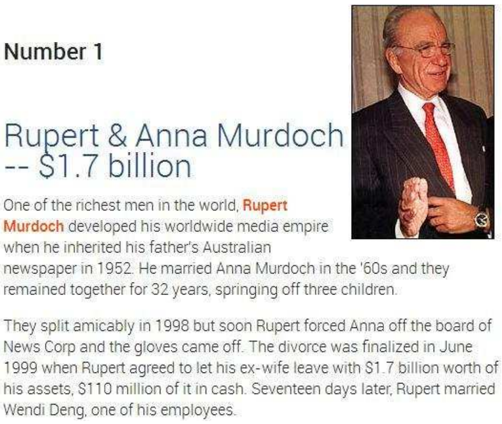
Men go to "girl / woman's house" to marry / win, and bring her to his home. That is a sort of winning her. When a boy gets a " Girl-Friend ", generally he and his friends consider that as an achievement. The boy who " got / won " a girl-friend feels proud. His male friends feel, jealous, competitive and envious. Millions of stories have been written on these themes. Lakhs of movies show this. Boys / Men go for " bike race ", or say " Car Race ", where the winner " gets " the most beautiful girl of the college.

(Men want to excel. Men are eager to fight, eager to rule, eager for war. Men want to drive. Men want to win.)

Prithviraj Chauhan ' went ` to " pickup " or " abduct " or " win " or " bring " his love. There was a Hindi movie (hit) song … " Pasand ho jaye, to ghar se utha laye ". It is not other way round. Girls do not go to Boy's house or man's house to marry. Nor the girls go in a gang to " pick-up " the boy / man and bring him to their home / place / den.

Random - 11

Rich people; often are very hard working. Successful business men, establish their business (empire), amass lot of wealth, with lot of difficulty. Lots of sacrifice, lots of hard work, gets into this. Rich people's wives had no contribution in this wealth creation. Women are smart, and successful upto the extent to choose the right/rich man to marry. So generally what happens in case of Divorces ? Search the net on " most costly divorces " and you will know. The women;(who had no contribution at all, in setting up the business / empire), often gets in Billions, or several Millions in divorce settlements.



Number 1

Rupert & Anna Murdoch -- $1.7 billion

One of the richest men in the world, Rupert Murdoch developed his worldwide media empire when he inherited his father's Australian newspaper in 1952. He married Anna Murdoch in the '60s and they remained together for 32 years, springing off three children.

They split amicably in 1998 but soon Rupert forced Anna off the board of News Corp and the gloves came off. The divorce was finalized in June 1999 when Rupert agreed to let his ex-wife leave with $1.7 billion worth of his assets, $110 million of it in cash. Seventeen days later, Rupert married Wendi Deng, one of his employees.

Ted Danson & Casey Coates -- $30 million

Ted Danson's claim to fame is undoubtedly his decade-long stint as Sam Malone on NBC's celebrated sitcom Cheers . While he did other TV shows and movies, he will always be known as the bartender of that place where everybody knows your name. He met his future first bride Casey, a designer, in 1976 while doing Erhard Seminars Training.

Ten years his senior, she suffered a paralyzing stroke while giving birth to their first child in 1979. In order to nurse her back to health, Danson took a break from acting for six months. But after two children and 15 years of marriage, the infatuation fell to pieces. Danson had started seeing Whoopi Goldberg while filming the comedy, Made in America and this precipitated the 1992 divorce. Casey got $30 million for her trouble.

See https://zookeepersblog.wordpress.com/misandry-and-men-issues-a-short-summary-at-single-place/

See http://skmclasses.kinja.com/save-the-male-1761788732

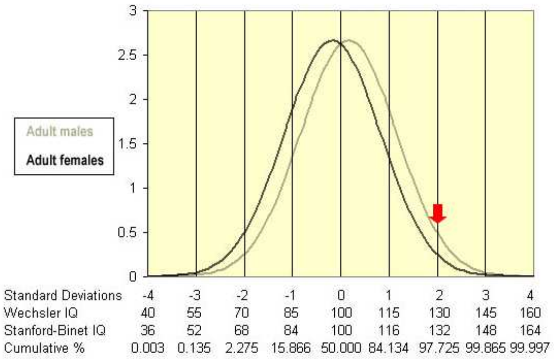
It was Boys and Men, who brought the girls / women home. The Laws are biased, completely favoring women. The men are paying for their own mistakes.

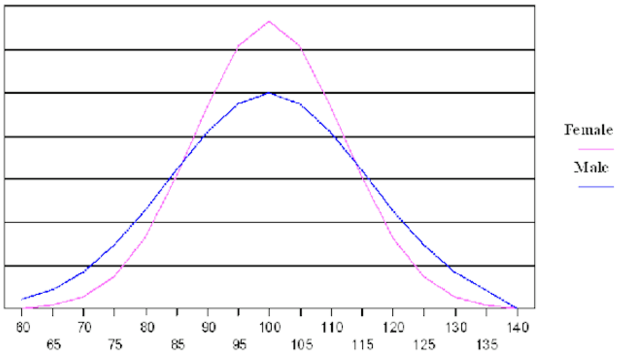
See https://zookeepersblog.wordpress.com/biased-laws/

(Man brings the Woman home. When she leaves, takes away her share of big fortune!)

Random - 12

A standardized test of Intelligence will never be possible. It never happened before, nor ever will happen in future; where the IQ test results will be acceptable by all. In the net there are thousands of charts which show that the intelligence scores of girls / women are lesser. Debates of Trillion words, does not improve performance of Girls.





I am not wasting a single second debating or discussing with anyone, on this. I am simply accepting ALL the results. IQ is only one of the variables which is required for success in life. Thousands of books have been written on “ Networking Skills “, EQ (Emotional Quotient), Drive, Dedication, Focus, “ Tenacity towards the end goal “ … etc. In each criteria, and in all together, women (in general) do far worse than men. Bangalore is known as “ ….. capital of India “. [Fill in the blanks]. The blanks are generally filled as “ Software Capital “, “ IT Capital “, “ Startup Capital “, etc. I am member in several startup eco-systems / groups. I have attended hundreds of meetings, regarding “ technology startups “, or “ idea startups “. These meetings have very few women. Starting up new companies are all “ Men’s Game “ / “ Men’s business “. Only in Divorce settlements women will take their goodies, due to Biased laws. There is no dedication, towards wealth creation, by women.

Random - 13

Many men, as fathers, very unfortunately treat their daughters as “ Princess “. Every “ non-performing “ woman / wife was “ princess daughter “ of some loving father. Pampering the girls, in name of “ equal opportunity “, or “ women empowerment “, have led to nothing.

See http://skmclasses.kinja.com/progressively-daughters-become-monsters-1764484338

See http://skmclasses.kinja.com/vivacious-vixens-1764483974

There can be thousands of more such random examples, where “ Bigger Shape / size “ of males have influenced our culture, our Society. Let us recall the reasons, that we already learned in standard 10 - 11, Biology text Books. In humans, women have a long gestation period, and also spends many years (almost a decade) to grow, nourish, and stabilize the child. (Million years of habit) Due to survival instinct Males want to inseminate. Boys and Men fight for the “ facility (of womb + care) “ the girl / woman may provide. Bigger size for males, has a winning advantage. Whoever wins, gets the “ woman / facility “. The male who is of “ Bigger Size “, has an advantage to win…. Leading to Natural selection over millions of years. In general “ Bigger Males “; the “ fighting instinct “ in men; have led to wars, and solving tough problems (Mathematics, Physics, Technology, startups of new businesses, Wealth creation, Unreasonable attempts to make things [such as planes], Hard work ….)

So let us see the IIT-JEE results of girls. Statistics of several years show that there are around 17, (or less than 20) girls in top 1000 ranks, at all India level. Some people will yet not understand the performance, till it is said that … year after year we have around 980 boys in top 1000 ranks. Generally we see only 4 to 5 girls in top 500. In last 50 years not once any girl topped in IIT-JEE advanced. Forget about Single digit ranks, double digit ranks by girls have been extremely rare. It is all about “ good boys “, “ hard working “, “ focused “, “**Bel-esprit** “ boys.

In 2015, Only 2.6% of total candidates who qualified are girls (upto around 12,000 rank). while 20% of the Boys, amongst all candidates qualified. The Total number of students who appeared for the exam were around 1.4 million for IIT-JEE main. Subsequently 1.2 lakh (around 120 thousands) appeared for IIT-JEE advanced.

IIT-JEE results and analysis, of many years is given at https://zookeepersblog.wordpress.com/iit-jee-iseet-main-and-advanced-results/

In Bangalore it is rare to see a girl with rank better than 1000 in IIT-JEE advanced. We hardly see 6-7 boys with rank better than 1000. Hardly 2-3 boys get a rank better than 500.

See http://skmclasses.weebly.com/everybody-knows-so-you-should-also-know.html

Thousands of people are exposing the heinous crimes that Motherly Women are doing, or Female Teachers are committing. See https://www.facebook.com/WomenCriminals/

Some Random Examples must be known by all

Mother Admits On Facebook to Sleeping with 15 Yr Old Son, They Have a Baby Together - Alwayzturntup

Sometimes it hard to believe w From Alwayzturntup

ALWAYZTURNTUP.ME

It is extremely unfortunate that the " woman empowerment " has created. This is the kind of society and women we have now. I and many other sensible Men hate such women. Be away from such women, be aware of reality.

'Sex with my son is incredible - we're in love and we want a baby'

Ben Ford, who ditched his wife when he met his mother Kim West after 30 years, claims what the couple are doing 'isn't incest'

MIRROR.CO.UK

Former Shelbyville ISD teacher who had sex with underage student gets 3 years in prison

After a two day break over the weekend, A Shelby County jury was back in the courtroom looking to conclude the trial of a former Shelbyville ISD teacher who had...

KLTV.COM | BY CALEB BEAMES

Woman sent to jail for the rest of her life after raping her four grandchildren is described as the 'most evil person' the judge has ever seen

Edwina Louis rape...

See More

Woman sent to jail for raping her four grandchildren

A Ohio grandmother has been sentenced to four consecutive life terms after being found guilty of the rape of her own grandchildren. Edwina Louis, 53, will spend the rest of her life behind bars.

DAILYMAIL.CO.UK

http://www.thenativecanadian.com/.../eastern-ontario-teacher-...

The N.C. Chronicles.: Eastern Ontario teacher charged with 36 sexual offences

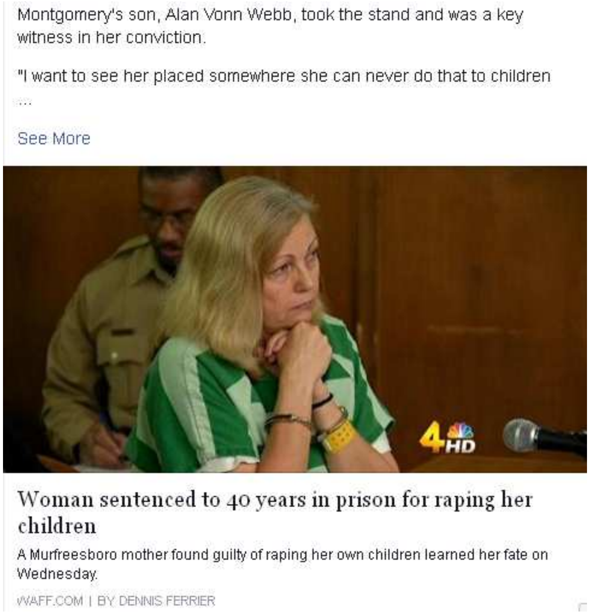
anti feminism, Child abuse, children's rights, Feminist hypocrisy,

THENATIVECANADIAN.COM | BY BLACKWOLF

Hyd woman kills newborn boy as she wanted daughter - Times of India

Having failed to bear a daughter for the third time, a shopkeeper's wife slit the throat of her 24day-old son with a shaving blade and left him to die in a street on Tuesday night.Purnima's first child was a stillborn boy, followed by another boy born five years ago.

TIMESOFINDIA.INDIATIMES.COM



Montgomery's son, Alan Vonn Webb, took the stand and was a key witness in her conviction.

"I want to see her placed somewhere she can never do that to children ...

See More

Woman sentenced to 40 years in prison for raping her children

A Murfreesboro mother found guilty of raping her own children learned her fate on Wednesday.

WAFF.COM | BY DENNIS FERRIER

gentler sex? Violence against men.'s photo.

Women, the gentler sex? Violence against men.

April 8 at 1:38am ·

In fact, the past decade has seen a dramatic increase in the number of incidents of women raping and sexually assaulting boys and men. On May 2014, Jezebel repo...

End violence against women . . . .

North Carolina Grandma Eats Her Daughter's New Born Baby After Smoking Bath Salts

Henderson, North Carolina– A North Carolina grandmother of 4 and recovering drug addict, is now in custody after she allegedly ate her daughter's newborn baby....

AZ-365.TOP

28-Year-Old Texas Teacher Accused of Sending Nude Picture to 14-Year-Old Former Student

BREITBART.COM

http://latest.com/.../attractive-girl-gang-lured-men-alleywa.../

Attractive Girl Gang Lured Men Into Alleyways Where Female Body Builder Would Attack Them

A Mexican street gang made up entirely of women has been accused of using their feminine wiles to lure men into alleyways and then beating them up and...

LATEST.COM

http://www.wfmj.com/.../youngstown-woman-convicted-of-raping-...

Youngstown woman convicted of raping a 1 year old is back in jail

A Youngstown woman who went to prison for raping a 1-year-old boy fifteen years ago is in trouble with the law again.

WFMJ.COM

End violence against women . . . .

Women are raping boys and young men

Rape advocacy has been maligned and twisted into a political agenda controlled by radicalized activists. Tim Patten takes a razor keen and well supported look into the manufactured rape culture and...

AVOICEFORMEN.COM | BY TIM PATTEN

Bronx Woman Convicted of Poisoning and Drowning Her Children

Lisette Bamenga researched methods on the Internet before she killed her son and daughter in 2012.

NYTIMES.COM | BY MARC SANTORA

A Russian-born newlywed slowly butchered her German husband — feeding strips of his flesh to their dog until he took his last breath. Svetlana Batukova, 46, was...

See More

She killed her husband and then fed him to her dog: police

A Russian-born newlywed butchered her German hubby — and fed strips of his flesh to her pooch, authorities said. Svetlana Batukova offed Horst Hans Henkels at their...

NYPOST.COM

Daily Mail
January 15, 2015

Mother charged with rape and sodomy of her son's 12-year-old friend

Mom, 30, 'raped and had oral sex with her son's 12-year-old friend'

Nicole Marie Smith, 30, (pictured) of St Charles County, Missouri, has been jailed after she allegedly targeted the 12-year-old boy at her home.

DAILYM.AI

April 4 at 4:48am

Female prison officers commit 90pc of sex assaults on male teens in US juvenile detention centres

Lawsuit in Idaho highlights the prevalence of sexual victimization of juvenile offenders.

IBTIMES.CO.UK | BY NICOLE ROJAS

This mother filmed herself raping her own son and then sold it to a man for $300. The courts just decide her fate. When you see what she got, you're going to be outraged.

Mother Who Filmed Herself Raping Her 1-Year-Old Son Receives Shocking Sentence

"...then used the money to buy herself a laptop..."

AMERICANEWS.COM

In several countries or rather in several regions of the world, family system has collapsed, due to bad nature and naughty acts of women. Particularly in Britain, and America, almost 50% people are alone, lonely, separated, divorced or failed marriages. In 2013, 48% children were born out of wedlock. It was projected that by 2016, more than 51% children will be born, to unmarried mothers. In these developed countries " paternity fraud " by women, are close to 20%. You can see several articles in the net, and in wikipedia etc. This means 1 out of 5 children are calling a wrong man as dad. The lonely, alone " mothers " are frustrated. They see the children as burden. Love in the Society in general is lost, long time ago. The types of " Mothers " and " Women " we have now ....

This is the type of women we have in this world. These kind of women were also someones daughter

Mother Stabs Her Baby 90 Times With Scissors After He Bit Her While Breastfeeding Him!

Eight-month-old Xiao Bao was discovered by his uncle in a pool of blood Needed 100 stitches after the incident; he is now recovering in hospital Reports say his...

MOMMABUZZ.COM

HURT FEMINISM BY
DOING NOTHING

- ✗ DON'T HELP WOMEN
- ✗ DON'T FIX THINGS FOR WOMEN
- ✗ DON'T SUPPORT WOMEN'S ISSUES
- ✗ DON'T COME TO WOMEN'S DEFENSE[1]
- ✗ DON'T SPEAK FOR WOMEN
- ✗ DON'T VALUE WOMEN'S FEELINGS
- ✗ DON'T PORTRAY WOMEN AS VICTIMS
- ✗ DON'T PROTECT WOMEN[2]

✓ WITHOUT WHITE KNIGHTS FEMINISM WOULD END TODAY

[1] Don't even nawalt ("Not All Women Are Like That")

[2] for example from criticism or insults

How Society prioritize Men

Rich women	They can get away with murder.
Women	They get all the rights with no responsibility and Shelters for Homeless women.
Rich Men	They get tax bail outs and short prison sentence.
Girls	They get educational benefits but no violence against kids Act.
Boys	They have some support but don't have any education that fits boys.
Animals	They have animal rights and PETA.
Prisoners	They get conjugal visits and 3 squares and a roof.
Men	Paid slaves.
Poor Men	Nothing.

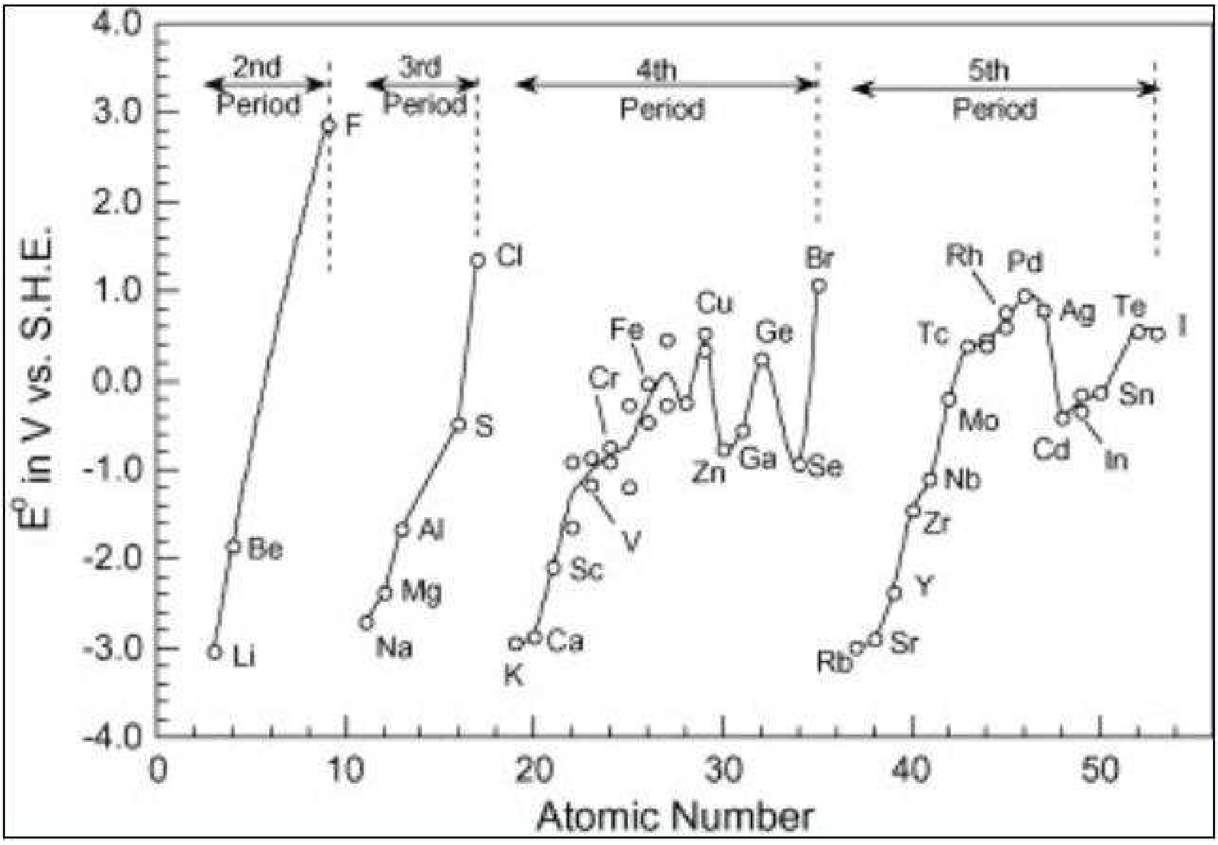
Who pays the most Taxes?
This is why MGTOW exist.

#MGTOW

Professor Subhashish Chattopadhyay

Spoon Feeding Series - Electrochemistry

We must first understand the most Important graph or Image of Chemistry



It is very strange, that so many Chemistry books exists in this world, which do not even have a single Periodic table in them. Almost all books do not have this graph either. This is the graph of electrode potential of various elements with respect to (standard) Hydrogen electrode.

All chemical reactions happen because of this electrode potential difference. When a Solid is added to a solution of another compound such as a Gold Spoon in $CuSO_4$ Solution, of a Copper container having $AgNO_3$ Solution, then the displacement reaction happens or not is decided by these potential values. Battery and Electrochemistry chapter uses this knowledge. Oxidation-Reduction reactions, titrations etc all need this understanding.

ELECTROCHEMICAL CELLS

An electrochemical cell consists of two electrodes (metallic conductors) in contact with an electrolyte (an ionic conductor). An electrode and its electrolyte comprise an Electrode Compartment.

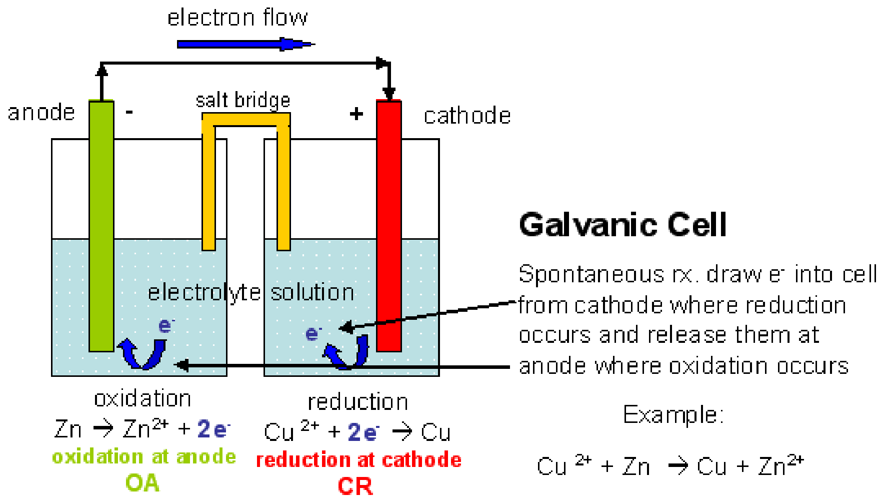
Electrochemical Cells can be classified as:

(i) Electrolytic Cells - in which a non-spontaneous reaction is driven by an external source of current.

(ii) Galvanic Cells - which produce electricity as a result of a spontaneous cell reaction a galvanic cell, cathode is positive with respect to anode.

In a electrolytic cell, anode is made positive with respect to cathode.

ELECTROCHEMICAL CELLS

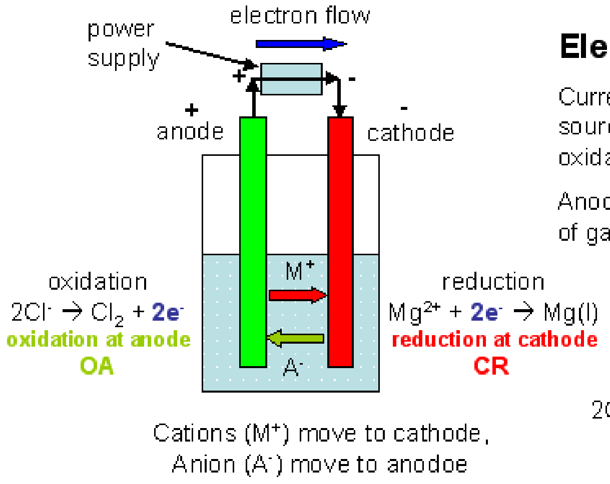


Galvanic Cell

Spontaneous rx. draw e- into cell from cathode where reduction occurs and release them at anode where oxidation occurs

Example:

$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$



Cations (M^+) move to cathode, Anion (A^-) move to anodoe

Electrolytic Cell

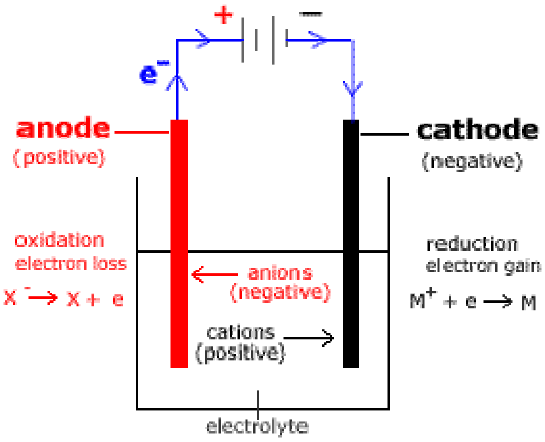
Current supplied by external source drive nonspontaneous oxidation/reduction reaction.

Anode + and cathode -, opposite of galvanic cell

Example:

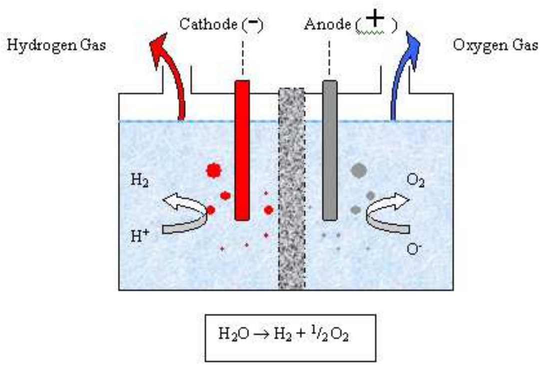
$2Cl^- + Mg^{2+} \rightarrow Cl_2 + Mg(l)$

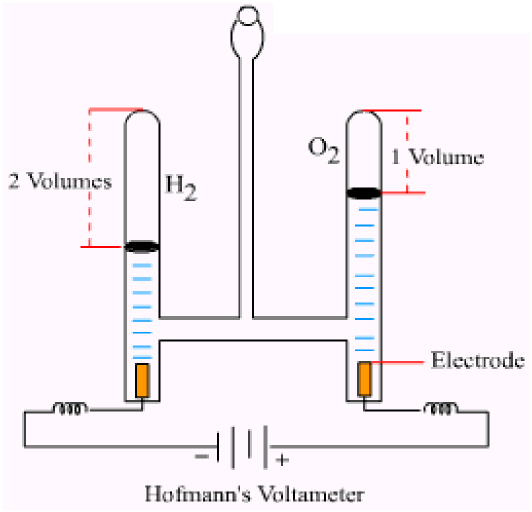
ELECTROLYSIS (Where a Positive current, of holes, is forced into the Anode. So electrons will come out of the Anode.)



The decomposition of electrolyte solution by passage of electric current, resulting into deposition of metals or liberation of gases at electrodes is known as electrolysis. Or in another words, **Electrolysis** is the chemical deposition of a compound into its constituent elements brought about by a flow of electric current. In the Electrolyte Cations (positively charged) move to Cathode as it is with excess electrons.

- Direct current is passed through the compound (the compound can be in molten or aqueous state).
- Electrical energy (From the direct current) is changed into chemical energy (the decomposition of the compound).
- One common example is the electrolysis of water, where water decomposes to hydrogen and oxygen.





ELECTROLYTIC CELL

This cell converts electrical energy into chemical energy. The entire assembly except that of the external battery is known as the electrolytic cell. So **Main components** of an electrolytic cell: Electrolytes, Electrodes and External Battery (or Source of DC Voltage).

ELECTRODES

The metal strip at which positive current enters is called anode; anode is positively charged in electrolytic cell. On the other hand, the electrode at which current leaves is called cathode. Cathodes are negatively charged. So The positive terminal of the **battery** is connected to the positive electrode (anode) while the negative terminal of the battery is connected to the negative electrode (cathode).

Spoon Feeding

Anode is positive. Here electrons are lost. So it is getting oxidized. Positive current enters.

Cathode is negative. Here electrons are gained. Positive Current leaves the cathode.

Electrolytes are usually made up of an ionic compound in solution or molten state OR aqueous solutions of acids or alkalis.

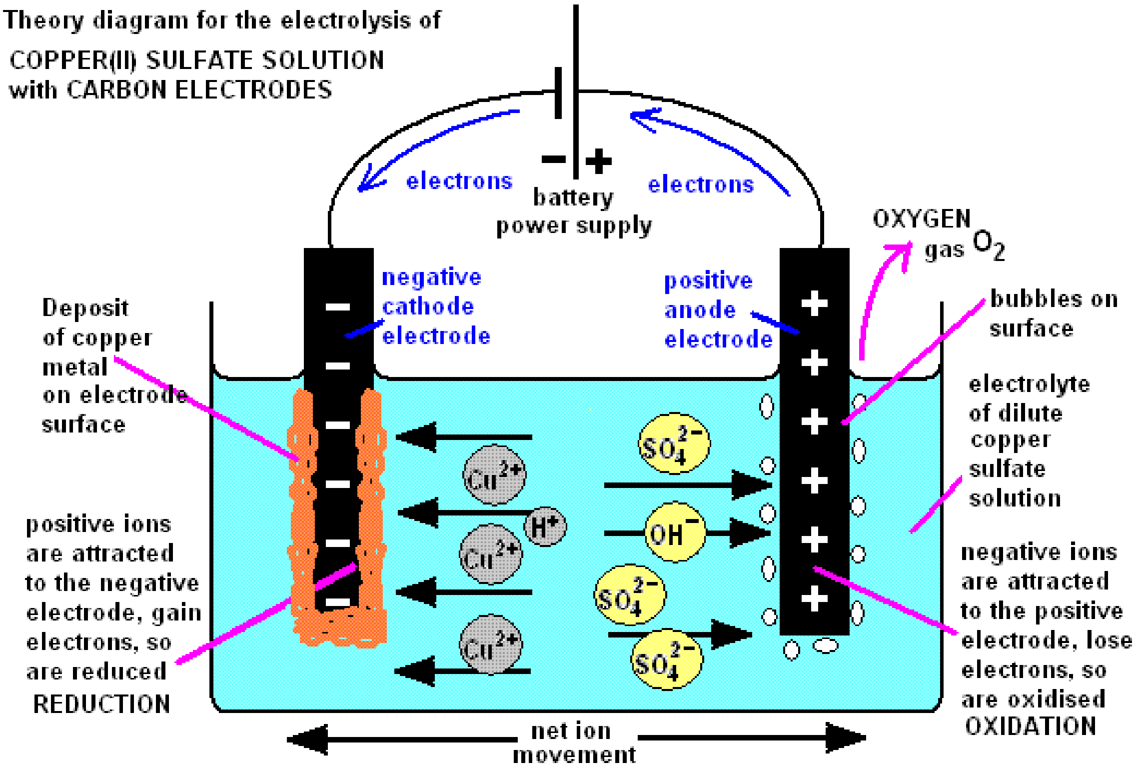
- Electrolytes conduct electricity with decomposition at the electrodes as it does so.
- Electrolytes can be classified into three categories: Non-electrolytes, weak electrolytes and strong electrolytes.
- Strong electrolytes = lots of ions to carry the charges from one electrode to the other. Examples of strong electrolytes: Strong acids or alkalis (sulphuric acid, aqueous sodium hydroxide), salt solutions (aqueous sodium chloride)
- Weak electrolytes = few ions to carry the charges from one electrode to the other. Examples of weak electrolytes: Weak acids or bases (Ethanoic acid, aqueous ammonia)
- Non-electrolytes = no ions available to carry the charges from one electrode to the other. Examples of non-electrolytes: Pure water, organic liquids or solvents

Electrodes are conductors through which electrons enter and leave the electrolyte.

- Anode is the POSITIVE (+) electrode from which electrons leave the electrolyte (or the electric current enters the electrolyte)
- Cathode is the NEGATIVE (-) electrode from which electrons enter the electrolyte (or the electric current leaves the electrolyte)
- Electrodes are typically made up of inert materials (which do not participate in any redox reactions), such as carbon, platinum, titanium, or stainless steel. (NOTE: There are some cases where the electrodes undergoes redox reactions during electrolysis.)

What happens during electrolysis?

- Negative ions (Anions) are attracted to the anode while the positive ions (cations) are attracted to the cathode.
- When the ions reaches their respective electrodes, they will be discharged. (They lose or gain electrons and form neutral atoms)
- Hence, at anode, anions are discharged through loss of electrons; while at the cathode, cations are discharged through gain of electrons.



ELECTROLYSIS OF MOLTEN SODIUM CHLORIDE

NaCl(molten) < == > $Na^+ + Cl^-$

Reactions at anode (oxidation) $2\,Cl^- \rightarrow Cl_2$ (gas) + $2e^-$ Recall Loosing electron is being oxidized

Reactions at cathode (reduction) $Na^+ + e^- = Na$

There are two types of electrodes used in the electrolytic cell,
namely attackable and non - attackable.

The attackable elecrodes participitate in the electrode reaction. They are made up of reactive metals like Zn, Cu, Ag etc. In such electrodes, atom of the metal gets oxidised into the corresponding cation, which is passed into the solution. Thus, such anodes get dissolved and their mass decreases. On the other hand, non-attackable electrodes do not participate in the electrode reaction as they made up of unreactive elements like Pt, graphite etc. Such electrodes do not dissolve and their mass remain same.

FARADAY'S LAWS OF ELECTROLYSIS:

(i) First law of electrolysis :

Amount of substance deposited or liberated at an electrode is directly proportional to amount of charge passed (utilized) through the solution.

$W \propto Q$

W = weight liberated, Q = charge in coulomb
$w = ZQ$

Z = electrochemical equivalent when Q = 1 coulomb, then w = Z

Thus, weight deposited by 1 coulomb charge is called electrochemical equivalent.

Let 1 ampere current is passed till 't' seconds .

Then, Q = I t
∴
w = Z I t or Z i t Some teachers prefer to write current in small case " i "

1 Faraday = 96500 coulomb = Charge of one mole electrons

One faraday is the charge required to liberate or deposit one gm equivalent of a substance at corresponding electrode.

Let 'E' is equivalent weight then 'E' gm will be liberated by 96500 coulomb.
∴ 1 Coulomb will liberate E / 96500 gm

So by definition Z = E/96500
W = I t E / 96500

When a gas is evolved at an electrode, then above formula changes as

$$V = \frac{I\,t\,V_e}{96500}$$

where V = volume of liberated gas, V_e = equivalent volume of gas.

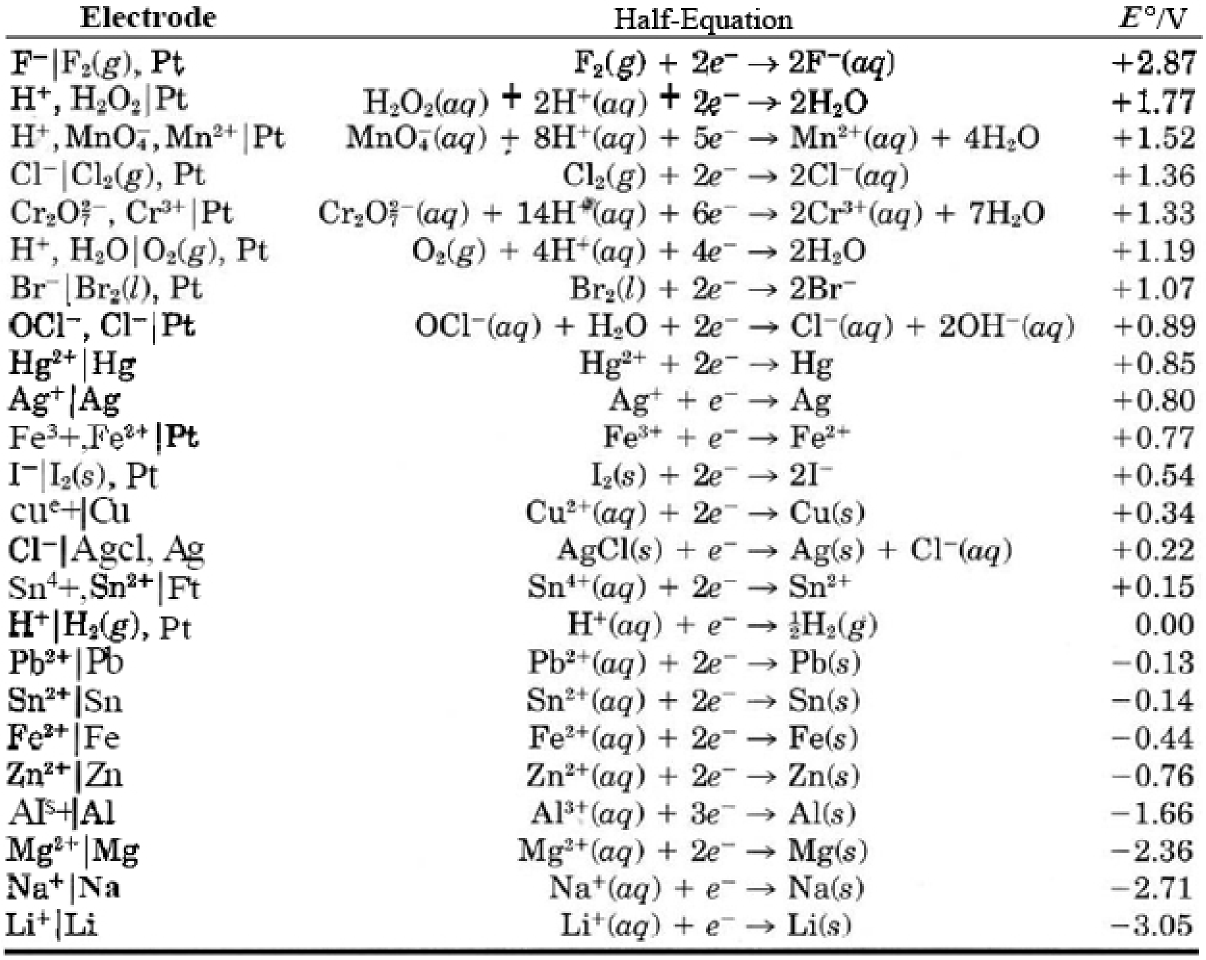
Equivalent volume may be defined as: The volume of gas liberated by 96500 coulomb at STP.

(ii) Second law of electrolysis :
When same amount of charge is passed through different electrolyte solutions connected in series then weight of substances deposited or dissolved at anode or cathode are in ratio of their equivalent weights. i.e. $W_1 / W_2 = E_1 / E_2$

QUALITATIVE ASPECTS OF ELECTROLYSIS

In the electrolysis process we have discussed above, we have taken molten salt as electrolyte, which contains only one cation and anion. Now, if the electrolyte taken contains more than one cation and anion (for example, aqueous solution of the ionic electrolyte), then the cation and anion that will get discharged depends on the ability of cation to get reduced and the ability of anion to get oxidised.

The ability of an ion to get oxidised or reduced depends upon the size, mass, positive charge, negative charge etc. Thus, it is not possible to predict qualitatively that which ion would be discharged first, as one factor might enhance the ability to discharge while the other factor may hamper it. This can only bepredicted on the basis of quantitative value assigned based on the cumulative effect of all the factors responsible for an ion's ability to discharge. The value is referred as standard potential, which is determined by keeping the concentration of ion as 1 M, pressure of gas at 1 atm, and the measurement done at 25°C. For a cation, the standard reduction potential (SRP) values are compared. The cation having higher standard reduction potential value is discharged in preference to cation with lower SRP value provided the ions are at 1 M concentration. For an anion, the standard oxidationpotential (SOP) values are compared and anion having higher SOP is preferentially discharged, if the concentration is 1 M for each of the ion. The SRP values at 25°C for some of the reduction half reactions are given in the tables.



Electrode	Half-Equation	$E°$/V
$F^-\|F_2(g)$, Pt	$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	+2.87
H^+, $H_2O_2\|Pt$	$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O$	+1.77
$H^+, MnO_4^-, Mn^{2+}\|Pt$	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O$	+1.52
$Cl^-\|Cl_2(g)$, Pt	$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}, Cr^{3+}\|Pt$	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$H^+, H_2O\|O_2(g)$, Pt	$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$	+1.19
$Br^-\|Br_2(l)$, Pt	$Br_2(l) + 2e^- \rightarrow 2Br^-$	+1.07
$OCl^-, Cl^-\|Pt$	$OCl^-(aq) + H_2O + 2e^- \rightarrow Cl^-(aq) + 2OH^-(aq)$	+0.89
$Hg^{2+}\|Hg$	$Hg^{2+} + 2e^- \rightarrow Hg$	+0.85
$Ag^+\|Ag$	$Ag^+ + e^- \rightarrow Ag$	+0.80
$Fe^3+,Fe^{2+}\|Pt$	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77
$I^-\|I_2(s)$, Pt	$I_2(s) + 2e^- \rightarrow 2I^-$	+0.54
$cu^e+\|Cu$	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$Cl^-\|$Agcl, Ag	$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	+0.22
$Sn^4+,Sn^{2+}\|Ft$	$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}$	+0.15
$H^+\|H_2(g)$, Pt	$H^+(aq) + e^- \rightarrow \frac{1}{2}H_2(g)$	0.00
$Pb^{2+}\|Pb$	$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	−0.13
$Sn^{2+}\|Sn$	$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	−0.14
$Fe^{2+}\|Fe$	$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	−0.44
$Zn^{2+}\|Zn$	$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	−0.76
$Al^s+\|Al$	$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	−1.66
$Mg^{2+}\|Mg$	$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	−2.36
$Na^+\|Na$	$Na^+(aq) + e^- \rightarrow Na(s)$	−2.71
$Li^+\|Li$	$Li^+(aq) + e^- \rightarrow Li(s)$	−3.05

When solution of an electrolyte contains more than one type of cations and anions at concentrations different than 1 M, the discharge of an ion does not depend solely on standard potentials but also depends on the concentration of ion in the solution. This value is refered as potential, called as reduction potential for cation and oxidation potential for anion. The relation between reduction potential and standard reduction potential is given by Nernst equation, as

$$E_{RP} = E^{\circ}_{RP} - \frac{RT}{nF} \ln \frac{[\text{concentration of product}]}{[\text{concentration of reac tan t}]}$$

Where E_{RP} = Reduction potential of cation

E°_{RP} = Standard Reduction potential of cation

Thus, it is possible that a cation (A^+) with lower standard reduction potential getting discharged in preference to cation (B^+) having higher standard reduction potential because their concentration might be such that the reduction potential of A^+ is higher than that of B^+ . When two metal ions in the solution have identical values of their reduction potentials, the simultaneous deposition of both the metals will occur in the form of an alloy.

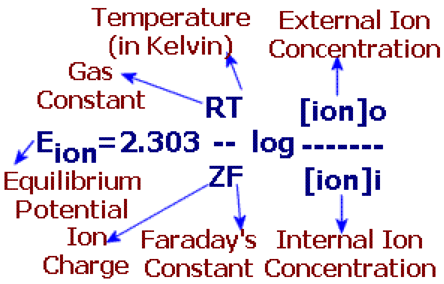
Note on Nernst Equation also uses Electrode potential

Walther Hermann Nernst (1864 - 1941) German Physicist & Chemist received the Nobel prize in 1920 Chemistry.

$$At\ 25^0C: E_{cell} = E^0_{cell} - \frac{0.059}{n}\log\frac{M}{[M^{n+}]} or \frac{1}{[M^{n+}]}$$

$$E_{cell} = E^0_{cell} - \frac{0.059}{n}\log[\frac{Products}{Reactants}] or Q.$$

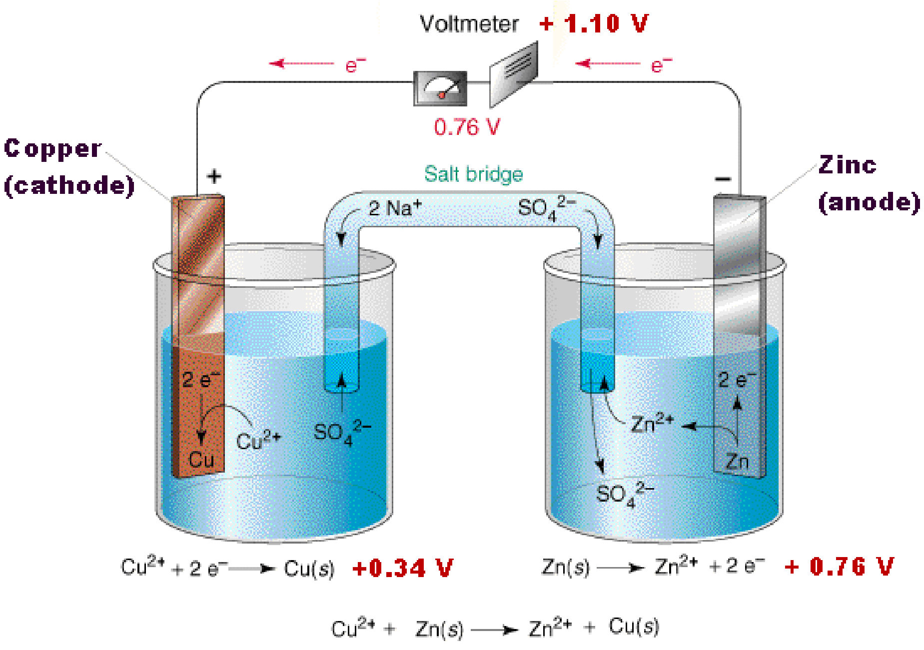
$$E_{cell} = E^0_{cathode} - E^0_{anode} - \frac{0.059}{n}\log\frac{[P]}{[R]}$$



-

GALVANIC CELL

This cell converts chemical energy into electrical energy.



Galvanic cell is made up of two half cells i.e., anodic and cathodic. The cell reaction is of redox kind. Oxidation takes place at anode and reduction at cathode. It is also known as voltaic cell. It may be represented as shown in Fig. Zinc rod immersed in ZnSO4 behaves as anode and copper rod immersed in CuSO4 behaves as cathode.

Remember :

In the electrode potential chart / list the elements higher up will act as Cathode compared to elements lower in the chart.

Observe that Cu has positive electrode potential, and is higher up compared to Hydrogen. So Cu rod acts as Cathode.

Zinc has negative electrode potential. Zinc is below SHE (Standard Hydrogen Electrode), so below Hydrogen, in the chart. So Zn rod acts as Anode.

-

In galvanic cell like Daniell cell; electrons flow from anode (zinc rod) to the cathode (copper rod) through external circuit; zinc dissolves as Zn^{2+} ; Cu^{2+} ion in the cathode cell picks up two electron and become deposited at cathode.

-

The e.m.f of the standard cell $Zn \mid Zn^{2+} \mid\mid Ag^{+} \mid Ag$ $E^{o}_{cell} = 1.562$ Volt

If the standard electrode potential of Zinc is - 0.762 Volt, then that of Silver is ?

Solution : $E^{o}_{cell} = E_{Right} - E_{Left} = E_{Ag+ \mid Ag} - E_{Zn2+ \mid Zn} = (E_{Reduction\ (\ Right\ )} - E_{Reduction\ (\ Left\ )})$

So $1.562 = E(Ag^{+} \mid Ag) - (- 0.762)$ => $E_{Ag+ \mid Ag} = 0.8$ Volt

-

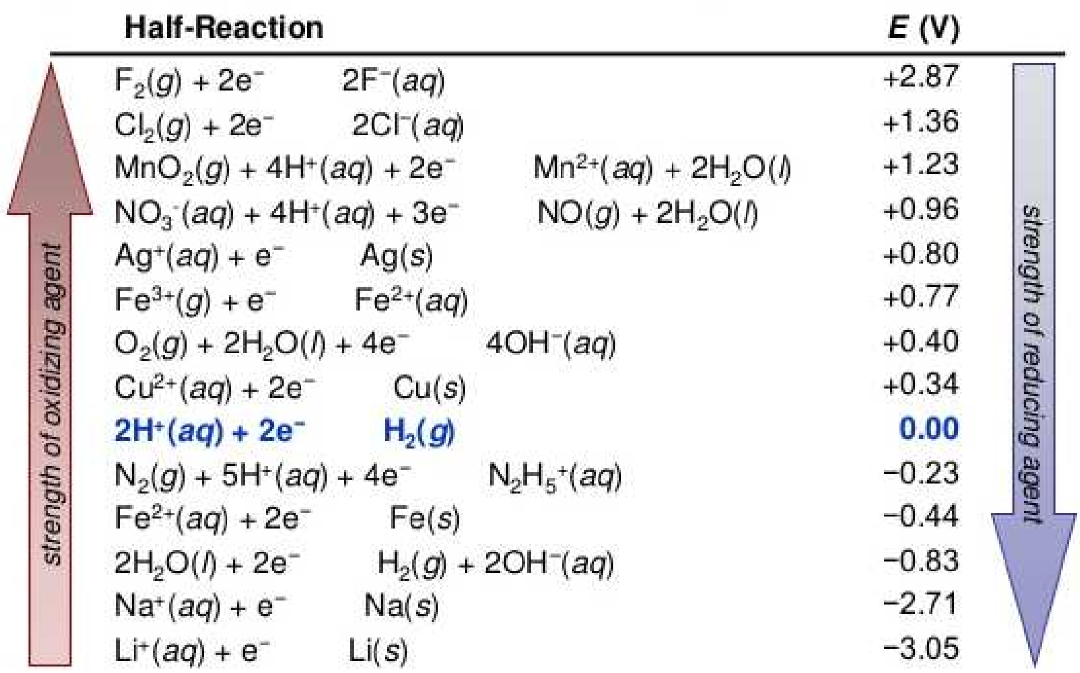
What will happen if a solution of copper sulphate put into an iron pot ?

Note : Electrode potential of Cu is more positive (so higher) than Fe (Iron).

A solution of copper sulphate put into an iron pot will damage. This is because the standard electrode potential for Fe2+/Fe is more negative than that for Cu2+/Cu. The iron oxidises first, while copper ions are reduced. Iron will corrode (rust). Or in more simple words it is easier to replace Cu ions by Fe ions from the pot. Any element lower in the series tends to replace the element which is higher up the series.

This is called a redox reaction, since the iron is being oxidised, and copper ions reduced.

Note : A solution of Iron Salt in a Copper Vessel would have just done fine. In this case copper is in solid form, as vessel. So will not replace the Iron ions.

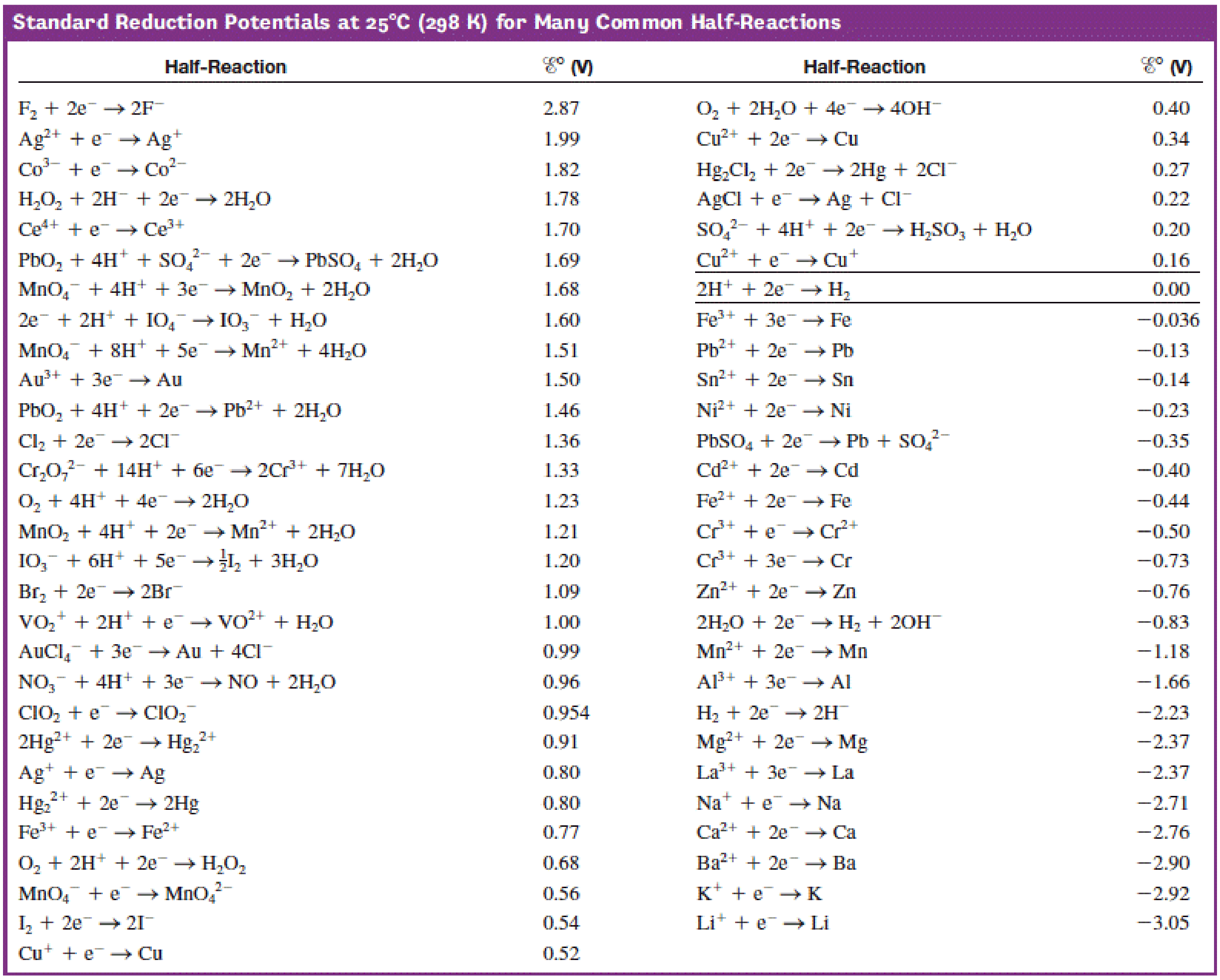


Half-Reaction		E (V)
$F_2(g) + 2e^-$	$2F^-(aq)$	+2.87
$Cl_2(g) + 2e^-$	$2Cl^-(aq)$	+1.36
$MnO_2(g) + 4H^+(aq) + 2e^-$	$Mn^{2+}(aq) + 2H_2O(l)$	+1.23
$NO_3^-(aq) + 4H^+(aq) + 3e^-$	$NO(g) + 2H_2O(l)$	+0.96
$Ag^+(aq) + e^-$	$Ag(s)$	+0.80
$Fe^{3+}(g) + e^-$	$Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H_2O(l) + 4e^-$	$4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^-$	$Cu(s)$	+0.34
$2H^+(aq) + 2e^-$	**$H_2(g)$**	**0.00**
$N_2(g) + 5H^+(aq) + 4e^-$	$N_2H_5^+(aq)$	−0.23
$Fe^{2+}(aq) + 2e^-$	$Fe(s)$	−0.44
$2H_2O(l) + 2e^-$	$H_2(g) + 2OH^-(aq)$	−0.83
$Na^+(aq) + e^-$	$Na(s)$	−2.71
$Li^+(aq) + e^-$	$Li(s)$	−3.05

strength of oxidizing agent

strength of reducing agent

A more detailed table



Standard Reduction Potentials at 25°C (298 K) for Many Common Half-Reactions

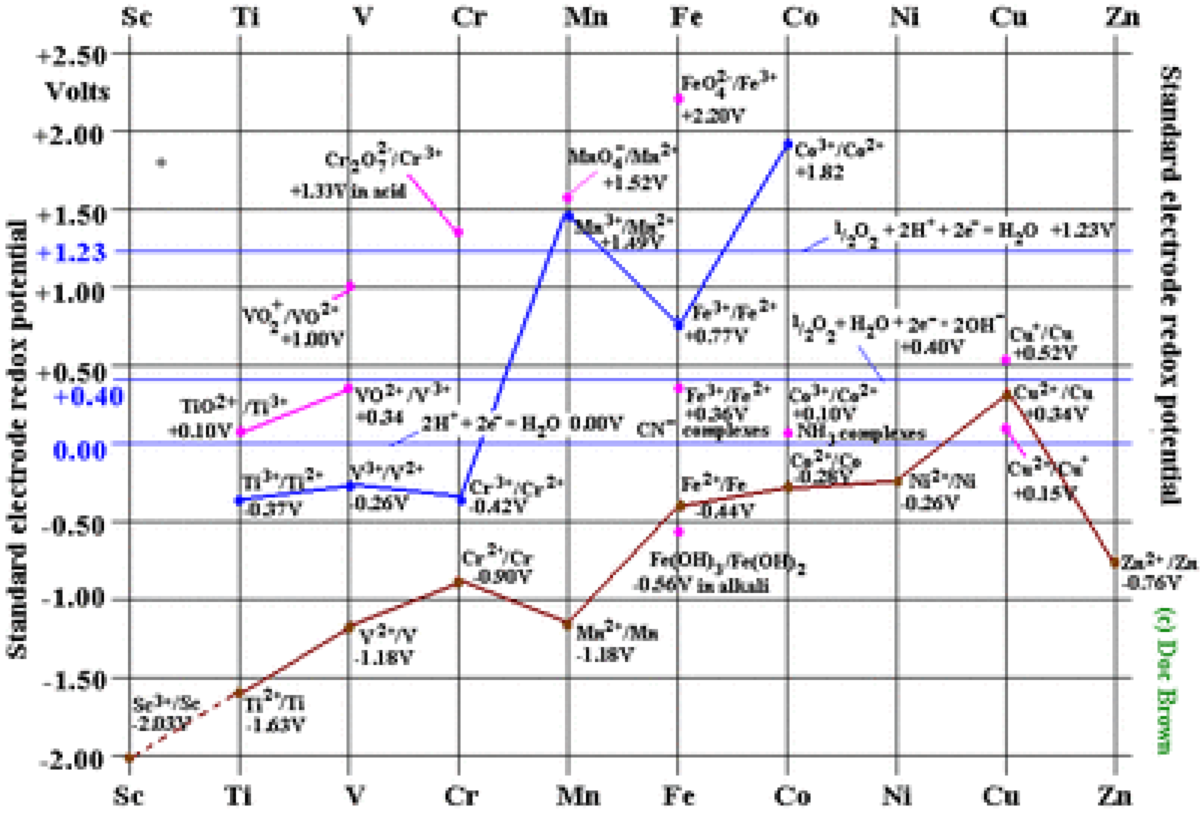
Half-Reaction	$\mathcal{E}^\circ$ (V)	Half-Reaction	$\mathcal{E}^\circ$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3-} + e^- \rightarrow Co^{2-}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^- + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$2e^- + 2H^+ + IO_4^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	−2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	−2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	−2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	−3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

Spoon Feeding

What will happen if a solution of Magnesium sulphate put into an Copper pot ?

Note : Magnesium looses electron very easily, metallic character, or basic character being high. Electrode potential is - 2.37 While we know Copper has +ve electrode potential. (This is an important exception and the data is better remembered as 0.5)

So Copper is solid in Copper pot (or even if a copper spoon was inserted, the same logic). Copper will not replace Magnesium ions. But if a Magnesium spoon was put into Copper-Sulphate solution then the Magnesium ions / atoms will start replacing the Cu ions and Copper will start getting precipitated. The Magnesium spoon, or container will start getting corroded or damaged.



SALT BRIDGE

Two electrolyte solutions in galvanic cells are separated using salt bridge joining the two sides. saltbridge is a device to minimize or eliminate the liquid junction potential. Saturated solution of salt like KCl, KNO3, NH4Cl and NH4NO3 etc. in agar-agar gel is used in salt bridge. Salt bridge contains high concentration of ions viz. K+ and NO3– at the junction with electrolyte solution. Thus, salt bridge carries whole of the current across the boundary; more over the K+ and NO3– ions have same speed. Hence, salt bridge with uniform and same mobility of cations and anions minimize the liquid junction potential & completes the electrical circuit & permits the ions to migrate.

Representation of a cell (IUPAC conventions): Let us illustrate the convention taking the example of Daniel cell.

(i) Anodic half cell is written on left and cathodic half cell on right hand side.

$$Zn(s) \mid ZnSO_4(sol) \parallel CuSO_4(sol) \mid Cu(s)$$

(ii) Two half cells are separated by double vertical lines: Double vertical lines indicate salt bridge or any type of porous partition.

(iii) EMF (electromotive force) may be written on the right hand side of the cell.

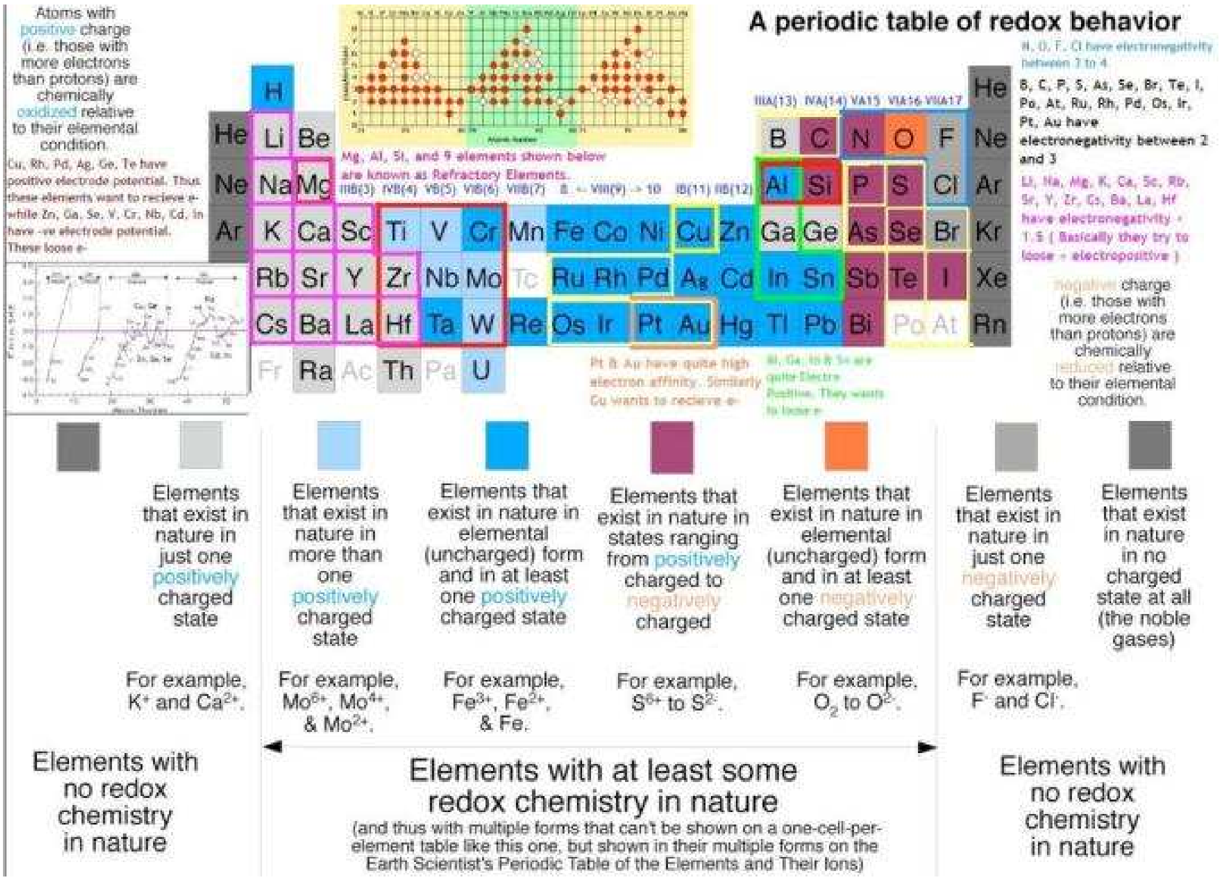
(iv) Single vertical lines indicate the phase separation between electrode and electrolyte solution.

$$Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$$

(Illustration of Phase boundary)

(v) Inert electrodes are reprsented in the bracket

$$Zn \mid ZnSO_4 \parallel H^+ \mid H_2, Pt$$



Consider the following set of half-reactions

Reduction	$Fe^{2+} + 2e^- \rightleftharpoons Fe$	$E^\circ_{red} = -0.44$ V
Oxidation	$Zn \rightleftharpoons Zn^{2+} + 2e^-$	$E^\circ_{ox} = +0.76$ V

Overall $Zn + Fe^{2+} \rightleftharpoons Zn^{2+} + Fe$ $E^\circ_{cell} = 0.32$ V

This is valid only if all species have concentrations of 1 *M*.

Le Châtelier's principle gives us some ideas. Look at the overall reaction. Consider the reaction to be at equilibrium (E_{cell} = 0 V). If we add more Fe^{2+} to the reaction mixture, The equilibrium will shift to the right to use up the excess Fe^{2+}. This will, of course cause a positive cell potential to be measurable.

Conversely, if we removed Fe^{2+} from the reaction mixture, the equilibrium would shift to the left to try to replace some of the missing Fe^{2+}. This would result in a measurable negative potential (reaction goes left).

If the reaction were not at equilibrium then these preceding two changes would me additive to the measured voltage (say standard voltage). So, if we add Fe^{2+} to a mixture at Standard Conditions, then the voltage would be more positive and if we removed some Fe^{2+} from a mixture at Standard Conditions the measured voltage would be lower (less positive).

The reverse results would be found for addition or removal of Zn^{2+} (a product). More Zn^{2+} would give a lower positive potential and *vice versa*.

Remember the relation: $\Delta G = \Delta G^\circ + RT \ln Q$ Nernst Equation for non-standard conditions

Substitute the new definition of ΔG and we get

$-nFE = -nFE^\circ + RT \ln Q$

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

(This is again called the *Nernst Equation of another form*).

Thus, we can calculate the cell potential of any cell, given only the initial conditions (to calculate Q) and the reduction potentials (to calculate E°)

We can calculate the voltage for the situation where the concentrations are not standard. For example, consider $[Fe^{2+}] = 0.1\ M$ and $[Zn^{2+}] = 1.9\ M$

For this reaction, we also know that there are two electrons transferred for each equation (n = 2).

$$\begin{aligned} E &= E^\circ - \frac{RT}{nF} \times \ln \frac{[Zn^{2+}]}{[Fe^{2+}]} \\ &= 0.32\text{V} - \frac{8.3145 \frac{\text{J}}{\text{mol K}} \times 298.15\text{K}}{2 \times 96485 \frac{\text{C}}{\text{mol}}} \times \ln \frac{1.9}{0.10} \\ &= 0.28\text{V} \end{aligned}$$

Although the reaction is 90% complete (from Standard Conditions initial) the cell potential has only dropped by a small amount (0.04 V). This is normal. For example, the batteries in your flashlight will put out almost full voltage until the last traces of chemical are almost used up at which point the voltage will drop off rather sharply. This is an especially useful characteristic of cells powering electronic equipment.

In general, for a redox cell reaction involving the transference of n electrons
$aA + bB \rightarrow cC + dD$, the EMF can be calculated as:

$$E_{Cell} = E^{\circ}_{Cell} - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Prediction and feasibility of spontaniety of a cell reaction.

Work done by the cell = nFE;

It is equivalent to decrease in free energy $\Delta G = -nFE$

Under standard state $\Delta G^0 = -nFE^0$ (i)

(i) From thermodynamics we know, ΔG = negative for spontaneous process. Thus from eq.(i) it is clear that the EMF should be +ve for a cell process to be feasible or spontaneous.

(ii) When ΔG = positive, E = negative and the cell process will be non spontaneous.

(iii) When $G = 0$, $E = 0$ and the cell will attain the equilibrium.

Reactions	**ΔG**	**E**
Spontaneous	(–)	(+)
Non- spontaneous	(+)	(–)
Equilibrium	0	0

Standard free energy change of a cell may be calculated by electrode potential data. Substituting the value of E0 (i.e., standard reduction potentialof cathode- standard reduction potential of anode) in eq. (i) we may get ΔG° .

THERMODYNAMIC TREATMENT OF NERNST EQUATION

Determination of equilibrium constant

: We know, that E = $E^0 - \frac{0.0591}{n} \log K_{eq}$ ….. (1)

At equilibrium, the cell potential is zero because cell reactions are balanced, i.e. E = 0

∴ From Eq. (i), we have

$$E^0 = \frac{0.0591}{n} \log K_{eq}$$

Or

$$K_{eq} = \text{anti} \log \left[\frac{nE^0}{0.0591} \right]$$

Recall antilog is 10 to the power

Heat of Reaction inside the cell:

Let n Faraday charge flows out of a cell of e.m.f. E, then

$-\Delta G = nFE$ ….. (i)

Gibbs Helmholtz equation (from thermodynamics) may be given as,

$$\Delta G = \Delta H + T\left[\frac{\partial \Delta G}{\partial T}\right]_p \qquad \text{(ii)}$$

From Eqs. (i) and (ii), we have

$$-nFE = \Delta H + T\left[\frac{\partial(-nFE)}{\partial T}\right]_p = \Delta H - nFT\left[\frac{\partial E}{\partial T}\right]_p$$

Thus

$$\Delta H = -nFE + nFT\left[\frac{\partial E}{\partial T}\right]_p$$

Entropy change inside the cell :

We know that G = H - TS or
$\Delta G = \Delta H - T\Delta S$ ...(i)

where
ΔG = Free energy change ;
ΔH = Enthalpy change and
ΔS = entropy change.

According to Gibbs Helmoholtz equation,

$$\Delta G = \Delta H + T\left[\frac{\partial \Delta G}{\partial T}\right]_p$$

$$\Delta G = \Delta H = T\left[\frac{\partial \Delta G}{\partial T}\right]_p$$

From Eqs. (i) and (ii), we have

$$-T\Delta S = T\left[\frac{\partial \Delta G}{\partial T}\right]_p \quad \text{or} \quad \Delta S = -\left[\frac{\partial \Delta G}{\partial T}\right]_p$$

$$\text{or} \qquad \Delta S = nF\left[\frac{\partial E}{\partial T}\right]_p$$

Where $\left[\frac{\partial E}{\partial T}\right]_p$ is called temperature coefficient of cell e.m.f.

Spoon Feeding Rule of Electrochemistry

$$\begin{array}{l} A \longrightarrow A^{+2} + 2e \quad \Delta G_1 = -0.2\text{kcal} \;....(i) \\ B \longrightarrow B^{+2} + 2e \; \Delta G_2 = +0.4\text{ kcal} \;....(ii) \end{array}$$

According to the rule of spontaneity, reaction (i) is spontaneous but reaction (ii) is non-spontaneous. To
gain full cell reaction, we convert non-spontaneous reaction into spontaneous reaction.

$$\begin{array}{lll} \textit{Same}: & A \longrightarrow A^{+2} + \cancel{2e}; & \Delta G_1 = -0.2\text{kcal} \\ \textit{Change}: & B^{+2} + \cancel{2e} \longrightarrow B; & \Delta G_2 = -0.4\text{ kcal} \\ \hline & A + B^{+2} \longrightarrow A^{+2} + B & \Delta G\text{rxn} \end{array}$$

ΔGrxn = ΔG1+ ΔG2 = (-0.2kcal) + (-0.4 kcal) = - 0.6 kcal

Recall ΔG = -nFE or E = - ΔG / nF

Spoon feeding Rule of Electrochemistry

If both half cell reactions are non-spontaneous, then we conv ert more non-spontaneous reaction into spontaneous reaction to gain full cell reaction

$$\begin{array}{l} A \longrightarrow A^{+2} + 2e \quad \Delta G_1 = +0.2\text{ kcal} \;....(i) \\ B \longrightarrow B^{+2} + 2e \quad \Delta G_2 = +0.5\text{ kcal} \;....(ii) \end{array}$$

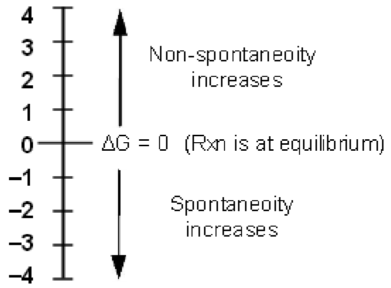
Reaction (i) is less non-spontaneous and reaction (ii) is more non-spontaneous.

$$\begin{array}{lll} \textit{Change}: & B^{+2} + \cancel{2e} \longrightarrow B & \Delta G_2 = -0.5\text{ kcal} \\ \textit{Same}: & A \longrightarrow A^{+2} + \cancel{2e} & \Delta G_1 = +0.2\text{ kcal} \\ \hline & B^{+2} + A \longrightarrow B + A^{+2} & \Delta G\text{rxn} \end{array}$$

$$\Delta G\text{rxn} = \Delta G_1 + \Delta G_2 = (-0.5) + (0.2)\text{ kcal} = -0.3\text{ kcal}$$

Recall Spontaneity of ΔG
More Positive lesser spontaneous

More negative more spontaneous



So If both half cell reactions are spontaneous then we convert less spontaneous reaction into non-spontaneous reaction.

$$A \longrightarrow A^{+2} + 2e \quad \Delta G_1 = -0.5 \text{ kcal} \quad \text{(more spontaneous)}$$
$$B \longrightarrow B^{+2} + 2e \quad \Delta G_2 = -0.2 \text{ kcal} \quad \text{(less spontaneous)}$$

$$\textit{Same :} \quad A \longrightarrow A^{+2} + \cancel{2e} \qquad \Delta G_1 = -0.5 \text{ kcal}$$
$$\textit{Change :} \quad B^{+2} + \cancel{2e} \longrightarrow B \qquad \Delta G_2 = +0.2 \text{ kcal}$$
$$A + B^{+2} \longrightarrow B + A^{+2} \quad \Delta G\text{rxn}$$

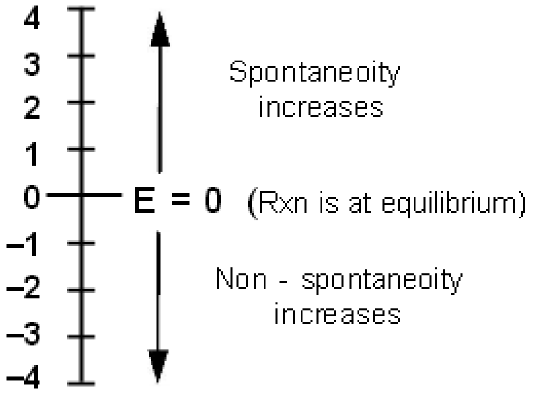
$$\Delta G \text{ rxn} = -\ 0.5 \text{ kcal} + 0.2 \text{ kcal} = -\ 0.3 \text{ kcal}$$

If ΔG° given in the half cells then spontaneity of the reaction not determined by ΔG°. We convert ΔG° into ΔG by following equation.

$$A \longrightarrow A^{+2} + 2e \quad \Delta G^o_1 = -0.2 \text{ kcal} \text{ ...(i)}$$
$$B \longrightarrow B^{+2} + 2e \quad \Delta G^o_2 = +0.5 \text{ kcal...(ii)}$$
$$\Delta G = \Delta G^o + RT \ln Q$$
$$\text{If } Q = 1 \text{ , then } \Delta G = \Delta G^o$$
$$\Delta G_1 = \Delta G^o_1 + RT \ln [A^{+2}] \text{ ....(i)}$$
$$\Delta G_2 = \Delta G^o_2 + RT \ln [B^{+2}] \text{ ....(ii)}$$

If emf of the half cell given in the problem then we predict the spontaneity of reaction by emf.
ΔG = - nFE

Spontaneity from E



Greater the reduction potential greater will be ease of reduction. Greater the oxidation potential greater will be ease of oxidation.

If the equations are given as mix of spontaneous voltage and non-spontaneous voltage, then convert them to same form

$$A \longrightarrow A^{+2} + 2e \quad E_{o.p} = -0.2\ \text{Volt} \quad (\text{non-spontaneous})$$
$$B \longrightarrow B^{+2} + 2e \quad E_{o.p} = +0.5\ \text{Volt} \quad (\text{Spontaneous})$$

$$\begin{array}{lll} \textit{Same}: & B \longrightarrow B^{+2} + \cancel{2e} & E_{O.P.} = +0.5\ \text{Volt} \\ \textit{Change}: & A^{+2} + \cancel{2e} \longrightarrow A & E_{R.P.} = +0.2\ \text{Volt} \\ \hline & B + A^{+2} \longrightarrow B^{+2} + A & E_{cell} \end{array}$$

$$E_{cell} = E_{O.P} + E_{R.P} = 0.5 + 0.2 = 0.7\ \text{Volt}$$

Spoon Feeding

$$A \longrightarrow A^{+2} + 2e \quad E_{O.P.} = +0.5\ \text{Volt} \quad (\textit{more spontaneous})$$
$$B \longrightarrow B^{+2} + 2e \quad E_{O.P.} = +0.3\ \text{Volt} \quad (\textit{Less spontaneous})$$

$$\begin{array}{lll} \textit{Same}: & A \longrightarrow A^{+2} + \cancel{2e} & E_{O.P.} = +0.5\ \text{Volt} \\ \textit{Change}: & B^{+2} + \cancel{2e} \longrightarrow B & E_{R.P.} = -0.3\ \text{Volt} \\ \hline & A + B^{+2} \longrightarrow B + A^{+2} & E_{cell} \end{array}$$

$$E_{cell} = E_{O.P.} + E_{R.P.} = +0.5 - 0.3\ \text{Volt} = +0.2\ \text{Volt}$$

Spoon Feeding

$$A \longrightarrow A^{+2} + 2e \quad E_{O.P.} = -0.5\ \text{Volt} \quad (\textit{more spontaneous})$$
$$B \longrightarrow B^{+2} + 2e \quad E_{O.P.} = -0.2\ \text{Volt} \quad (\textit{Less spontaneous})$$

$$\begin{array}{lll} \textit{Same}: & B \longrightarrow B^{+2} + \cancel{2e} & E_{O.P.} = -0.2\ \text{Volt} \\ \textit{Change}: & A^{+2} + \cancel{2e} \longrightarrow A & E_{R.P.} = +0.5\ \text{Volt} \\ \hline & A + B^{+2} \longrightarrow B + A^{+2} & E_{cell} \end{array}$$

$$E_{cell} = E_{O.P.} + E_{R.P.} = -0.2 + 0.5\ \text{Volt} = +0.3\ \text{Volt}$$

Spoon Feeding

Spontaneity of reaction not determined by standard emf. it is determined by following equation.

$$E_{O.P.} = E^{0}_{O.P.} - (0.0592/n)\log[A^{+2}]$$
$$E_{O.P.} = E^{0}_{O.P.} - (0.0592/n)\log[B^{+2}]$$

$$A \longrightarrow A^{+2} + 2e \quad E^{o}_{O.P.} = +0.5\ \text{Volt}.....(i)$$
$$B \longrightarrow B^{+2} + 2e \quad E^{o}_{O.P.} = -0.2\ \text{Volt}.....(ii)$$

Greater the O.P. greater will be ease of oxidation.

Rule for converting oxidation half cell into reduction half cell and vice-versa

We determined spontaneity of reaction by E° value, however it is not correct. These are two possible result one is correct and other is incorrect. If Emf of the cell is +ve then our result is correct, but Emf of the cell is –ve, then our result is incorrect, to gain correct result we convert oxidation half cell into reduction half cell and reduction half cell into oxidation half cell.

$A \longrightarrow A^{+2} + 2e \quad E_{O.P.} = -0.2$ Volt

If you want to gain reduction half cell then

$A^{+2} + 2e \longrightarrow A \quad E_{R.P.} = +0.2$ Volt

$B \longrightarrow B^{+2} + 2e \quad E_{O.P.} = +0.5$ Volt

If you want to gain reduction half cell then

$B^{+2} + 2e \longrightarrow B \quad E_{R.P.} = -0.5$ Volt

To calculate Ecell we convert all the half cell reactions are in same type (either oxidation half or reduction half)

$A \longrightarrow A^{+2} + 2e \quad E_{O.P.} = 0.2$ Volt
$B^{+2} + 2e \longrightarrow B \quad E_{R.P.} = 0.5$ Volt

Ecell = ?

(i) Convert both reaction into oxidation half

$A \longrightarrow A^{+2} + 2e \quad E_{O.P.} = 0.2$ Volt
$B \longrightarrow B^{+2} + 2e \quad E_{O.P.} = -0.5$ Volt

(ii) Convert both reaction into reduction half cell

$A^{+2} + 2e \longrightarrow A \quad E_{R.P.} = -0.2$ Volt
$B^{+2} + 2e \longrightarrow B \quad E_{R.P.} = 0.5$ Volt

Same : $B^{+2} + \cancel{2e} \longrightarrow B \quad E_{R.P.} = 0.5$ Volt
Change : $A \longrightarrow A^{+2} + \cancel{2e} \quad E_{O.P.} = +0.2$ Volt

$B^{+2} + A \longrightarrow A^{+2} + B \quad E_{cell} = 0.7$ Volt

For following type half cell reaction hybrid reaction quotients (mixture of Qp and Qc) used in place of Qc or Qp

$H_2 \longrightarrow 2H^+ + 2e$ (no. of electron used = 2)

$$Q_{Hybrid} = \frac{[H^+]^2 \; mol/litre}{(P_{H_2}) \; atm}$$

$1/2H_2 \longrightarrow H^+ + 1e$ (no. of electron used = 1)

$$Q_{Hybrid} = \frac{[H^+]}{(P_{H_2})^{1/2}}$$

$Cl_2 + 2e \longrightarrow 2Cl^-$ (no. of electron used = 2)

$$Q_{Hybrid} = \frac{[Cl^-]^2}{(P_{Cl_2})}$$

$Cl^- \longrightarrow Cl_2 + 1e$ (no. of electron used = 1)

$$Q_{Hybrid} = \frac{(P_{Cl_2})^{1/2}}{[Cl^-]}$$

Emf is mass or mole independent property (intensive property), but free energy is mass or mole dependent
property (Extensive property)

$H_2 \longrightarrow 2H^+ + 2e$; $E_{O.P.} = x$ volt, $\Delta G = -2Fx$

$1/2H_2 \longrightarrow H^+ + 1e$; $E_{O.P.} = x$ volt, $\Delta G = -Fx$

Emf of the reaction not depends on stoichiometry coeff.

Example: $2X + 3y \longrightarrow 5A$ $E_{cell} = x$ volt

$X + y \longrightarrow A$ $E_{cell} = x$ volt

If reaction is spontaneous in forward direction then non-spontaneous in reverse direction and vice-versa.
Magnitude of Emf and ΔG are same but sign is reverse.

$A \longrightarrow A^{+2} + \cancel{2e}$; $E_{O.P.} = X$ volt, $\Delta G = -2FX$

$A^{+2} + \cancel{2e} \longrightarrow A$ $\Delta G = +2FX$, $\Delta G = -nFE$

$\Delta G = -nFE_{R.P.}$

$$E_{R.P.} = \Delta G/-nF = 2FX/-2F = -X \text{ volt}$$

If two half cell (no. of electron same or different) produces full cell reaction then for simplicity we adddirectly emf of half cell not ΔG. Addition of ΔG gives same result but process is lengthy.

$$A \longrightarrow A^{+2} + \cancel{2e} \qquad E_1$$
$$B^{+2} + \cancel{2e} \longrightarrow B \qquad E_2$$

$$B^{+2} + A \longrightarrow A^{+2} + B \qquad E_{cell} = E_1 + E_2$$

If we proceed this problem by ΔG then.

$$A \longrightarrow A^{+2} + \cancel{2e} \qquad \Delta G_1 = -2FE_1$$
$$B^{+2} + \cancel{2e} \longrightarrow B \qquad \Delta G_2 = -2FE_2$$

$$B^{+2} + A \longrightarrow A^{+2} + B \qquad \Delta G rxn = \Delta G_1 + \Delta G_2$$

$$-2FEcell = -2FE_1 - 2FE_2$$

$$\boldsymbol{E_{cell} = E_1 + E_2}$$

If no. of electron involved and apparent in reaction then reaction is half cell. But if no. of electron involved but not apparent in the reaction then reaction is full cell reaction.

Example:

$Fe \longrightarrow Fe^{+3} + 3e$ oxidation half cell, n=3

$Fe^{+3} + 1e \longrightarrow Fe^{+2}$ reduction half cell, n= 1

$2Fe^{+3} + 3I^{-} \longrightarrow 2Fe^{+2} + I_3^{-}$ full cell rxn, n=2

$MnO_4^{-} + 4H^{+} + 3e \longrightarrow 2H_2O + MnO_2$

reduction half cell, n = 3

$Fe^{+2} \longrightarrow Fe^{+3} + 1e$ oxidation half cell, n=1

If two half cell reaction having different no. of electron provide full cell reaction then we also add Emf for simplicity.

Example :

$$2\times (A \longrightarrow A^{+3} + 3e) \quad E_1, \quad \Delta G_1 = -6FE_1$$
$$3\times (B^{+2} + 2e \longrightarrow B)\, E_2, \quad \Delta G_2 = -6FE_2$$

$$2A + 3B^{+2} \longrightarrow 2A^{+3} + 3B, \ \Delta G rxn = -6FE_3$$

$$\Delta G rxn = \Delta G_1 + \Delta G_2 = -6FE_1 - 6FE_2 = -6FE_3$$

$$E_3 = E_1 + E_2$$

If two half cell produces third half cell then we should not added Emf directly. To calculate emf of third half cell we add ΔG,

$$A \longrightarrow A^{+3} + 3e\ ; \qquad E_1,\ \Delta G_1 = -3FE_1$$
$$B^{+2} + 2e \longrightarrow B\ ; \qquad E_2,\ \Delta G_2 = -2FE_2$$
$$A + B^{+2} \longrightarrow A^{+3} + B + 1e \qquad E_3\ {}^{1}\ E_1 + E_2$$
$$\Delta G_3 = \Delta G_1 + \Delta G_2 \ \eth\ -1FE_3 = -3FE_1 + (-2FE_2)$$
$$E_3 = 3E_1 + 2E_2$$

For writing shorthand notation or cell representation of electrochemical cell following conventions are used.

$$A \longrightarrow A^{+2} + \cancel{2e} \qquad E_{O.P} = 0.5\ \text{volt}$$
$$B^{+2} + \cancel{2e} \longrightarrow B \qquad E_{R.P} = 0.2\ \text{volt}$$
$$A + B^{+2} \longrightarrow B + A^{+2} \qquad E_{cell} = 0.7\ \text{volt}$$

DIFFERENT TYPES OF HALF-CELLS AND THEIR REDUCTION POTENTIAL

(1) Gas-Ion Half Cell:

In such a half cell, an inert collector of electrons, platinum or graphite is in contact with gas and a solution containing a specified ion. One of the most important gas-ion half cell is the hydrogen-gas-hydrogen ion half cell. In this half cell, purified H2 gas at a constant pressure is passed over a platinum electrode which is in contact with an acid solution.

H^+ + (aq) + e^- -> ½ H_2

So

$$E_{H^+/H_2} = E^0_{H^+/H_2} - \frac{0.0591}{1} \log \frac{(pH_2)^{1/2}}{[H^+]}$$

(2) Metal-Metal Ion Half Cell:

This type of cell consist of a metal M in contact with a solution containing M^{n+} ions.

M^{n+} (aq) + ne -> M(s)

$$E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$$

(3) Metal-Insoluble Salt - Anion Half Cell:
In this half cell, a metal coated with its insoluble salt is in contact with a solution containing the anion of the insoluble salt. eg. Silver-Silver Chloride Half Cell:

This half cell is represented as $Cl^-/AgCl/Ag$. The equilibrium reaction that occurs at the electrode is $AgCl(s) + e \rightarrow Ag(s) + Cl^- \ (aq)$

$$E_{Cl^- / AgCl / Ag} = E^0_{Cl^- / AgCl / Ag} - \frac{0.0591}{1}\log\left[Cl^-\right]$$

potential of such cells depends upon the concentrate ion of anions. Such cells can be used as Reference Electrode.

(4) Oxidation-reduction Half Cell:

This type of half cell is made by using an inert metal collector, usually platinum, immersed in a solution which contains two ions of the same element in different states of oxidation.
eg. $Fe^{2+} \rightarrow Fe^{3+}$ half cell.

$Fe^{3+} (aq) + e \rightarrow Fe^{2+} (aq)$

$$E_{Fe^{3+} / Fe^{2+}} = E^0_{Fe^{3+} / Fe^{2+}} - \frac{0.0591}{1}\log\frac{\left[Fe^{2+}\right]}{\left[Fe^{3+}\right]}$$

CONCENTRATION CELL

The cells in which electrical current is produced due to transport of a substance from higher to lower concentration. Concentration gradient may arise either in electrode material or in electrolyte. Thus there are two types of concentration cell.

(i) Electrode concentration cell
(ii) Electrolyte concentration cell

Electrode Gas concentration cell :
$Pt, H_2(P1) \mid H^+(C) \mid H_2(P2), Pt$

Here, hydrogen gas is bubbled at two different partial pressures at electrode dipped in the solution of same electrolyte.

Cell Process : ½ H_2 (P1) -> H^+ (c) + e^- (Anode Process)

$$\frac{H^+ (c) + e^- > 1/2 \ H_2 (P_2)}{1/2 \ H (P_1) < -- > 1/2 \ H_2 (P_2)}$$

So E = $-\left[\frac{2.303RT}{F}\right]\log\left[\frac{p_2}{p_1}\right]^{1/2}$ Recall - Log (a / b) is log (b / a)

Or or $E = \left[\frac{2.303RT}{2F}\right]\log\left[\frac{p_1}{p_2}\right]$, At 25^0C , $E = \frac{0.059}{2F}\log\left[\frac{p_1}{p_2}\right]$

For spontaneity of such cell reaction, p1>p2

Electrolyte concentration cells:

$$Zn(s) \mid ZnSO_4\,(C_1) \parallel ZnSO_4\,(C_2) \mid Zn(s)$$

In such cells, concentration gradient arise in electrolyte solutions. Cell process may be given as,

$$Zn(s) \rightarrow Zn^{2+}(C_1) + 2e \qquad \text{(Anodic process)}$$

$$\frac{Zn^{2+}(C_2) + 2e \longrightarrow Zn(s)}{Zn^{2+}(C_2) \rightarrow Zn^{2+}(C_1)} \qquad \text{(Over all process)}$$

∴ From Nernst equation, we have

$$E = 0 - \frac{2.303RT}{2F}\log\left[\frac{C_1}{C_2}\right] \quad \text{or} \quad E = \frac{2.303RT}{2F}\log\left[\frac{C_2}{C_1}\right]$$

For spontanity of such cell reaction, C2> C_1

Conductance

Introduction:

Both metallic and electrolytic conductors obey Ohm's law i.e.
V = IR

where V = Potential difference in volt; I = Current in ampere ; R = resistance in Ohm

We know, resistance is directly proportional to length of conductor and inversely proportional to cross sectional area of the conductor.

$$R \propto \frac{l}{A} \quad \text{or} \quad R = \rho\frac{l}{A} \qquad (\ \rho = \text{Specific resistance}\ )$$

Specific resistance is the resistance of a conductor having lengths of 1 cm and corss sectional area of 1 cm^2 .

Unit of R is ohm and unit of specific resistance is ohm cm Reciprocal of resistance is called as conductance and reciprocal of specific resistance is called as specific conductance.

$\frac{1}{R} = \frac{1}{\rho}\frac{A}{l}$ or C = KA / L

where C = conductance ohm^{-1} ; K = specific conductance ohm^{-1} cm^{-1} .
Mho and siemens are other units of conductance

So $K = LC / A$

Specific conductance= Cell constant x Conductance

Specific Conductance is conductance of 1 Cm^3 of an electrolyte Solution.

In case of electrolytic solution, the specific conductance is defined as the conductance of a solution of definite concentration enclosed in a cell having two electrodes of unit area separated by 1 cm apart.

1. Equivalent Conductance

Equivalent conductance is the conductance of an electrolyte solution containing 1 gm equivalent of electrolyte. It is denoted by $\wedge$.

$\wedge = K \times V$

$(\wedge = ohm^{-1}\ cm^{-1} \times cm^3 = ohm^{-1}\ cm^2)$

Usually concen ration of electrolyte solution is expressed as C gm equivalent per litre.

Thus, $V = 1000 / C$

Also $\wedge = K \times 1000 / C$

2. Molar Conductance

Molar conductance may be defined as conductance of an electrolyte solution having 1 gm mole electrolyte in a litre. It is denoted by $\wedge_m$.

$\wedge_m = K \times V$

Usually concentration of electrolyte solution is expressed as ‘M’ gm mole elecrtrolyte per litre.

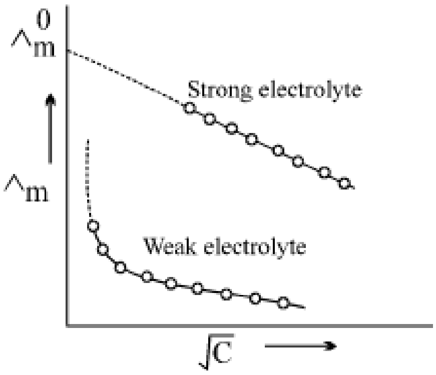
Thus, $V = \frac{1000}{M}$

Hence, $\wedge_m = K x \frac{1000}{M}$

Relation between $\wedge$ and $\wedge_m$: $\wedge_m = n \times \wedge$

Determination of $\wedge_m^0$ **OR** $\wedge^0$

A plot of $\wedge_m$ vs $\sqrt{C}$ as found experimentally; is as shown below.



The $\wedge_m$ vs $\sqrt{C}$ plot of strong electrolyte being linear it can be extrapolated to zero concentration.

Thus, ∧m values of the solution of the test electrolyte are determined at various concentrations the concentrations should be as low as good.

∧m values are then plotted against √C when a straight line is obtained. This is the extrapolated to zero concentration. The point where the straight line intersects ∧m axis is ∧° m of the strong electrolyte.

However, the plot in the case weak electrolyte being non linear, shooting up suddenly at some low concentration and assuming the shape of a straight line parallel to ∧m axis. Hence extrapolation in this case is not possible. Thus, ∧0 of a weak electrolyte cannot be determined experimentally. It can, however, be done with the help of Kohlrausch's law.

Kohlrausch's Law of Independent Migration of Ions

Kohlrausch determined ∧0 values of pairs of some strong electrolytes containing same cation say KF and KCl, NaF and NaCl etc., and found that the difference in ∧0 values in each case remains the same:

$$\wedge_m^0(KCl) - \wedge_m^0(KF) = \wedge_m^0(NaCl) - \wedge_m^0(NaF)$$

He also detemined ∧0 values of pairs of strong electrolytes containing same anion say KF and NaF, KCl and NaCl etc.and found that the difference in ∧0 values in each case remains the same.

$$\wedge_m^0(KF) - \wedge_m^0(NaF) = \wedge_m^0(KCl) - \wedge_m^0(NaCl)$$

This experimental data led him to formulate the following law called Kohlrausch's law of independent migration of ions.

At infinite dilution when dissociation is complete, every ion makes some definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion which with it is associated and that the molar conductance at infinite dilution for any electrolyte is given by the sum of the contribution of the two ions. Thus,

$$\wedge_m^0 = \lambda_+^0 + \lambda_-^0$$

Where λ_+^0 is the contribution of the cation and λ_-^0 s the contribution of the anion towards the molar conductance at infinite dilution. These contributions are called molar ionic conductances at infinite dilution. Thus, λ_+^0 is the molar ionic conductance of cation and λ_-^0 is the molar ionic conductance of anion, at infinite dilution. The above equation is, however, correct only for binary electrolyte like NaCl, MgSO4 etc.

Application of Kohlrausch's law :

(1) Determination of $\wedge_m^0$ of a weak electrolyte:

In order to calculate $\wedge_m^0$ of a weak electrolyte say CH_3COOH, we determine experimentally $\wedge_m^0$ values of the following three strong electrolytes:

(a) A strong electrolyte containing same cation as in the test electrolyte, say HCl

(b) A strong electrolyte containing same anion as in the test electrolyte, say CH_3COONa

(c) A strong electrolyte containing same anion of (a) and cation of (b) i.e. NaCl.

$\wedge_m^0$ of CH_3COOH is then given as:

$$\wedge_m^0 (CH_3COOH) = \wedge_m^0 (HCl) + \wedge_m^0 (CH_3COONa) - \wedge_m^0 (NaCl)$$

Proof:

$$\wedge_m^0 (HCl) = \lambda_H^0 + \lambda_{Cl^-} \qquad ....(i)$$

$$\wedge_m^0 (CH_3COO\mathbf{Na}) = \lambda^0_{\mathbf{CH_3COO^-}} + \lambda_{Na^+} \qquad ...(ii)$$

$$\wedge_m^0 (\mathbf{Nacl}) = \lambda^0_{Na^+} + \lambda^0_{Cl^-} \qquad ...(iii)$$

Adding equation (i) and equation (ii) and subtracting (iii) from them:

$$\wedge_m^0 \mathbf{(HCl)} + \wedge^0_{(CH_3COONa)} - \wedge^0_{\mathbf{(NaCl)}} = \lambda^0_{(H^+)} + \lambda^0_{(CH_3COO^0)} = \wedge_{0(CH_3COOH)}$$

(2) Determination of degree of dissociation (α) :

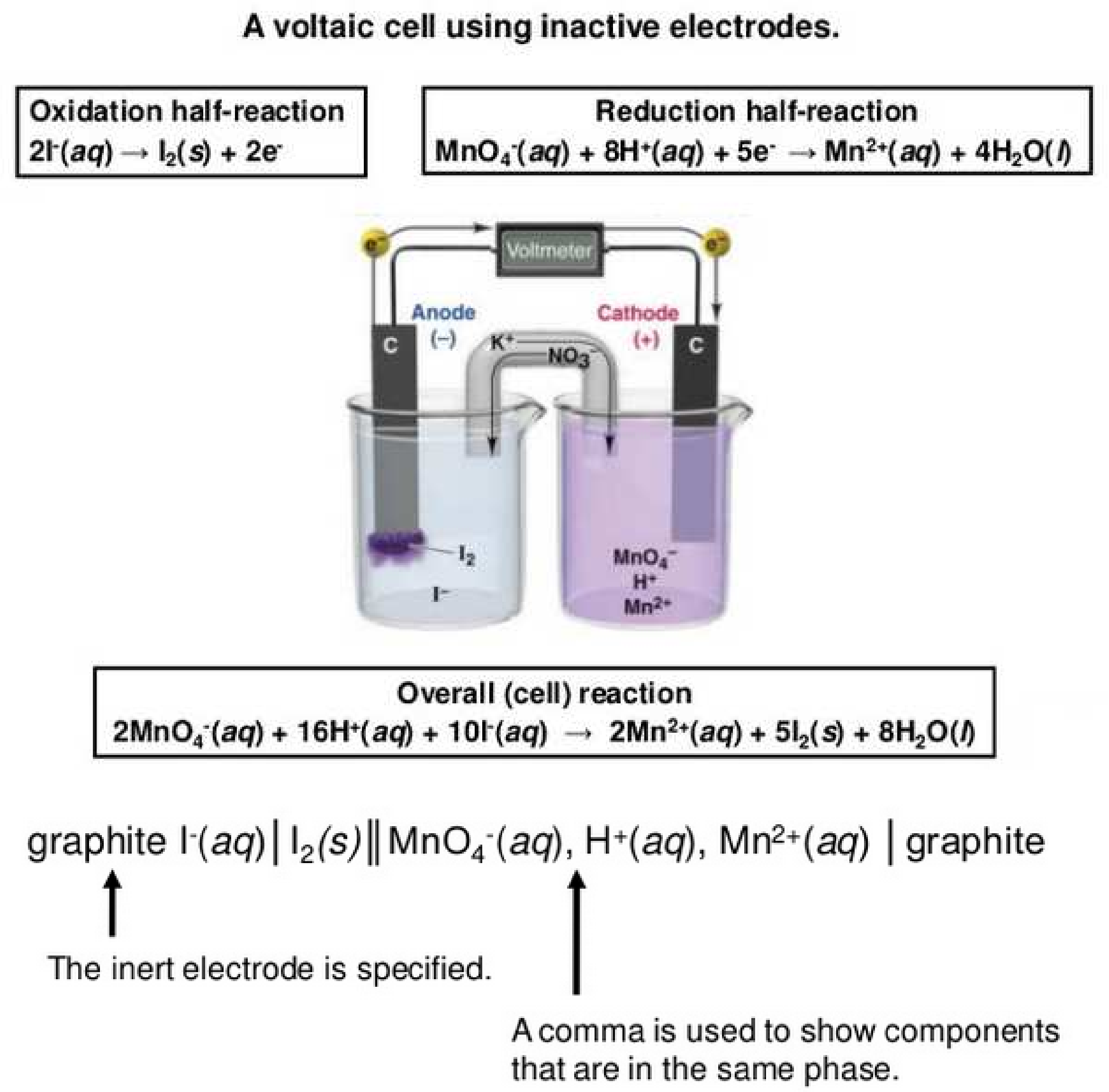
$$\alpha = \frac{\textbf{No. of molecules ionised}}{\textbf{Total no. of molecules dissolved}} = \frac{\wedge_m}{\wedge_m^{\mathbf{0}}}$$

(3) Determination of solubility of sparingly soluble Salt

The specific conductivity of a saturated solution of the test electrolyte (sparingly soluble) made in conductivity water is determined by the method as described above. From this the specific conductivity of conductivity water is deducted. The molar conductance of the saturated solution is taken to be equal to $\wedge_m^{\mathbf{0}}$ as the saturated solution of a sparingly soluble salt is extremely dilute. Hence from equation (4).

$$\wedge_m^0 = \frac{1000\kappa}{C},$$

where C is the molarity of solution and hence the solubility.



A voltaic cell using inactive electrodes.

Oxidation half-reaction
$2I^-(aq) \rightarrow I_2(s) + 2e^-$

Reduction half-reaction
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

Overall (cell) reaction
$2MnO_4^-(aq) + 16H^+(aq) + 10I^-(aq) \rightarrow 2Mn^{2+}(aq) + 5I_2(s) + 8H_2O(l)$

graphite $I^-(aq) | I_2(s) \| MnO_4^-(aq), H^+(aq), Mn^{2+}(aq)$ | graphite

The inert electrode is specified.

A comma is used to show components that are in the same phase.

A voltaic cell is made of aqueous Bromine and Zinc. Given -

$Br_2(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + 2Br^-(aq)$ $E_{cell} = 1.83$ V.

Calculate $E_{bromine}$, given that $E_{zinc} = -0.76$ V

Solution :

$Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$ [reduction; cathode]

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ [oxidation; anode] $E°_{zinc} = -0.76$ V

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

$1.83 = E_{bromine} - (-0.76)$

$1.83 - 0.76 = E_{bromine}$ **= 1.07 Volt**

-

What is the equilibrium constant for the reaction of copper metal with bromine to form copper(II) ions and bromide ions in aqueous solution at 25 °C?

Cathode $Br_2 + 2e^- \rightleftarrows 2\ Br^-$ $E°_{red} = 1.09$ V

Anode $Cu \rightleftarrows Cu^{2+} + 2e^-$ $E°_{ox} = -E°_{red} = -0.34$ V

Cell $Cu + Br_2 \rightleftarrows Cu^{2+} + 2\ Br^-$ $E°_{cell} = 0.75$

$$\ln K = \frac{nFE°}{RT} = \frac{2 \times 96458 \frac{C}{mol} \times 0.75\ V}{8.31451 \frac{J}{mol\ K} \times 298.15 K} = 58.38_{208}$$

$$K = e^{58.38_{208}} = 2.2 \times 10^{25}$$

-

Using half reactions write the spontaneous Redox reactions

$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ $E°_{tin} = -0.14$ V

$Ag^+(aq) + e^- \rightarrow Ag(s)$ $E°_{silver} = 0.80$ V

We have to multiply the Silver reaction with 2 to balance and match electrons

Note : This does not change the voltage obtained

$\mathbf{2}Ag^+(aq) + \mathbf{2}e^- \rightarrow \mathbf{2}Ag(s)$ $E°_{silver} = 0.80$ V

Now we need to add the half reactions to eliminate the electrons, but subtract to get the Voltage correctly. **Recall** $E^o_{cell} = E_{Right} - E_{Left} = E_{Cathode} - E_{Anode} = (E_{Reduction\ (\ Right\ )} - E_{Reduction\ (\ Left\ )})$

$$\begin{array}{ll}
Sn(s) \rightarrow Sn^{2+}(aq) + 2e^{-} & E^{\circ}_{tin} = -0.14\ V \\
2Ag^{+}(aq) + 2e^{-} \rightarrow 2Ag(s) & E^{\circ}_{silver} = 0.80\ V \\
\hline
Sn(s) + 2Ag^{+}(aq) \rightarrow 2Ag(s) + Sn^{2+}(aq) & E^{\circ}_{cell} = 0.94\ V
\end{array}$$

$$E^{\circ}_{cell} = E^{\circ}_{silver} - E^{\circ}_{tin} = 0.80 - (-0.14) = 0.94\ V$$

Cathode provides electrons. Ag ions are receiving electrons at Cathode. Anode is positive where electrons are lost. See Tin is more metallic (than Silver) and is looses electrons in Anode.

It is easier to visualize the Voltage as gap in electrode potential. Silver is higher up than Hydrogen in the series. Thus has positive electrode potential. While Tin is more metallic, below Hydrogen in the series. The gap is of 0.94 Volts.

-

Zinc and Magnesium Oxide Battery

Anode (oxidation): $Zn(s) + 2OH^{-}(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^{-}$

Cathode (reduction): $MnO_2(s) + 2H_2O(l) + 2e^{-} \rightarrow Mn(OH)_2(s) + 2OH^{-}(aq)$

Overall (cell) reaction:

$$Zn(s) + MnO_2(s) + H_2O(l) \rightarrow ZnO(s) + Mn(OH)_2(s) \quad E_{cell} = 1.5\ V$$

-

Zinc and Magnesium Oxide Battery

Anode (oxidation): $Zn(s) + 2OH^{-}(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^{-}$

Cathode (reduction): $Ag_2O(s) + H_2O(l) + 2e^{-} \rightarrow 2Ag(s) + 2OH^{-}(aq)$

Overall (cell) reaction: $Zn(s) + Ag_2O(s) \rightarrow ZnO(s) + 2Ag(s)$

$$E_{cell} = 1.6\ V$$

The mercury battery uses HgO as the oxidizing agent instead of Ag_2O and has cell potential of 1.3 V.

-

The Lithium Batteries use Silver Vanadium Pentoxide as cathode

Anode (oxidation):

$$3.5Li(s) \rightarrow 3.5Li^{+} + 3.5e^{-}$$

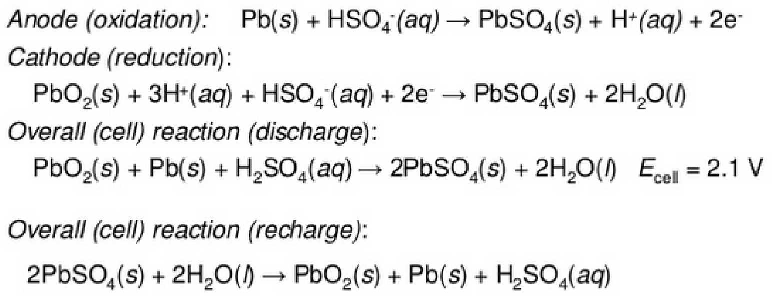
Cathode (reduction):

$$AgV_2O_{5.5} + 3.5Li^{-} + 3.5e^{-} \rightarrow Li_{3.5}V_2O_{5.5}$$

Overall (cell) reaction:

$$AgV_2O_{5.5} + 3.5Li(s) \rightarrow Li_{3.5}V_2O_{5.5}$$

The most commonly used Battery is Lead-Acid Battery



Anode (oxidation): $Pb(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2e^-$

Cathode (reduction):

$PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

Overall (cell) reaction (discharge):

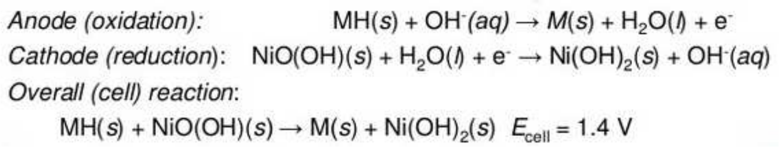
$PbO_2(s) + Pb(s) + H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l) \quad E_{cell} = 2.1\ V$

Overall (cell) reaction (recharge):

$2PbSO_4(s) + 2H_2O(l) \rightarrow PbO_2(s) + Pb(s) + H_2SO_4(aq)$

-

Nickel Metal Hydride Battery



Anode (oxidation): $MH(s) + OH^-(aq) \rightarrow M(s) + H_2O(l) + e^-$

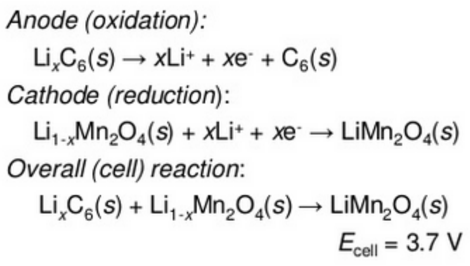
Cathode (reduction): $NiO(OH)(s) + H_2O(l) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)$

Overall (cell) reaction:

$MH(s) + NiO(OH)(s) \rightarrow M(s) + Ni(OH)_2(s) \quad E_{cell} = 1.4\ V$

-

Laptops, Cell-phones most commonly use Lithium ion Batteries



Anode (oxidation):

$Li_xC_6(s) \rightarrow xLi^+ + xe^- + C_6(s)$

Cathode (reduction):

$Li_{1-x}Mn_2O_4(s) + xLi^+ + xe^- \rightarrow LiMn_2O_4(s)$

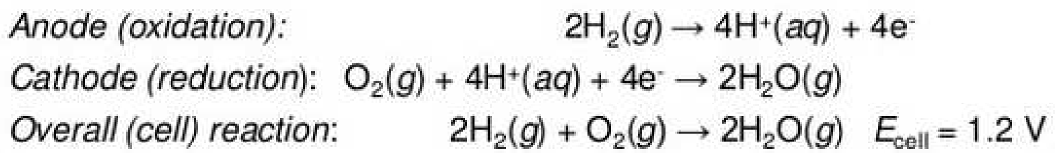
Overall (cell) reaction:

$Li_xC_6(s) + Li_{1-x}Mn_2O_4(s) \rightarrow LiMn_2O_4(s)$

$E_{cell} = 3.7\ V$

-

Hydrogen Fuel Cell



Anode (oxidation): $2H_2(g) \rightarrow 4H^+(aq) + 4e^-$

Cathode (reduction): $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(g)$

Overall (cell) reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \quad E_{cell} = 1.2\ V$

-

What is the value of the solubility product constant for AgCl?

We could calculate this by breaking the overall K_{sp} reaction into a series of redox reactions as follows:

Anode	$Ag(s) \rightarrow Ag^+ + e^-$	$E^\circ_{ox} = -0.80$ V
Cathode	$AgCl + e^- \rightarrow Ag(s) + Cl^-$	$E^\circ_{red} = 0.22$ V
Overall **(° K_{sp} reaction)**	$AgCl \rightleftarrows Ag^+ + Cl^-$	$E^\circ_{cell} = -0.58$ V (not very spontaneous)

$$\ln K = \frac{nFE^\circ}{RT} = \frac{1 \times 96485\frac{C}{mol}(-0.58\,V)}{8.3145\frac{J}{mol\,K} \times 298.15K} = 22.5_{744}$$

$K = 6.3 \times 10^{-9}$

-

Ion Concentrations can also be calculated...

Consider the Platinum-Hydrogen electrode coupled with a copper/copper(II) electrode.

The overall reaction is $Cu^{2+} + H_2 \rightarrow Cu + 2H^+$.

The Nernst equation is

$$E = E^\circ - \frac{8.31451\frac{J}{mol\,K} \times 298.15\,K}{2\,mol \times 96485\frac{C}{mol}} \times \ln\left(\frac{a(H^+)^2}{a(Cu^{2+}) \times a(H_2)}\right)$$

$$E = E^\circ - \frac{.0257\,V}{2} \times \ln\left(\frac{a(H^+)^2}{a(Cu^{2+}) \times a(H_2)}\right) \qquad \text{since}$$

$$\frac{8.31451\frac{J}{mol\,K} \times 298.15\,K}{96485\frac{C}{mol}} = .0256_{928}\,V$$

If $[Cu^{2+}] = 1\,M$ and $P(H_2) = 1$ bar (both their activities are 1) then

$$E = E^\circ - \frac{0.0257\,V}{2} ln[H^+]^2$$

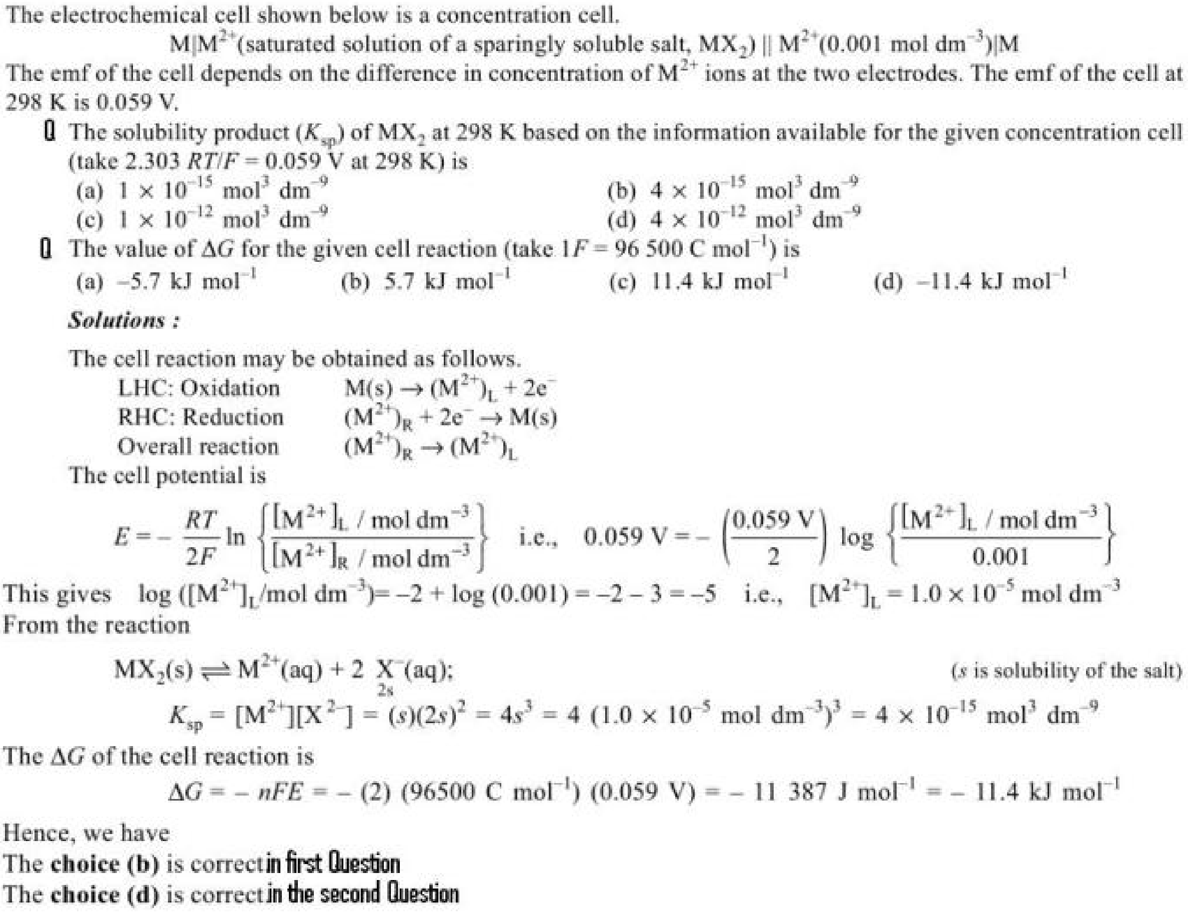
$E = E^\circ - 0.0257$ V ln $[H^+]$ (Note: ln $Y = 2.303 \times \log Y$ and .-257×2.303=.05917)

$E = E^\circ + 0.05917$ V (-log $[H^+]$)

$E = E^\circ + 0.05917\text{ V} \times \text{pH}$.

We see here that the cell potential is a function of pH. The probes in pH meters are set up this way. A complete electrochemical cell is contained within the probe casing. All chemicals are at standard conditions and a porous glass membrane allows only H^+ ions to pass through.

Electrochemical Cell



The electrochemical cell shown below is a concentration cell.

$$M|M^{2+}(\text{saturated solution of a sparingly soluble salt, } MX_2)\ ||\ M^{2+}(0.001\text{ mol dm}^{-3})|M$$

The emf of the cell depends on the difference in concentration of M^{2+} ions at the two electrodes. The emf of the cell at 298 K is 0.059 V.

- The solubility product (K_{sp}) of MX_2 at 298 K based on the information available for the given concentration cell (take $2.303\,RT/F = 0.059$ V at 298 K) is
  (a) 1×10^{-15} mol³ dm⁻⁹ — written as $1 \times 10^{-15}\text{ mol}^3\text{ dm}^{-9}$
  (b) $4 \times 10^{-15}\text{ mol}^3\text{ dm}^{-9}$
  (c) $1 \times 10^{-12}\text{ mol}^3\text{ dm}^{-9}$
  (d) $4 \times 10^{-12}\text{ mol}^3\text{ dm}^{-9}$
- The value of ΔG for the given cell reaction (take $1F = 96\,500\text{ C mol}^{-1}$) is
  (a) -5.7 kJ mol^{-1} (b) 5.7 kJ mol^{-1} (c) 11.4 kJ mol^{-1} (d) -11.4 kJ mol^{-1}

Solutions :

The cell reaction may be obtained as follows.

LHC: Oxidation $M(s) \rightarrow (M^{2+})_L + 2e^-$
RHC: Reduction $(M^{2+})_R + 2e^- \rightarrow M(s)$
Overall reaction $(M^{2+})_R \rightarrow (M^{2+})_L$

The cell potential is

$$E = -\frac{RT}{2F}\ln\left\{\frac{[M^{2+}]_L / \text{mol dm}^{-3}}{[M^{2+}]_R / \text{mol dm}^{-3}}\right\} \quad \text{i.e.,} \quad 0.059\text{ V} = -\left(\frac{0.059\text{ V}}{2}\right)\log\left\{\frac{[M^{2+}]_L / \text{mol dm}^{-3}}{0.001}\right\}$$

This gives $\log([M^{2+}]_L/\text{mol dm}^{-3}) = -2 + \log(0.001) = -2 - 3 = -5$ i.e., $[M^{2+}]_L = 1.0 \times 10^{-5}\text{ mol dm}^{-3}$

From the reaction

$$MX_2(s) \rightleftharpoons M^{2+}(aq) + 2\underset{2s}{X^-}(aq); \qquad (s \text{ is solubility of the salt})$$

$$K_{sp} = [M^{2+}][X^{2-}] = (s)(2s)^2 = 4s^3 = 4\,(1.0 \times 10^{-5}\text{ mol dm}^{-3})^3 = 4 \times 10^{-15}\text{ mol}^3\text{ dm}^{-9}$$

The ΔG of the cell reaction is

$$\Delta G = -nFE = -(2)\,(96500\text{ C mol}^{-1})\,(0.059\text{ V}) = -11\,387\text{ J mol}^{-1} = -11.4\text{ kJ mol}^{-1}$$

Hence, we have
The **choice (b)** is correct in first Question
The **choice (d)** is correct in the second Question

Let us always remember the basics. If something, say M, looses electrons, it is getting oxidized. Metals are basic. Metals loose electrons and gets oxidized. The metals which loose electron very easily, get oxidized very easily. So these are better reducing agent.

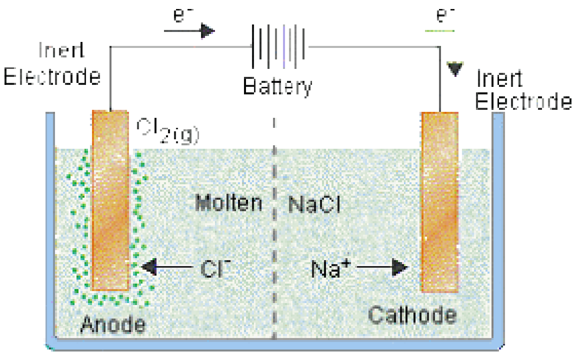
Adding of Oxygen, or Halogens (F, Cl, Br, I) or other p-Block elements which accept electrons, is oxidation. So if Potassium (K) gets Oxygen (attaches to O) to form K_2O or KO_2 (Superoxide), K is getting oxidized. If Cs attaches with F then Cs is getting oxidized, while F is being reduced. Cs is a reducing agent as it is loosing electrons. F is an oxidizing agent as it is gaining electrons.

Adding of Hydrogen is reduction. So if Ethene receives Hydrogen to become Ethane, then Ethene is being reduced. Raney Nickel is Nickel with molecular level pores. Raney Ni with HCl gives Hydrogen atoms, (some teachers say this as Nascent Hydrogen) locally, meaning near the molecule where the reaction is needed. So Raney Ni + HCl is a good reducing agent. Same for Zinc dust + HCl. But then what is Birch reduction ?

As my experience of teaching more than 25 years, almost every student understands these. Knowing this is essential but does not ensure success in Organic chemistry. There are many kinds of details of oxidizing agent or Reducing agent that vary from reactions / situations.

A simple binary ionic compounds contains only two elements - a metal and a non-metal. When the ionic compound is in the molten state, the locked ions within the ionic structure will be free to move about (conduct electricity).

A typical setup for electrolysis of molten compounds is shown below:



The metallic ions (cations - M^{n+}) will be discharged at the cathode to form a metal atom. The metallic ions are REDUCED to metal at the cathode. (because they gain electrons)

$$Mn++ne-\longrightarrow M$$

The non-metallic ions (anions - N^{n-}) will be discharged at the anode to form a non-metallic atom. The non-metallic ions are OXIDISED to non-metallic atom at the anode. (because they lose electrons)

$$N^{n-} \rightarrow N + ne-$$

Case Study: Electrolysis of molten sodium chloride, *NaCl*

Electrodes: Carbon rods (Graphite)

Electrolytes: Molten sodium chloride

Ions present in electrolytes: Sodium ions ($Na+$), Chloride ions ($Cl-$)

Reaction at the CATHODE:

- $Na+$ ions are attracted to the cathode.

- Each $Na+$ ion gains one electron from the cathode to form one sodium atom.

- Molten sodium is formed at the anode.

- equation: $Na^+(l)+e^-\longrightarrow Na(s)$ (Reduction)

Reaction at the ANODE:

- Cl^- ions are attracted to the anode.

- Each Cl^- ions loses one electrons to the anode to form one chlorine atom.
- Chlorine gas is liberated at anode.
- equation: $2Cl^-(l)\rightarrow Cl_2(g)+2e^-$ (Oxidation)

Overall reaction:

- Every 2 moles of sodium chloride produce 2 moles of sodium metal and 1 mole of chlorine gas
- $2NaCl(l)\rightarrow 2Na(s)+Cl_2(g)$

Case Study: Electrolysis of molten magnesium oxide, MgO

Electrodes: Carbon rods (Graphite)

Electrolyte: Molten magnesium oxide

Ions present in electrolyte: Magnesium ions (Mg^{2+}), Oxygen ions (O^{2-})

Reaction at the CATHODE:

- Mg^{2+} ions are attracted to the cathode.

- Each Mg^{2+} ion gains two electrons from the cathode to form one magnesium atom.
- $Mg^{2+}(l)+2e^-\longrightarrow Mg(s)$

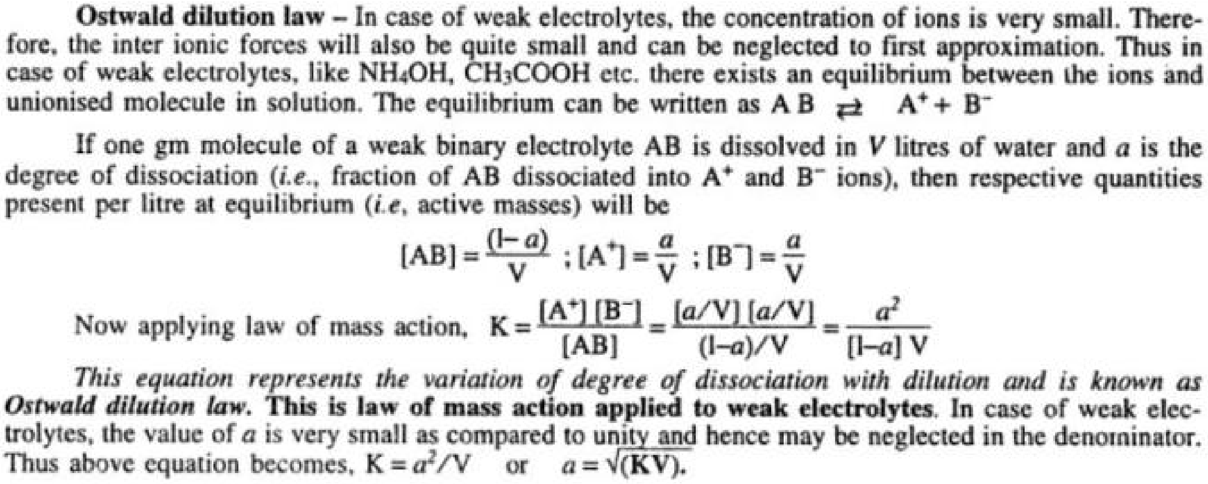
Reaction at the ANODE:

- O^{2-} ions are attracted to the anode.

- Each O^{2-} ion loses two electrons to the anode to form one oxygen atom.
- $2O^{2-}(l)\rightarrow O_2(g)+4e^-$

Overall reaction:

- Every two moles of magnesium oxide produce two moles of magnesium metal and one mole of oxygen gas.
- $2MgO(l)\rightarrow 2Mg(s)+O_2(g)$



Ostwald dilution law – In case of weak electrolytes, the concentration of ions is very small. Therefore, the inter ionic forces will also be quite small and can be neglected to first approximation. Thus in case of weak electrolytes, like NH_4OH, CH_3COOH etc. there exists an equilibrium between the ions and unionised molecule in solution. The equilibrium can be written as $AB \rightleftarrows A^+ + B^-$

If one gm molecule of a weak binary electrolyte AB is dissolved in *V* litres of water and *a* is the degree of dissociation (*i.e.*, fraction of AB dissociated into A^+ and B^- ions), then respective quantities present per litre at equilibrium (*i.e*, active masses) will be

$$[AB] = \frac{(1-a)}{V}\ ;\ [A^+] = \frac{a}{V}\ ;\ [B^-] = \frac{a}{V}$$

Now applying law of mass action, $K = \frac{[A^+]\,[B^-]}{[AB]} = \frac{[a/V]\,[a/V]}{(1-a)/V} = \frac{a^2}{[1-a]\,V}$

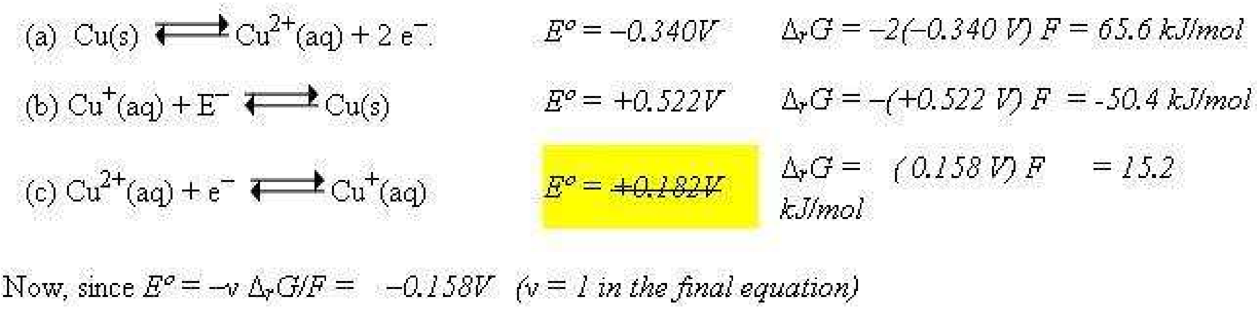
This equation represents the variation of degree of dissociation with dilution and is known as ***Ostwald dilution law.*** **This is law of mass action applied to weak electrolytes**. In case of weak electrolytes, the value of *a* is very small as compared to unity and hence may be neglected in the denominator. Thus above equation becomes, $K = a^2/V$ or $a = \sqrt{(KV)}$.

Gyan Question :

Determine the standard potential of the Cu^{2+}/Cu^+ cell from two other standard cell potentials.
$E°(Cu^{2+}/Cu) = +0.340V$ and $E°(Cu^+/Cu) = +0.522$ V.

Since Hess' Law allows us to add Gibbs energies for the reactions to arrive at the Gibbs energy of the desired reaction, we should go via Gibbs energies. Convert our standard potentials into Gibbs energies, perform the addition and then convert back to a standard potential.

The two reactions that will occur are:



(a) $Cu(s) \rightleftarrows Cu^{2+}(aq) + 2\ e^-$. $E^o = -0.340V$ $\Delta_r G = -2(-0.340\ V)\ F = 65.6\ kJ/mol$

(b) $Cu^+(aq) + E^- \rightleftarrows Cu(s)$ $E^o = +0.522V$ $\Delta_r G = -(+0.522\ V)\ F = -50.4\ kJ/mol$

(c) $Cu^{2+}(aq) + e^- \rightleftarrows Cu^+(aq)$ $E^o =$ ~~$+0.182V$~~ $\Delta_r G = (0.158\ V)\ F = 15.2\ kJ/mol$

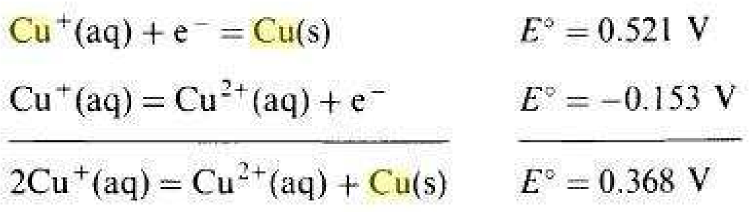
Now, since $E^o = -v\ \Delta_r G/F = -0.158V$ ($v = 1$ in the final equation)

We cannot simply add the electrode potentials in this case because, the final reaction is still a half-reaction.

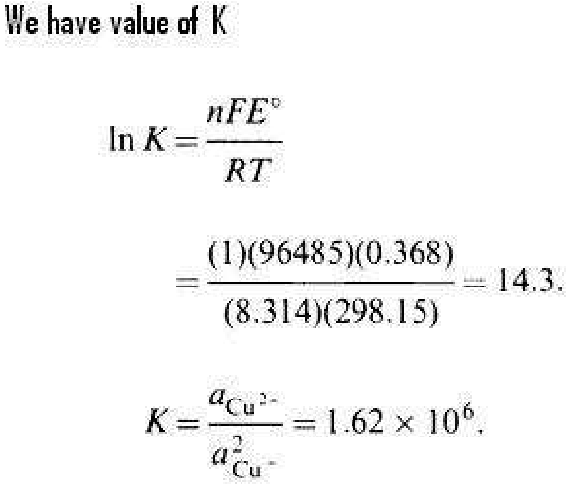
If the final reaction is a complete cell reaction, with no electrons remaining, then we can skip to just adding the cell potentials because the factor v would be the same in all equations and hence, cancel out.

(1): $Cu^+ (aq) + e^- \rightarrow Cu (s) \quad E^o = 0.521$ V
(2): $Cu^{2+} (aq) + e^- \rightarrow Cu^+ (aq) \quad E^o = 0.153$V

(1) is reduction and drives (2) as oxidation
$2\ Cu^+ (aq) \rightarrow Cu^{2+} (aq) + Cu (s) \quad E^o_{cell} = 0.521 - 0.153 = 0.368$ V (>0)
Which means $E^o_{rxn} > 0$ and $\Delta G^o_{rxn} < 0$ spontaneous. Yes it disproportionates.



$$Cu^+(aq) + e^- = Cu(s) \qquad E^\circ = 0.521\ V$$
$$Cu^+(aq) = Cu^{2+}(aq) + e^- \qquad E^\circ = -0.153\ V$$
$$2Cu^+(aq) = Cu^{2+}(aq) + Cu(s) \qquad E^\circ = 0.368\ V$$

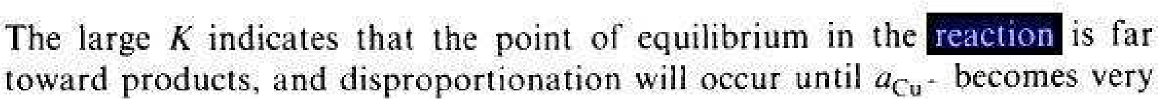


We have value of K

$$\ln K = \frac{nFE^\circ}{RT}$$

$$= \frac{(1)(96485)(0.368)}{(8.314)(298.15)} = 14.3.$$

$$K = \frac{a_{Cu^{2+}}}{a^2_{Cu^+}} = 1.62 \times 10^6.$$



The large K indicates that the point of equilibrium in the reaction is far toward products, and disproportionation will occur until a_{Cu^+} becomes very

small

Discuss Disproportion of Iron

Decide whether Fe^{2+} (*aq*) in its standard state at 25°C is stable w/r/t disproportionation.

In Appendix E we find:
(1): $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)\ E^o = 0.771V$
(2): $Fe^{2+}(aq) + 2e^- \rightarrow Fe\,(s)\ E^o = -\,0.447V$

In order for Fe^{2+} (*aq*) to disproportionate reaction (1) would have to be driven backwards (oxidation): $3Fe^{2+} \rightarrow Fe\,(s) + 2Fe^{3+}(aq)$
And $E^o = -0.447 - (+0.771) = -1.218$ V (< 0) and $\Delta G^o_{rxn} > 0$ (non-spontaneous) and therefore stable against disproportionation.

0.01 M Solution of HCN has a specific resistance of x ohm cm Its equivalent conduction would be ?

(a) 10 x (b) 100x (c) 10^5 / x (d) 10^5 x

$$C = 0{\cdot}01\ M = 0{\cdot}01\ N\ (\text{for HCN})$$

$$\therefore \quad V = \frac{1}{0{\cdot}01} = 100\ \text{litres/eq}$$

$$\text{or,} \quad V = 100 \times 1000\ cm^3$$

$$kv = \frac{1}{\text{Specific resistance}}$$

$$= \frac{1}{x}\ ohm^{-1}\ cm^{-1}$$

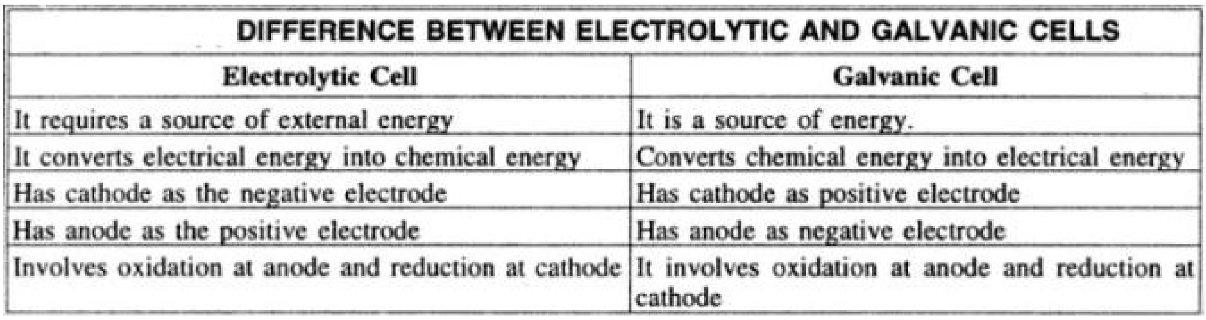
Equivalent conductance

$$\lambda v = kv \times V$$

$$= \frac{1}{x} \times 100 \times 1000$$

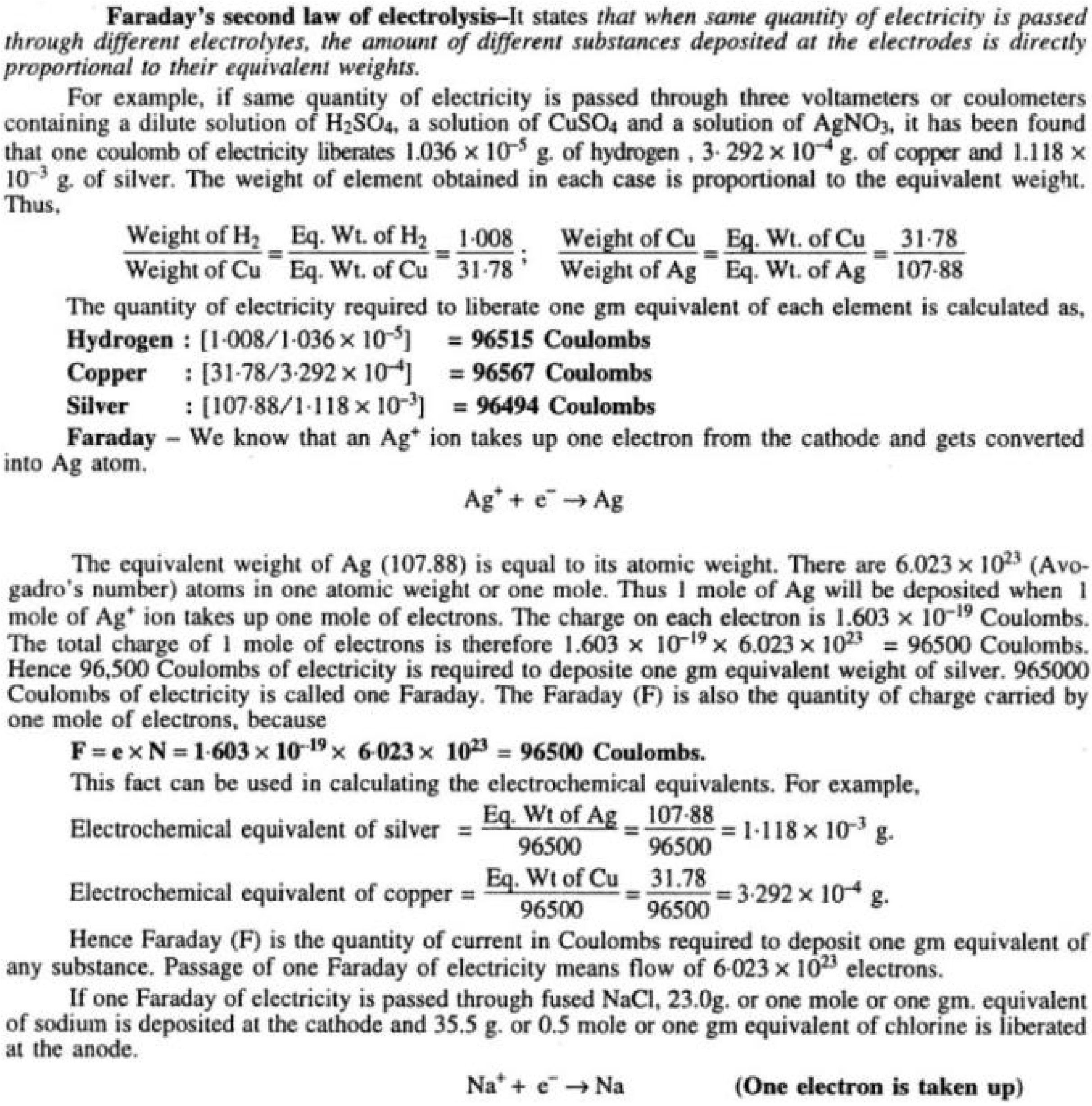
$$= \frac{10^5}{x}\ ohm^{-1}\ cm^2$$

Recall again



DIFFERENCE BETWEEN ELECTROLYTIC AND GALVANIC CELLS

Electrolytic Cell	Galvanic Cell
It requires a source of external energy	It is a source of energy.
It converts electrical energy into chemical energy	Converts chemical energy into electrical energy
Has cathode as the negative electrode	Has cathode as positive electrode
Has anode as the positive electrode	Has anode as negative electrode
Involves oxidation at anode and reduction at cathode	It involves oxidation at anode and reduction at cathode



Faraday's second law of electrolysis–It states *that when same quantity of electricity is passed through different electrolytes, the amount of different substances deposited at the electrodes is directly proportional to their equivalent weights.*

For example, if same quantity of electricity is passed through three voltameters or coulometers containing a dilute solution of H_2SO_4, a solution of $CuSO_4$ and a solution of $AgNO_3$, it has been found that one coulomb of electricity liberates 1.036×10^{-5} g. of hydrogen , $3{\cdot}292 \times 10^{-4}$ g. of copper and 1.118×10^{-3} g. of silver. The weight of element obtained in each case is proportional to the equivalent weight. Thus,

$$\frac{\text{Weight of } H_2}{\text{Weight of Cu}} = \frac{\text{Eq. Wt. of } H_2}{\text{Eq. Wt. of Cu}} = \frac{1{\cdot}008}{31{\cdot}78}; \quad \frac{\text{Weight of Cu}}{\text{Weight of Ag}} = \frac{\text{Eq. Wt. of Cu}}{\text{Eq. Wt. of Ag}} = \frac{31{\cdot}78}{107{\cdot}88}$$

The quantity of electricity required to liberate one gm equivalent of each element is calculated as,

Hydrogen : $[1{\cdot}008/1{\cdot}036 \times 10^{-5}]$ **= 96515 Coulombs**

Copper : $[31{\cdot}78/3{\cdot}292 \times 10^{-4}]$ **= 96567 Coulombs**

Silver : $[107{\cdot}88/1{\cdot}118 \times 10^{-3}]$ **= 96494 Coulombs**

Faraday – We know that an Ag^+ ion takes up one electron from the cathode and gets converted into Ag atom.

$$Ag^+ + e^- \rightarrow Ag$$

The equivalent weight of Ag (107.88) is equal to its atomic weight. There are 6.023×10^{23} (Avogadro's number) atoms in one atomic weight or one mole. Thus 1 mole of Ag will be deposited when 1 mole of Ag^+ ion takes up one mole of electrons. The charge on each electron is 1.603×10^{-19} Coulombs. The total charge of 1 mole of electrons is therefore $1.603 \times 10^{-19} \times 6.023 \times 10^{23} = 96500$ Coulombs. Hence 96,500 Coulombs of electricity is required to deposite one gm equivalent weight of silver. 965000 Coulombs of electricity is called one Faraday. The Faraday (F) is also the quantity of charge carried by one mole of electrons, because

$$\mathbf{F = e \times N = 1{\cdot}603 \times 10^{-19} \times 6{\cdot}023 \times 10^{23} = 96500 \text{ Coulombs.}}$$

This fact can be used in calculating the electrochemical equivalents. For example,

$$\text{Electrochemical equivalent of silver} = \frac{\text{Eq. Wt of Ag}}{96500} = \frac{107{\cdot}88}{96500} = 1{\cdot}118 \times 10^{-3} \text{ g.}$$

$$\text{Electrochemical equivalent of copper} = \frac{\text{Eq. Wt of Cu}}{96500} = \frac{31.78}{96500} = 3{\cdot}292 \times 10^{-4} \text{ g.}$$

Hence Faraday (F) is the quantity of current in Coulombs required to deposit one gm equivalent of any substance. Passage of one Faraday of electricity means flow of $6{\cdot}023 \times 10^{23}$ electrons.

If one Faraday of electricity is passed through fused NaCl, 23.0g. or one mole or one gm. equivalent of sodium is deposited at the cathode and 35.5 g. or 0.5 mole or one gm equivalent of chlorine is liberated at the anode.

$$Na^+ + e^- \rightarrow Na \qquad \textbf{(One electron is taken up)}$$

If one Faraday of electricity is passed through $CuCl_2$ solution, one gm. equivalent weight of copper ions is discharged at the cathode. This is only 1/2 mole of copper, since copper is bivalent.

$Cu^{2+} + 2e^- \rightarrow Cu$ **(Two electrons are taken up)**

If one Fraday of electricity is passed through $AlCl_3$ solution, one gm. equivalent of Al^{3+} ions is discharged at the cathode. This is only 1/3 mole of Al^{3+} ions, because Al is trivalent.

$Al^{3+} + 3e^- \rightarrow Al$ **(Three electrons are taken up)**

In other words, for depositing one mole of Na atoms, one mole of copper atoms and one mole of aluminium atoms, we need one, two and three moles of electrons respectively. In general, to deposit one mole of atoms of any metal of valency Z, we need Z moles of electrons. Thus,

$$M = e.Z.F \qquad ...... (3)$$

where M is the mass of **one mole.** Now we know $W = e.Q$ where $Q = c \times t$ Thus,

$$\frac{W}{M} = \frac{e.Q}{e.ZF} = \frac{Q}{Z.F} = \frac{c \times t}{Z.F} \qquad ...... (4)$$

If weight deposited (W), the mass of one mole (M) and Z, the number of electrons in the process are known, the quantity of electricity Q (=c× t) can be measured by using equation (4) by using a device, known as **coulometer.** We have seen that for depositing one gm atomic weight (1 mole) of copper, 2 Faradays of electricity are required. The amount of copper that can be deposited by one faraday is

$$\frac{\text{1 gm. Atomic Weight}}{2} = \frac{63.5}{2} = 31{\cdot}8\text{ g.}$$

Thus the equivalent weight (E) of copper is 31.8 g. **In general, equivalent weight (E) of an element is,**

$$E = \frac{\text{Gram Atomic Weight of Element}}{Z}$$

where Z is the number of electrons in the process. For example, Na^+ and Ag^+ ions require one electron for reduction. Hence their equivalent weights are equal to their atomic weights. Similarly, Cl^- ion loses one electron to oxidise into Cl atom. Hence its atomic weight is equal to its equivalent weight, i.e., 35.5 g. Hence

$$E = \frac{\text{1 Gm Mole}}{Z} = \frac{M}{Z} \qquad ...... (5)$$

When atoms of the element are deposited, M is called gm atomic weight, and when molecules are evolved or discharged *M* is called gm molecular weight.

Applications of electrolysis – There are various industrial applications of electrolysis. For example, **(a) Electrometallurgy –** The metals like Na, K, Mg, Al etc. are obtained by the electrolysis of fused electrolytes. **(b) Electrorefining of metals –** A large number of metals, such as Cu, Ag, Au, Al, Sn etc. are purified by electrolysis. **(c) Manufacture of compounds –** Electrolysis has also been used in the large scale production of various compounds such as NaOH, KOH, KCl, Na_2CO_3, H_2O_2 etc. **(d) Manufacture of non-metals –** Electrolysis has been employed also in the manufacture of H_2, Cl_2, F_2 etc. **(e) Electroplating** – Deposition of precious metals like Ag, Au, Pt etc. on less expensive metals like Cu is known as **electroplating.** This is also carried out by electrolysis. **(f) Preparation of alloys and electrotyping–** Electrolysis is very useful in the preparation of alloys and also in electrotyping.

Electrical conductivity – Electrical conductivity is the conductivity in mhos of a solution containing one gm equivalent of solute when placed between two sufficiently large electrodes which are one cm apart. It is denoted by λ_V. The equivalent conductivity is related to the specific conductivity by the expression

$$\lambda_V = K_V \times V \qquad \text{...... (9)}$$

where V is the volume in c.c. of the solution containing one gm equivalent of an electrolyte.

Molecular conductivity – It is the conductivity in mhos of a solution containing one gm mole of the solute when placed between two sufficientaly large electrodes which are exactly one cm apart. It is denoted by λ_m and is numerically equivalent to the product of sp. conductivity and the volume V in c.c. of the solution containing one gm. mole of the electrolyte. Thus

$$\lambda_m = K_V \times V \qquad \text{.... (10)}$$

Cell constant – The conductivity of a solution is measured by a cell, known as **conductivity cell.** The electrodes in this cell may not be exactly one cm apart and may not have an area of one sq. cm. Thus the value of observed conductivity will not be equal to the specific conductivity, but a value proportional to it. It is therefore essential to calculate a factor for the conductivity cell, called the **cell constant**, which when multiplied by the observed conductivity gives the value of specific conductivity. The value of the conductivity will, therefore, have to be multiplied by a certain factor inorder to get specific conductivity. This factor is known as **cell constant**. We know

$$R = \rho \times l/a = \rho \times x, \text{ where } x = l/a = \text{cell constant}$$

$$\text{Thus } \mathbf{x} \text{ (}\textbf{cell constant}\text{)} = \frac{R}{\rho} = \frac{1/\text{observed conductivity}}{1/\text{sp. conductivity}}.$$

So, Specific Conductivity = Cell constant (x) × Obs. Conductivity

Inorder to determine the cell constant, the conductivity cell is filled with exact N/50 solution of chemically pure KCl. The specific conductivity of this solution at 25^{0}C has been found to be 0.002765 mhos. The cell is placed in a thermostat at 25^{0}C and the resistance and hence the conductivity of the solution is determined. Thus

$$\textbf{Cell Constant} = \frac{0{\cdot}002765}{\text{Observed conductivity}}$$

The cell constant is expressed in **cm^{-1}**.

The important conditions for the cell to be reversible are :

(a) *If the external e.m.f. or potential is equal to the e.m.f. of the cell, no current flows through the cell and no chemical reaction occurs at all.*

(b) *If the external e.m.f. or potential is slightly smaller than the e.m.f. of the cell, a small current flows out of the cell and a small amount of chemical reaction takes place in the cell.*

(c) *If the external e.m.f. or potential is slightly more than the e.m.f. of the cell, current flows into the cell and cell reaction is reversed.*

(d) *A cell which does not fulfil the above conditions is said to be irreversible.*

Effect of dilution on conductivity – (a) The conductivity of the solution increases with dilution, because it depends upon the number of ions present in the solution. On dilution, the degree of ionisation of electrolyte increases and more ions are produced in the solution. **The greater the number of ions, the greater is the conductivity.**

(b) The specific conductivity decreases on dilution. This is due to the fact that although the total number of ions increases with dilution owing to increased dissociation, the number of current carrying particles or ions per c.c. decreases. This causes a decrease in specific conductivity.

(c) Equivalent and molecular conductivity both increase with dilution as these are the products of specific conductivity (K_V) and volume V of the solution containing one gm equivalent and one gm mole of the solute dissolved respectively. On dilution, more and more electrolyte ionises (degree of ionisation increases). When whole of the substance has ionised further dilution produces little or no change in the equivalent and molecular conductivities. This limiting value of equivalent conductivity (or molecular conductivity) is called the **equivalent conductivity at infinite dilution.** The ratio of equivalent conductivity at any dilution to that at infinite dilution (λ_∞) is called the **conductivity ratio** (α). Thus $\alpha = \lambda_V/\lambda_\infty$

It should be noted that increase in equivalent conductivity in the case of **strong electrolytes** like KCl, NaCl, HCl etc is not so large (because these are already highly ionised) as in case of **weak electrolytes** such as CH_3COOH, NH_4OH etc (becase they are slightly ionised and their ionisation increases with dilution).

Migration of ions – Electricity is carried through the solution of an electrolyte by migration of ions. The ions are present independently in solution and when a current of electricity is passed through the solution, the ions present in it move towards the oppositely charged electrodes. Thus,

(a) The ions move towards the oppositely charged electrodes at different speeds.

(b) During electrolysis, the ions are discharged or liberated in equivalent amounts at the two electrodes, no matter what their relative speed is.

(c) Concentration of the electrolyte changes around the electrodes as a result of difference in the speed of the ions.

(d) Loss of concentration around any electrode is proportional to the speed of the ion that moves away from the electrode. Thus,

$$\frac{\text{Fall Round Anode}}{\text{Fall Round Cathode}} = \frac{\text{Speed of Cation}}{\text{Speed of Anion}}$$

This relation is valid on the assumption that the discharged ions do not react with the atoms or material of the electrodes. But in many cases, they do combine with the electrode and in such cases, the concentration around such an electrode shows an increase, rather than a decrease. Electrolysis of $AgNO_3$ solution using silver electrodes is an example of such a case. On electrolysis, it has been observed that instead of fall, the concentration of $AgNO_3$ around the anode increases, because every NO_3^- ion that reaches at the anode dissolves from it one Ag^+ ion to form $AgNO_3$.

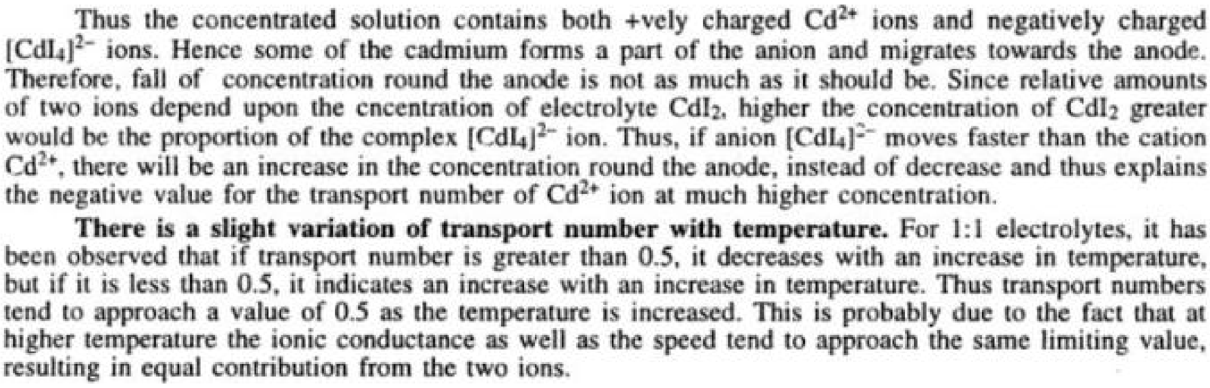
Transport number or transference number – The fraction of the current carried by an ion is termed as its transport number or transference number. If n_a and n_c are the transport numbers of anion and cation respectively then

$$n_a = \frac{\text{Current Carried by Anion}}{\text{Total Current Carried}} \qquad n_c = \frac{\text{Current Carried by Cation}}{\text{Total Current Carried}}$$

and $n_a + n_c = 1$

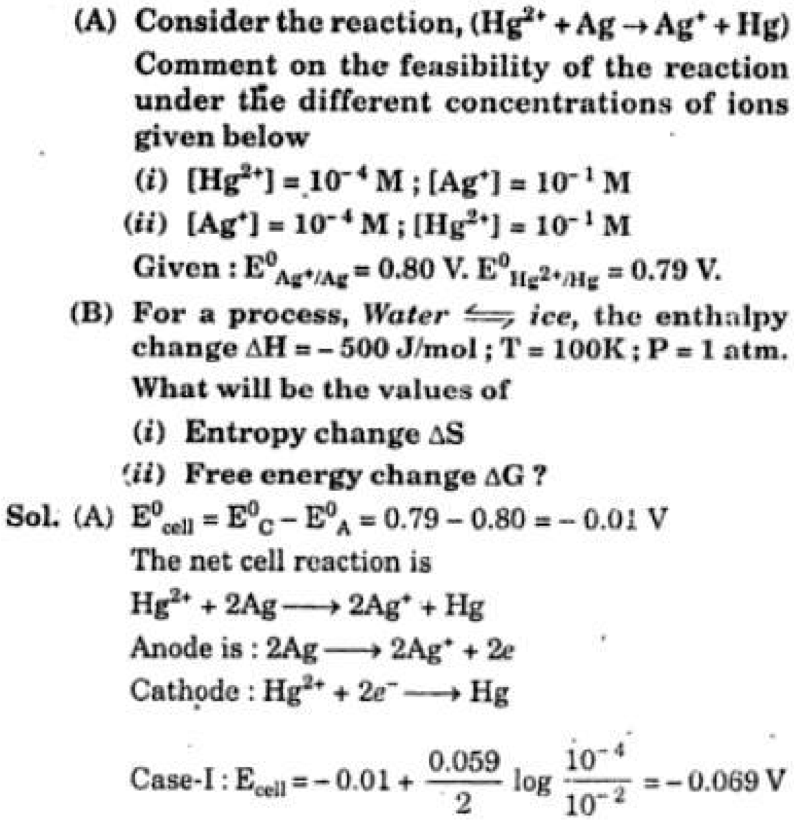
Concentration has marked effect on the transport number, especially in the case of some partially dissociated electrolytes such as ZnI_2, CdI_2 etc. For example, concentration has a marked effect on the transport number of cadmium ion in CdI_2. The value decreases from 0.49 at low concentration to almost zero at higher concentrations and the values become negative at still higher concentrations. The transport numbers of cadmium ions in 0.01N. 0.05N, 0.02N and 0.50N CdI_2 at 25°C are 0.449, 0.402,0.131, and 0.005 respectively. This abnormal behaviour can be explained by assuming:

(a) That in very dilute solution, CdI_2 ionises to Cd^{2+} ions and I^- ions and thus Cd^{2+} shows the usual transport number. $CdI_2 \rightleftarrows Cd^{2+} + 2I^-$. (b) That with increase in concentration, CdI_2 takes on I^- ions and forms complex, $CdI_2 + 2I^- \rightleftarrows [CdI_4]^{2-}$



Thus the concentrated solution contains both +vely charged Cd^{2+} ions and negatively charged $[CdI_4]^{2-}$ ions. Hence some of the cadmium forms a part of the anion and migrates towards the anode. Therefore, fall of concentration round the anode is not as much as it should be. Since relative amounts of two ions depend upon the cncentration of electrolyte CdI_2, higher the concentration of CdI_2 greater would be the proportion of the complex $[CdI_4]^{2-}$ ion. Thus, if anion $[CdI_4]^{2-}$ moves faster than the cation Cd^{2+}, there will be an increase in the concentration round the anode, instead of decrease and thus explains the negative value for the transport number of Cd^{2+} ion at much higher concentration.

There is a slight variation of transport number with temperature. For 1:1 electrolytes, it has been observed that if transport number is greater than 0.5, it decreases with an increase in temperature, but if it is less than 0.5, it indicates an increase with an increase in temperature. Thus transport numbers tend to approach a value of 0.5 as the temperature is increased. This is probably due to the fact that at higher temperature the ionic conductance as well as the speed tend to approach the same limiting value, resulting in equal contribution from the two ions.



(A) Consider the reaction, ($Hg^{2+} + Ag \rightarrow Ag^+ + Hg$) Comment on the feasibility of the reaction under the different concentrations of ions given below

(i) $[Hg^{2+}] = 10^{-4}$ M ; $[Ag^+] = 10^{-1}$ M

(ii) $[Ag^+] = 10^{-4}$ M ; $[Hg^{2+}] = 10^{-1}$ M

Given : $E^0_{Ag^+/Ag} = 0.80$ V. $E^0_{Hg^{2+}/Hg} = 0.79$ V.

(B) For a process, *Water* ⇋ *ice*, the enthalpy change $\Delta H = -500$ J/mol ; T = 100K ; P = 1 atm. What will be the values of

(i) Entropy change ΔS

(ii) Free energy change ΔG ?

Sol. (A) $E^0_{cell} = E^0_C - E^0_A = 0.79 - 0.80 = -0.01$ V

The net cell reaction is

$Hg^{2+} + 2Ag \longrightarrow 2Ag^+ + Hg$

Anode is : $2Ag \longrightarrow 2Ag^+ + 2e$

Cathode : $Hg^{2+} + 2e^- \longrightarrow Hg$

$$\text{Case-I} : E_{cell} = -0.01 + \frac{0.059}{2} \log \frac{10^{-4}}{10^{-2}} = -0.069 \text{ V}$$

So Reaction not feasible as E(cell) is negative

$$\text{Case-II} : E_{cell} = -0.01 + \frac{0.059}{2} \log \frac{10^{-2}}{10^{-4}} = +0.049\,V$$

∴ Feasible because E_{cell} is + ve.

(B) The given process is

$H_2O(l) \rightleftharpoons H_2O(s)$

(*i*) $\Delta S = \frac{\Delta H}{T} = \frac{-500}{100} = -5 J\,mol^{-1}\,K^{-1}$

(*ii*) At equilibrium $\Delta G = 0$.

Kohlrausch law – This law states that the value of equivalent conductivity at infinite dilution (λ_∞) may be regarded as made up of the sum of two independent factors, one characteristic of cation and other to anion. Thus,

$$\lambda_\infty = \lambda_a + \lambda_c \qquad ...(12)$$

If we consider a salt NaCl, its equivalent conductivity at infinite dilution is the sum of two terms, one due to Na^+ ion (λ_{Na^+}) and other due to Cl^- ion (λ_{Cl^-}). **These terms are known as ionic mobilities of anion and cation. The ratio of ionic mobilities is equal to their transport numbers.** Thus,

$$\frac{\lambda_a}{\lambda_c} = \frac{n_a}{n_c} = \frac{n_a}{(1-n_a)} \quad (\text{Since } n_a + n_c = 1) \qquad ...(13)$$

*The **absolute velocity** of an ion may be defined as the velocity of an ion in cm per sec. when it moves under an electric field due to two electrodes placed one cm. apart and having a potential difference of one volt between them (i.e.,under unit potential gradient).*

Hence unit of absolute velocity is **cm.per sec. (volts per.cm), i.e, cm² per. sec. per volt.** The absolute velocity is numerically equal to the ionic mobility divided by one **Faraday (96500 Coulombs).** Thus,

$$U = \frac{\lambda_a}{96500} \qquad V = \frac{\lambda_c}{96500}$$

From equation(13) We have $\frac{\lambda_a}{\lambda_c} = \frac{n_a}{1-n_a}$ or $\lambda_a - n_a\lambda_a = n_a\lambda_c$

$$\lambda_a = n_a(\lambda_a + \lambda_c) = n_a \times \lambda_\infty \quad (\text{since } \lambda_a + \lambda_c = \lambda_\infty) \qquad ..(14)$$

Hence conductance of an ion is obtained by multiplying the equivalent conductivity at infinite dilution of any strong electrolyte containing that ion by its transport number. Similarly,

$$\lambda_c = n_c \times \lambda_\infty$$

Applications of Kohlrausch law – (1) In the determination of ionic mobilities and absolute velocity of ions, (2) Calculation of equivalent conductivities of weak electrolytes at infinite dilution. (3) Determination of degree of dissociation, since, α, the degree of dissociation of an electrolyte at the dilution V is given by $\alpha = \lambda_V/\lambda_\infty$ (where $\lambda_\infty = \lambda_a + \lambda_c$)

Gyan Question :

Q : What is carborundum ? Does it conduct electricity ?

Ans :

Silicon carbide, also known as carborundum, is a compound of silicon and carbon with chemical formula SiC. It occurs in nature as the extremely rare mineral moissanite. Silicon carbide powder has been mass-produced since 1893 for use as an abrasive.

Grains of silicon carbide can be bonded together by sintering to form very hard ceramics that are widely used in applications requiring high endurance, such as car brakes, car clutches and ceramic plates in bulletproof vests. Electronic applications of silicon carbide as light-emitting diodes (LEDs) and detectors in early radios were first demonstrated around 1907, and today SiC is widely used in high-temperature/high-voltage semiconductor electronics.

Relative tendencies of electrodes to liberate electrons – When two electrodes are connected to from a cell, a competition sets in between the two electrodes to liberate electrons. For example, if the cell consists of zinc and copper electrodes, as in Daniell cell, the electrons flow from negative zinc electrode to positive copper electrode, because zinc has a greater tendency to liberate electrons than copper. If the cell is constituted with copper and silver electrodes, then copper has a greater tendency to liberate electrons than silver. This indicates that copper is negative electrode and silver is positive electrode and electrons flow from copper to silver electrode. If a cell is set up with Zn and H_2 (g) electrodes, then zinc has a greater tendency to liberate electrons than the H_2(g) electrode. This indicates that electrons will flow from negative zinc electrode to positive H_2(g) electrode. If the cell is constituted with copper and H_2(g) electrodes, **then H_2(g) electrode has a greater tendency to liberate electrons than the copper electrode.** This indicates that electrons will flow from negative H_2(g) electrode to positive copper electrode. Thus in the above cases, the tendency of the electrodes to release electrons decreases in the order **Zn > H_2(g) >Cu > Ag**

It should be noted that electrode at which electrons are released is written on the left, while that at which electrons are taken up is written on the right. for example,

$$Cu \mid Cu^{2+} \parallel Ag^{+} \mid Ag \qquad Zn \mid Zn^{2+} \parallel H^{+}, \mid H_2(g)$$

$AgNO_3$ solution turns blue when a piece of copper is dded to it, because copper metal can be oxidised by Ag^+ ions. Ag can not be oxidised by Cu^{2+} ions.

Also remember that the metal which goes into the solution in the form of its salt is undergoing oxidation and thus will act as negative electrode (anode), while the other metal acts as positive electrode (cathode). For example, in the reaction $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$, the Zn is oxidised to $ZnSO_4$, hence zinc will be negative electrode or anode and the cell will be constructed as:

$$Zn \mid ZnSO_4 \parallel H_2SO_4 \mid H_2, Pt$$

Role of salt bridge – Most often salt bridges, which are U- shaped tubes are made with agar-agar gel containing KCl or KNO_3. Sometimes NH_4NO_3 is also used. The reason of using these salts is that the ions of these salts, *e.g.*, KCl (K^+ ion and Cl^-) have almost the same speed as well as almost same transport numbers. If a **salt bridge is not used**, say, in the Daniell cell, the electrons released by the zinc electrode ($Zn \rightarrow Zn^{2+} + 2e^-$) can flow to the copper electrode through the external circuit. These electrons neutralise or reduce some Cu^{2+} ions of the $CuSO_4$ solution ($Cu^{2+} + 2e^- \rightarrow Cu$). As a result, copper sulphate solution acquires a negative charge for a short while, due to discharge of positively charged Cu^{2+} ions. In the mean time zinc sulphate solution becomes positively charged because of the formation of Zn^{2+} ions from the zinc electrode. Hence there will be accumulation of charges near the two electrodes, which prevents further flow of current. Hence the electrochemical change stops and **current drops to zero.**

The **salt bridge** provides a passage for the flow of charges in the internal circuit and thus prevents the accumulation of charges. In the presence of salt bridge, the charges present flow towards the oppositely charged electrodes. The –ve ions move from the copper electrode end through the $CuSO_4$ solution, salt bridge and zinc sulphate solution to the zinc rod. The positive ions move in the reverse direction, *i.e.*, zinc rod to copper rod. Hence flow of electricity is maintained when the salt bridge is used in the Galvanic cell.

To calculate the E°_{CELL} of Daniell Cell :

$$Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$$

We know $E^\circ_{CELL} = E^\circ_{RHE} - E^\circ_{LHE}$ (Both Reduction potentials)

Reaction at LHE $\quad Zn \rightleftarrows Zn^{2+} + 2e^-$ $\quad$ (Oxidation)

Reaction at RHE $\quad Cu^{2+} + 2e^- \rightleftarrows Cu$ $\quad$ (Reduction)

Now $E^\circ_{LHE} = E^\circ_{Zn^{2+}, Zn} = -0.76V$ and $E^\circ_{RHE} = E^\circ_{Cu^{2+}, Cu} = +0.34V$. Thus

$E^\circ_{CELL} = E^\circ_{RHE} - E^\circ_{LHE} = E^\circ_{Cu^{2+}, Cu} - E^\circ_{Zn^{2+}, Zn} = 0.34\ V - (-0.76V) =$ **1.10Volts.**

Since E°_{CELL} is positive, the cell reaction, $Zn + Cu^{2+} \rightleftarrows Zn^{2+} + Cu$ is **spontaneous.**

To calculate the E°_{CELL} *of the cell* $Zn \mid Zn^{2+} \parallel Pb^{2+} \mid Pb$

Reaction at LHE $Zn \rightarrow Zn^{2+} + 2e^-$ (Oxidation)
Reaction at RHE $Pb^{2+} + 2e^- \rightarrow Pb$ (Reduction)
Cell Reaction $Zn + Pb^{2+} \rightleftarrows Zn^{2+} + Pb$

$E^0_{CELL} = E^0_{RHE} - E^0_{LHE} = E^0_{(Pb^{2+}, Pb)} - E^0_{(Zn^{2+}, Zn)} = -0.130 - (-0.76) = -0.130 + 0.76 =$ **+0.640 V.**
As the E^0_{CELL} is **positive,** the above reaction is **spontaneous and thus cell is a source of electricity.**

To calculate E°_{CELL} *of the cell* $Cu \mid Cu^{2+} \mid Zn^{2+} \mid Zn$

$E^{\circ}_{CELL} = E^{\circ}_{RHE} - E^{\circ}_{LHE} = E^{\circ}_{(Zn^{2+}, Zn)} - E^{\circ}_{(Cu^{2+}, Cu)} = -0.76 - (+0.34) = -1.10$ Volts.
Since the E°_{CELL} is **negative**, the reaction, $Cu + Zn^{2+} \rightleftarrows Cu^{2+} + Zn$ is **non-spontaneous.**

Reaction at LHE $Cu \rightarrow Cu^{2+} + 2e^-$ (Oxidation)
Reaction at RHE $Zn^{2+} + 2e^- \rightarrow Zn$ (Reduction)

To calculate E°_{CELL} *of the cell* $Cu \mid Cu^{2+} \parallel Ag^+ \mid Ag$

Reaction at RHE- $2Ag^+ + 2e^- \rightarrow 2Ag$ (Reduction)
Reaction at LHE- $Cu \rightarrow Cu^{2+} + 2e^-$ (Oxidation)
Cell Reaction- $Cu + 2Ag^+ \rightleftarrows Cu^{2+} + 2Ag$

$E^{\circ}_{CELL} = E^{\circ}_{RHE} - E^{\circ}_{LHE} = E^{\circ}_{(Ag^{2+}, Ag)} - E^{\circ}_{(Cu^{2+}, Cu)} = 0.8 - 0.34 =$ **0.46V**
Since the E^0_{CELL} is **positive,** the cell reaction is **spontaneous.**

To calculate E°_{CELL} *of the cell* $Ag \mid Ag^+ \parallel Cu^{2+} \mid Cu$

$E^{\circ}_{CELL} = E^{\circ}_{RHE} - E^{\circ}_{LHE} = (0.34 - 0.80) =$ **– 0.46V**

Reaction at LHE- $2Ag \rightarrow 2Ag^+ + 2e^-$ (Oxidation)
Reaction at RHE- $Cu^{2+} + 2e^- \rightarrow Cu$ (Reduction)
Cell Reaction- $2Ag + Cu^{2+} \rightleftarrows 2Ag^+ + Cu$

Since E°_{CELL} is **negative**, the above reaction is **non-spontaneous.**

Displacement of metals – The reduction potentials of electrodes given in table 1 are very useful in predicting whether a metal can displace another from its salt solution. When a metal M_1 displaces another metal M_2 from its salt solution, M_1 gets oxidised as $M_1 \rightarrow M_1^+ + e^-$ and M_2^+ is reduced as $M_2^+ + e^- \rightarrow M_2$. If M_1 has the higher oxidation potential than that of M_2, then M_1 has a greater tendency to get oxidised and hence M_1 can displace M_2 from its salt solution. For example, zinc displaces silver from $AgNO_3$ solution, because standard oxidation potential of zinc (+0.76V) is greater than that of silver (–0.80 V). Similarly aluminium can displace nickel from nickel salt solution because oxidation potential of $Al \mid Al^{3+}$ (+1.66V) is greater than $Ni \mid Ni^{2+}$ (0.25 V). Copper can not displace zinc from copper sulphate solution when zinc piece is added to copper sulphate solution, because standard oxidation potential of copper (–0.34V) is less than the standard oxidation potential (+0.76V) of zinc. **This also indicates that more electropositive metals displace less electropositive metals from their salt solutions. Copper is thus less electropositive than zinc.**

the strongest reducing agent and the one at the bottom is the weakest reducting agent. Hence lower the reduction potential stronger the reducing agent. The decreasing order of the reducing property of some of the metals is Na > Mg > Zn > Fe > Cu > Ag (More the reduction potential lesser is the reducing power). Note that this is also the arrangement of metals (as given in the electrochemical series) when arranged in the order of their electrode potentials. The arrangement of metals in the order of decreasing tendency of their atoms to give electrons (i.e. undergoing oxidation) is also known as electrochemical series.

Reaction of metals with acids – By making use of standard potentials it is also possible to predict whether a metal would react with an acid to liberate hydrogen or not. For example, consider the reaction between zinc and dilute sulphuric acid. The reaction may be represented as,

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2 \qquad \text{or} \qquad Zn(s) + 2H^+ \rightarrow Zn^{2+} + H_2(g)$$

This reaction is a combination of two half cells.

$$Zn(s) \rightarrow Zn^{2+} + e^- \quad \textbf{(Oxidation)} \qquad \text{or} \qquad 2H^+ + 2e^- \rightarrow H_2(g) \quad \textbf{(Reduction)}$$

In a Galvanic cell oxidation occurs at the left hand electrode and reduction at the right hand electrode. Thus the cell can be represented as, $Zn, Zn^{2+} \mid H^+, H_2(g), Pt$

Thus $E^0_{CELL} = E^0_{RHE} - E^0_{LHE} = E^0_{(H^+, H_2)} - E^0_{(Zn^{2+}, Zn)} = 0 - (-0.76V) = \mathbf{+0.76\ V}$

Since E^0_{CELL} is positive, the reaction of zinc with hydrogen is spontaneous or feasible. Now consider the reaction of silver with dilute sulphuric acid.

$$2Ag + H_2SO_4 \rightarrow Ag_2SO_4 + H_2 \qquad \text{or} \qquad 2Ag(s) + 2H^+ \rightarrow 2Ag^+ + H_2(g)$$

The cell may be represented as $Ag, Ag^+ \parallel H^+, H_2(g), Pt$

$$E^o_{CELL} = E^o_{(H^+,H_2)} - E^o_{(Ag^+,Ag)} = 0-(0.80) = \mathbf{-0.80\ V}$$

Since E^o_{CELL} is negative, the reaction of silver with dilute H_2SO_4 is non-spontaneous or not feasible. In general, any metal lying above hydrogen electrode will reduce H^+ ions to give H_2 gas, while any metal lying below hydrogen electrode will not reduce H^+ ions to give H_2 gas. Thus metals like Zn, Cd, Fe etc., lying above hydrogen are capable of reacting with dilute acids such as H_2SO_4, HCl etc. while metals like Ag, Cu etc., which lie below hydrogen electrode, can not evolve hydrogen with dilute acids.

Secondary cells – A secondary cell once used can be recharged by passing current through it and it may, therefore, be used over and over again. Certain chemical changes occur when the cell is **charged** with electricity and these changes are reversed during **discharge**.

The production of electricity or electric energy at the cost of chemical energy inside is called **discharging** of the cell. When the external electrical energy is used into the cell to be transformed into chemical energy, the process is called **charging** of the cell.

The Leclanche or dry cell – This is a primary cell used in torches, radio, transistors, hearing aids etc and consists of a negative zinc electrode, a carbon electrode acting as positive electrode, surrounded by a paste of MnO_2 and $ZnCl_2$ as an electrolyte. The zinc plate usually forms the outer covering of the cell. The **oxidation** taking place at the negative zinc electrode (**anode**) is

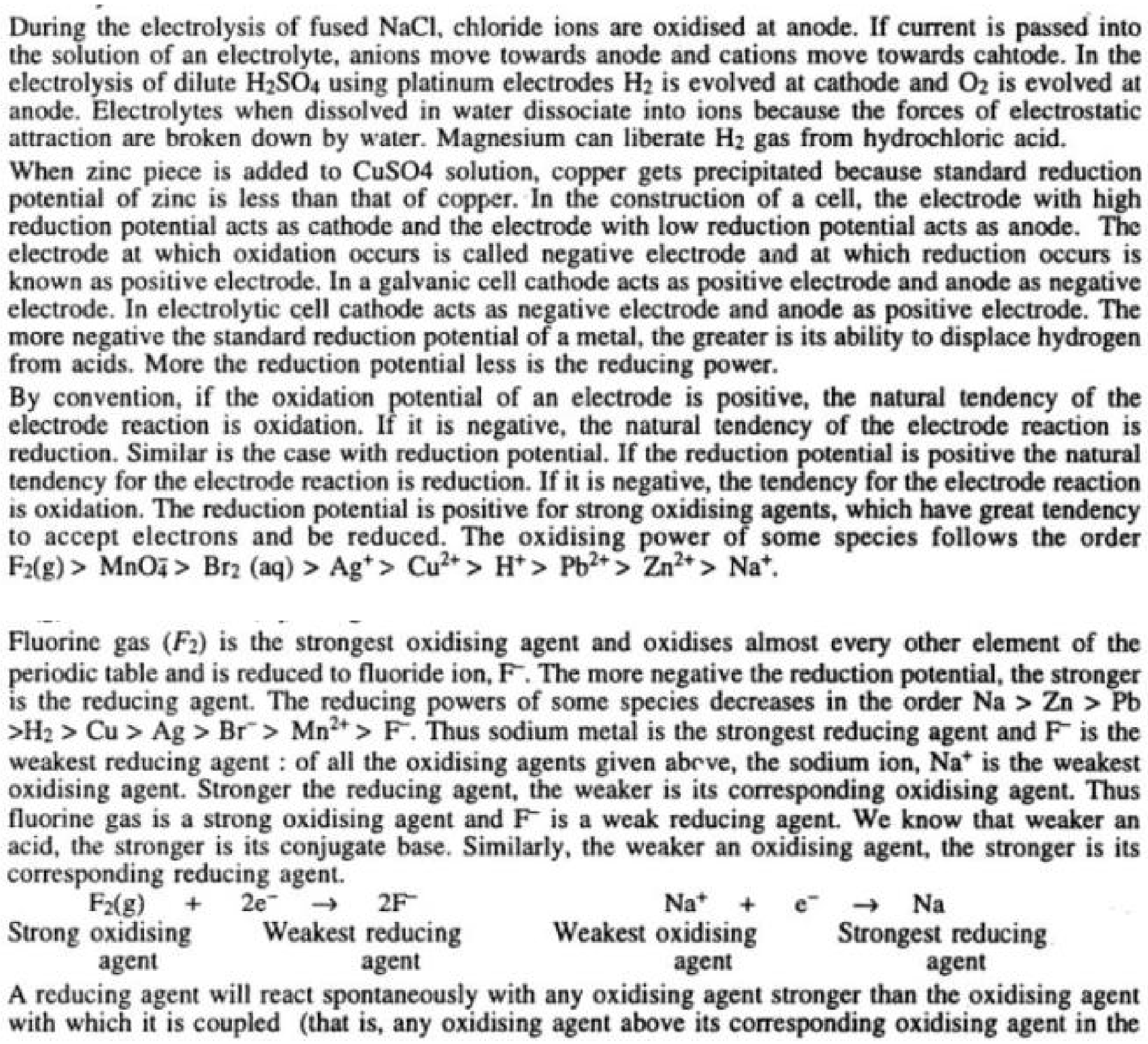
$$Zn + 2MnO_2 + H_2O \rightarrow Zn^{2+} + Mn_2O_3 + 2OH^-$$

The **reduction** taking place at positive electrode (**cathode**) is

$$2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^-$$

The **net cell reaction** is :

$$Zn + 2MnO_2(s) + H_2O \rightleftarrows Zn^{2+} + Mn_2O_3 + 2OH^-$$



During the electrolysis of fused NaCl, chloride ions are oxidised at anode. If current is passed into the solution of an electrolyte, anions move towards anode and cations move towards cahtode. In the electrolysis of dilute H_2SO_4 using platinum electrodes H_2 is evolved at cathode and O_2 is evolved at anode. Electrolytes when dissolved in water dissociate into ions because the forces of electrostatic attraction are broken down by water. Magnesium can liberate H_2 gas from hydrochloric acid.

When zinc piece is added to CuSO4 solution, copper gets precipitated because standard reduction potential of zinc is less than that of copper. In the construction of a cell, the electrode with high reduction potential acts as cathode and the electrode with low reduction potential acts as anode. The electrode at which oxidation occurs is called negative electrode and at which reduction occurs is known as positive electrode. In a galvanic cell cathode acts as positive electrode and anode as negative electrode. In electrolytic cell cathode acts as negative electrode and anode as positive electrode. The more negative the standard reduction potential of a metal, the greater is its ability to displace hydrogen from acids. More the reduction potential less is the reducing power.

By convention, if the oxidation potential of an electrode is positive, the natural tendency of the electrode reaction is oxidation. If it is negative, the natural tendency of the electrode reaction is reduction. Similar is the case with reduction potential. If the reduction potential is positive the natural tendency for the electrode reaction is reduction. If it is negative, the tendency for the electrode reaction is oxidation. The reduction potential is positive for strong oxidising agents, which have great tendency to accept electrons and be reduced. The oxidising power of some species follows the order $F_2(g) > MnO_4^- > Br_2\,(aq) > Ag^+ > Cu^{2+} > H^+ > Pb^{2+} > Zn^{2+} > Na^+$.

Fluorine gas (F_2) is the strongest oxidising agent and oxidises almost every other element of the periodic table and is reduced to fluoride ion, F^-. The more negative the reduction potential, the stronger is the reducing agent. The reducing powers of some species decreases in the order $Na > Zn > Pb > H_2 > Cu > Ag > Br^- > Mn^{2+} > F^-$. Thus sodium metal is the strongest reducing agent and F^- is the weakest reducing agent : of all the oxidising agents given above, the sodium ion, Na^+ is the weakest oxidising agent. Stronger the reducing agent, the weaker is its corresponding oxidising agent. Thus fluorine gas is a strong oxidising agent and F^- is a weak reducing agent. We know that weaker an acid, the stronger is its conjugate base. Similarly, the weaker an oxidising agent, the stronger is its corresponding reducing agent.

$$\underset{\text{Strong oxidising agent}}{F_2(g)} + 2e^- \rightarrow \underset{\text{Weakest reducing agent}}{2F^-} \qquad \underset{\text{Weakest oxidising agent}}{Na^+} + e^- \rightarrow \underset{\text{Strongest reducing agent}}{Na}$$

A reducing agent will react spontaneously with any oxidising agent stronger than the oxidising agent with which it is coupled (that is, any oxidising agent above its corresponding oxidising agent in the table of standard reduction potentials). Hence Pb will reduce H^+(aq), Cu^{2+}, Ag^+, Br_2 etc but not react with Zn^{2+} or Na^+. An oxidising agent will react with any reducing agent stronger than the reducing agent with which it is coupled (that is, any reducing agent below its corresponding reducing agent in the table of standard reduction potentials). Hence Br_2 will oxidise Ag, Cu, H_2, Pb, Zn and Na, but it will not react with Mn^{2+} or F^- ions. For example Cu will reduce Ag^+ ions because Ag^+ is stronger oxidising agent than Cu^{2+} because Ag^+ is above Cu^{2+} in the table). Similarly Cu will not reduce Pb^{2+} ions, because Pb^{2+} is below Cu^{2+} in the table.

In general, a strong oxidising agent is a species which is readily reduced and hence has a large positive standard reduction potential. Such species are $F_2 > Co^{3+} > H_2O_2$. The halogens above fluorine decrease in oxidising power in the order $Cl_2 > Br_2 > I_2$. Strong reducing agents are those which are easily oxidised. They have large positive standard oxidation potentials. They include Li > K > Na > ; Ba > Ca > Mg ; Al and some of the transition metals, Zn > Fe > Cd. Hydrogen gas, (SOP) = 0 is moderately good reducing agent. Species below H_2 (which all have negative standard oxidation potentials) are relatively weak reducing agents.

According to preferential discharge theory, out of a number of ions the one which requires least energy will be the first to be discharged at a given electrode.

Greater the standard oxidation potential, stronger the reducing agent will it be or greater would be its reducing power. Greater the reduction potential, greater is the tendency to gain electrons and hence greater is the tendency to be reduced. For example, the reduction potentials of H^+, Na^+, K^+ and Mg^{2+} ions are 0.000, –2.715, –2.924 and –2.370 respectively. Among these the reduction potential of H^+ ion is more. Thus H^+ ion has maximum tendency to gain electrons.

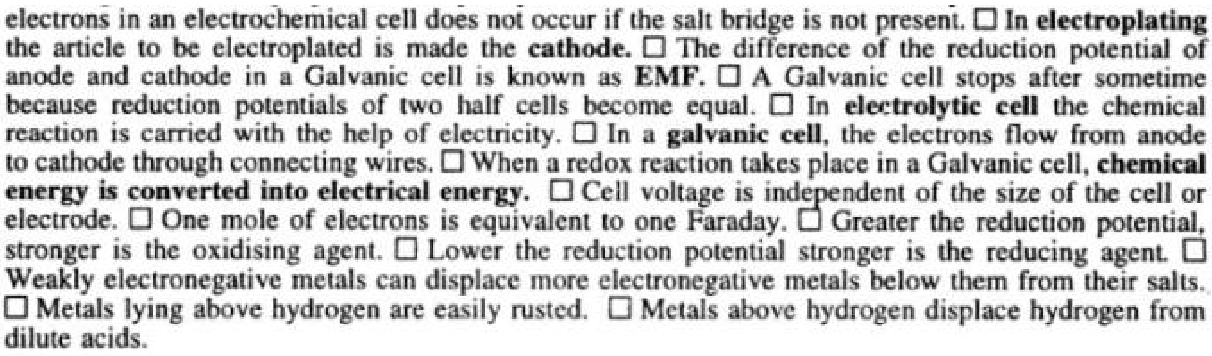
Lesser the standard reduction potential of a metal more readily it loses electron and hence greater is its reducing power. Hence more difficult is to reduce it.

The metal having lesser value of standard reduction potential can displace the other from its aqueous salt solution. Thus Sn can displace lead from aqueous lead bromide solution because standard reduction potential of Sn is less than that of Pb. When Zn piece is kept in $CuSO_4$ solution, copper gets precipitated because standard reduction potential of zinc is less than copper.

The metal having maximum positive value of standard reduction potential is deposited in maximum amount on the cathode. For example, the standard reduction potentials of $Ag \mid Ag^+ = 0.8$ V, 2Hg $Hg^{2+} = 0.79$. V, $Cu \mid Cu^{2+} = 0.34$ V and $Mg \mid Mg^{2+} = -2.37$ V. Thus the sequence of deposition of metals at the cathode is Ag, Hg, Cu, Mg. Hence greater the positive standard reduction potential of a metal, greater would be the amount deposited at the cathode.

In general, a metal can displace another metal, lying below it in the electrochemical series. For example, zinc displaces copper from copper sulphate solution because copper lies below zinc in the electrochemical series.

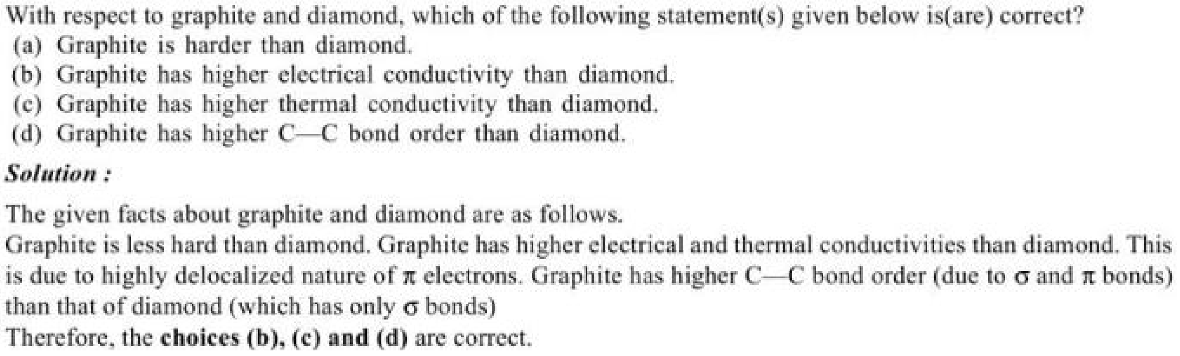
One coulomb = 6.28×10^{28} electrons. ☐ **One electric charge** $= 1.6 \times 10^{-19}$ coulombs. ☐ In galvanic cell electrical energy is generated at the expense of chemical energy. ☐ In an electrolytic cell the chemical energy is generated at the expense of electrical energy. ☐ **In an electrolytic cell current flows from anode to cathode inside the cell.** ☐ The electrode which pushes the electrons into the external circuit is called **anode.** ☐ The electrodes which do not participate in the chemical changes are called **inert electrodes.** ☐ **The electrode at which electrons flow into an electrolyte is called cathode.** ☐ **Cathode is negatively charged electrode while anode is positively charged.** ☐ Unless oxidising and reducing agents are kept separate, electric current will not be produced. ☐ Flow of



electrons in an electrochemical cell does not occur if the salt bridge is not present. ☐ In **electroplating** the article to be electroplated is made the **cathode.** ☐ The difference of the reduction potential of anode and cathode in a Galvanic cell is known as **EMF.** ☐ A Galvanic cell stops after sometime because reduction potentials of two half cells become equal. ☐ In **electrolytic cell** the chemical reaction is carried with the help of electricity. ☐ In a **galvanic cell**, the electrons flow from anode to cathode through connecting wires. ☐ When a redox reaction takes place in a Galvanic cell, **chemical energy is converted into electrical energy.** ☐ Cell voltage is independent of the size of the cell or electrode. ☐ One mole of electrons is equivalent to one Faraday. ☐ Greater the reduction potential, stronger is the oxidising agent. ☐ Lower the reduction potential stronger is the reducing agent. ☐ Weakly electronegative metals can displace more electronegative metals below them from their salts. ☐ Metals lying above hydrogen are easily rusted. ☐ Metals above hydrogen displace hydrogen from dilute acids.

Topic wise grouping of information kind of Dictionary of General Chemistry

Graphite and Diamond comparison



With respect to graphite and diamond, which of the following statement(s) given below is(are) correct?

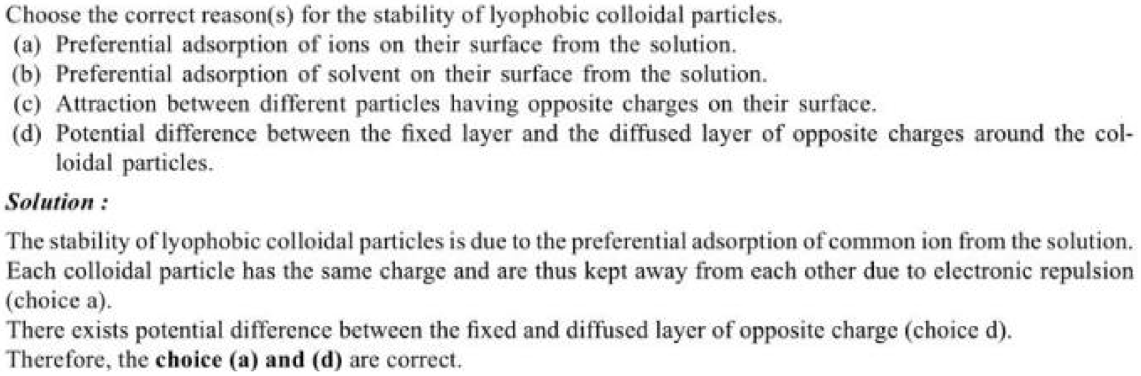
(a) Graphite is harder than diamond.
(b) Graphite has higher electrical conductivity than diamond.
(c) Graphite has higher thermal conductivity than diamond.
(d) Graphite has higher C—C bond order than diamond.

Solution :

The given facts about graphite and diamond are as follows.
Graphite is less hard than diamond. Graphite has higher electrical and thermal conductivities than diamond. This is due to highly delocalized nature of π electrons. Graphite has higher C—C bond order (due to σ and π bonds) than that of diamond (which has only σ bonds)
Therefore, the **choices (b), (c) and (d)** are correct.

-

Stability of lyophobic colloidal particles



Choose the correct reason(s) for the stability of lyophobic colloidal particles.

(a) Preferential adsorption of ions on their surface from the solution.
(b) Preferential adsorption of solvent on their surface from the solution.
(c) Attraction between different particles having opposite charges on their surface.
(d) Potential difference between the fixed layer and the diffused layer of opposite charges around the colloidal particles.

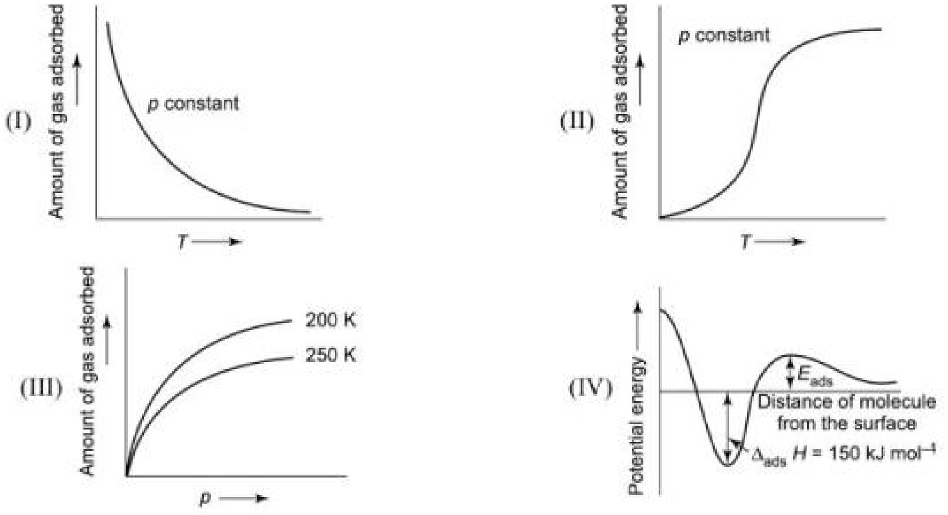
Solution :

The stability of lyophobic colloidal particles is due to the preferential adsorption of common ion from the solution. Each colloidal particle has the same charge and are thus kept away from each other due to electronic repulsion (choice a).
There exists potential difference between the fixed and diffused layer of opposite charge (choice d).
Therefore, the **choice (a) and (d)** are correct.

-

Physiorption and Chemisorption comparison

The given graph/data I, II, III and IV represent general trends observed for different physisorption and chemisorption processes under mild conditions of temperature and pressure. Which of the following choice(s) about I, II, III and IV is(are) correct.



(a) I is physisorption and II is chemisorption
(b) I is physisorption and III is chemisorption
(c) IV is chemisorption and II is chemisorption
(d) IV is chemisorption and III is chemisorption

Solution:

We have the following facts.

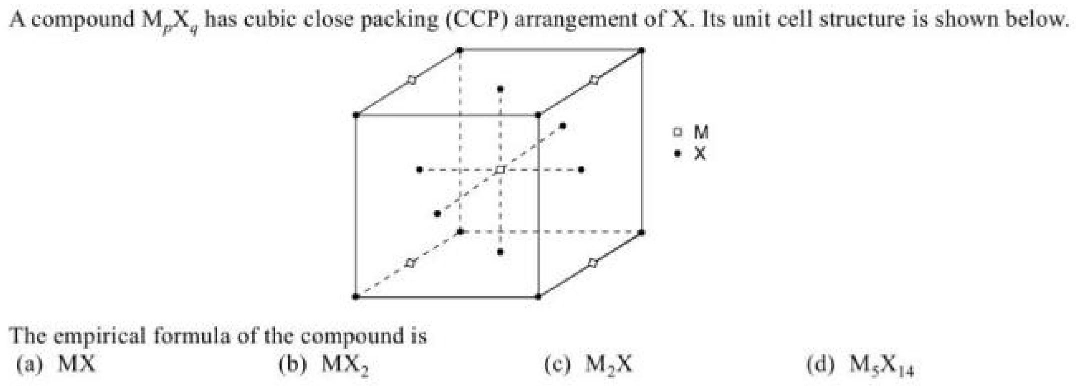
- Adsorption decreases with increase in temperature at constant pressure in case of physisorption
- Adsorption increases initially with increase in temperature at constant pressure in case of chemisorption as more molecules satisfy the energy of activation.
- The enthalpy change during chemisorptions is high due to the bond formation between adsorbent and adsorbate.

With these guidelines, we will have

Graph I represents physisorption
Graph II represents chemisorption
Graph III represents physisorption
Graph IV represents chemisorptions

Therefore, The **choices (a) and (c)** are correct.

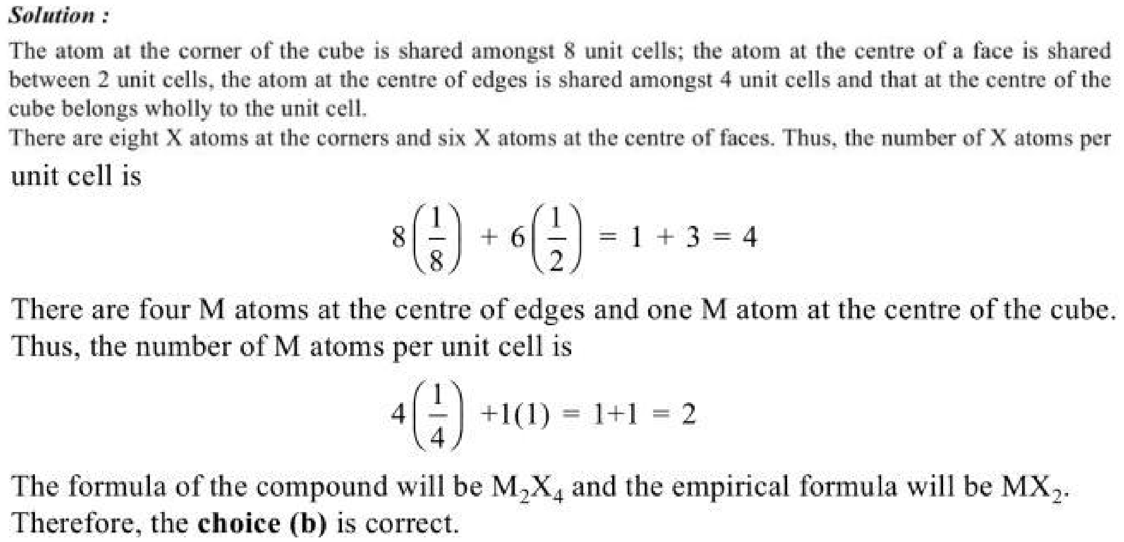
-



A compound M_pX_q has cubic close packing (CCP) arrangement of X. Its unit cell structure is shown below.

The empirical formula of the compound is

(a) MX (b) MX_2 (c) M_2X (d) M_5X_{14}



Solution :

The atom at the corner of the cube is shared amongst 8 unit cells; the atom at the centre of a face is shared between 2 unit cells, the atom at the centre of edges is shared amongst 4 unit cells and that at the centre of the cube belongs wholly to the unit cell.

There are eight X atoms at the corners and six X atoms at the centre of faces. Thus, the number of X atoms per unit cell is

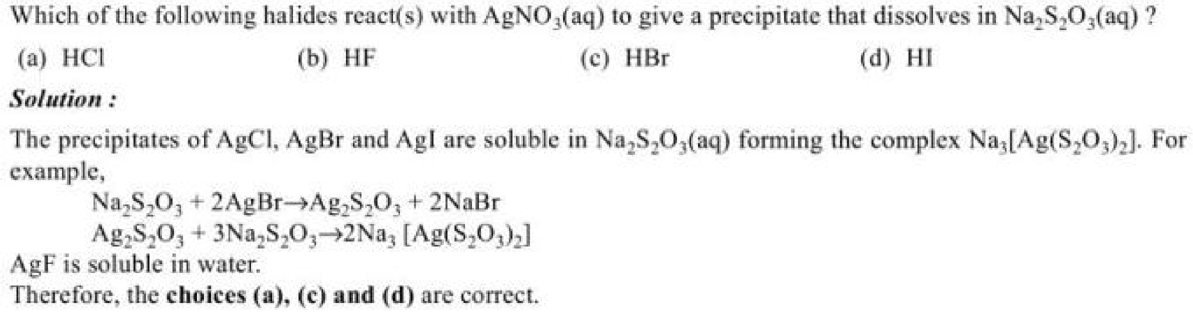
$$8\left(\frac{1}{8}\right) + 6\left(\frac{1}{2}\right) = 1 + 3 = 4$$

There are four M atoms at the centre of edges and one M atom at the centre of the cube. Thus, the number of M atoms per unit cell is

$$4\left(\frac{1}{4}\right) + 1(1) = 1+1 = 2$$

The formula of the compound will be M_2X_4 and the empirical formula will be MX_2. Therefore, the **choice (b)** is correct.

HCl HBr and HI react with AgNO3 to give a precipitate that dissolves in Na2S2O3



Which of the following halides react(s) with $AgNO_3(aq)$ to give a precipitate that dissolves in $Na_2S_2O_3(aq)$?

(a) HCl (b) HF (c) HBr (d) HI

Solution :

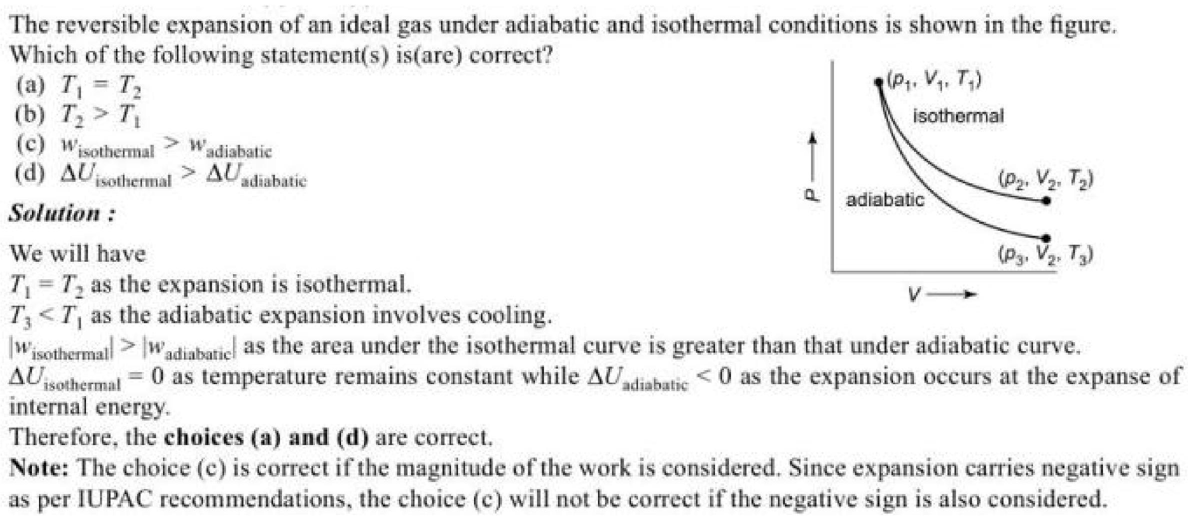
The precipitates of AgCl, AgBr and AgI are soluble in $Na_2S_2O_3(aq)$ forming the complex $Na_3[Ag(S_2O_3)_2]$. For example,

$$Na_2S_2O_3 + 2AgBr \rightarrow Ag_2S_2O_3 + 2NaBr$$
$$Ag_2S_2O_3 + 3Na_2S_2O_3 \rightarrow 2Na_3\,[Ag(S_2O_3)_2]$$

AgF is soluble in water.

Therefore, the **choices (a), (c) and (d)** are correct.

Reversible expansion of an ideal gas



The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is(are) correct?

(a) $T_1 = T_2$
(b) $T_2 > T_1$
(c) $w_{\text{isothermal}} > w_{\text{adiabatic}}$
(d) $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$

Solution :

We will have

$T_1 = T_2$ as the expansion is isothermal.

$T_3 < T_1$ as the adiabatic expansion involves cooling.

$|w_{\text{isothermal}}| > |w_{\text{adiabatic}}|$ as the area under the isothermal curve is greater than that under adiabatic curve.

$\Delta U_{\text{isothermal}} = 0$ as temperature remains constant while $\Delta U_{\text{adiabatic}} < 0$ as the expansion occurs at the expanse of internal energy.

Therefore, the **choices (a) and (d)** are correct.

Note: The choice (c) is correct if the magnitude of the work is considered. Since expansion carries negative sign as per IUPAC recommendations, the choice (c) will not be correct if the negative sign is also considered.

Acid Ionization Constant	$K_a = \frac{[H^+][A^-]}{[HA]}$
Adibiatic change	$PV = k$
Base Ionization Constant	$K_b = \frac{[OH^-][HB^+]}{[B]}$
Bohr Radius	$a_0 = \frac{\hbar^2}{m_e k e^2}$
Boiling Point Elevation	$\Delta T_b = i K_b \times molality$
Buffer Design Equation	$pH \approx pK_a - \log \frac{[HA]_0}{[A^-]_0}$
Cell Voltage	$E_{cell} = E^{\circ}_{cell} - \frac{RT}{n\Im} \ln Q = E^{\circ}_{cell} - \frac{0.0592}{n} \log Q$
Charles' Law	$\frac{V}{t} = k$

Atomic Structure

DESCRIPTION	EQUATION
Bohr Radius	$a_0 = \frac{\hbar^2}{m_e k e^2}$
De Broglie Wavelength	$\lambda = \frac{h}{mv}$
Linear Momentum	$p = mv$
Planck's Quantized (Quantum) Energy Equation	$\Delta E = h\nu$
Radii of stable orbits in the Bohr model	$r = n^2 \frac{\hbar^2}{m_e k Z e^2} = n^2 \frac{a_0}{Z}$
Relationship between Energy and Principal Quantum Number	$E_n = -R_H \left(\frac{1}{n^2}\right) = \frac{-2.178 \times 10^{-18}}{n^2} joule$
Rydberg Equation	$\Delta E = R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$
Speed of Light to Wavelength and Frequency Relationship	$c = \lambda\nu$

Electrochemistry

DESCRIPTION	EQUATION
Cell Voltage	$E_{cell} = E^{\circ}_{cell} - \frac{RT}{n\mathfrak{F}} \ln Q = E^{\circ}_{cell} - \frac{0.0592}{n} \log Q$
Electric Current	$I = \frac{q}{t}$
Reaction Quotient	$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ $where \quad aA + bB \rightarrow cC + dD$
Relationship between Equilibrium Constant and Cell Voltage	$\log K = \frac{nE^{\circ}}{0.0592}$

Equilibrium

DESCRIPTION	EQUATION
Acid Ionization Constant	$K_a = \frac{[H^+][A^-]}{[HA]}$
Base Ionization Constant	$K_b = \frac{[OH^-][HB^+]}{[B]}$
Buffer Design Equation	$pH \approx pK_a - \log \frac{[HA]_0}{[A^-]_0}$
Gas Pressure and Concentration Relationship	$K_p = K_c (RT)^{\Delta n}$
Ion Product Constant for Water	$K_w = [OH^-][H^+] = K_a \times K_b = 1.0 \times 10^{-14} \quad at \quad 25°C$
pH and pOH Relationship	$14 = pH + pOH$
pH Defined	$pH = -\log [H^+]$
pK$_a$ Definition	$pK_a = -\log K_a$
pK$_b$ Definition	$pK_b = -\log K_b$
pOH and Base Ionization Equilibrium Constant Relationship	$pOH = pK_b + \log \frac{[HB^+]}{[B]}$

Gases, Liquids, and Solutions

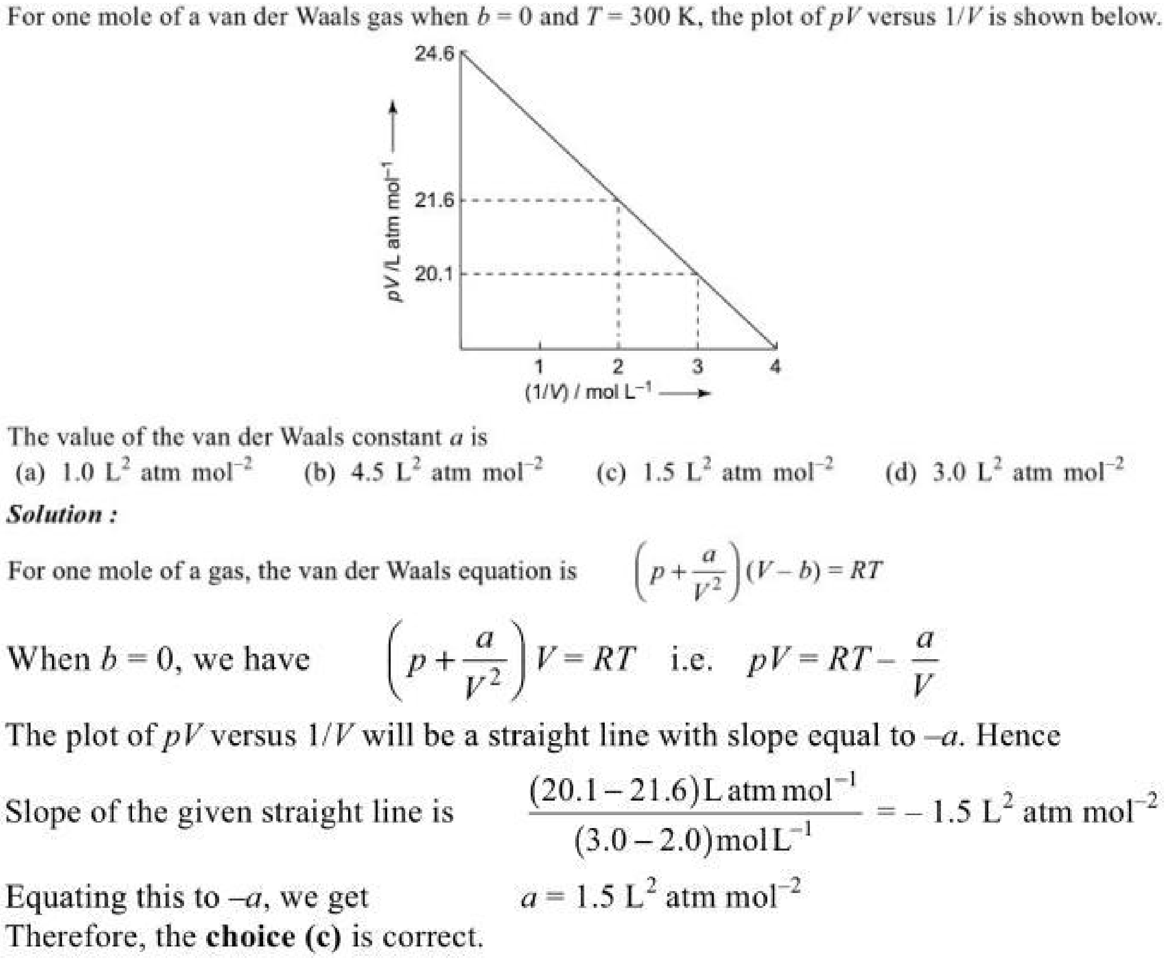
DESCRIPTION	EQUATION
Adibiatic change	$PV = k$
Boiling Point Elevation	$\Delta T_b = iK_b \times molality$
Charles' Law	$\frac{V}{t} = k$
Combined Gas Law	$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$
Density of a Material	$D = \frac{m}{V}$
Freezing Point Depression	$\Delta T_f = iK_f \times molality$

Graham's Law of Effusion	$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$
Ideal gas equation	$PV = nRT$
Kinetic Energy per Mole	$\frac{KE}{mole} = \frac{3}{2}RTn$
Kinetic Energy per Mole	$\frac{KE}{mole} = \frac{3}{2}RTn$

Thermochemistry

DESCRIPTION	EQUATION
Acid Ionization Constant	$K_a = \frac{[H^+][A^-]}{[HA]}$
Adibiatic change	$PV = k$
Base Ionization Constant	$K_b = \frac{[OH^-][HB^+]}{[B]}$
Bohr Radius	$a_0 = \frac{\hbar^2}{m_e k e^2}$
Boiling Point Elevation	$\Delta T_b = iK_b \times molality$
Buffer Design Equation	$pH \approx pK_a - \log\frac{[HA]_0}{[A^-]_0}$
Cell Voltage	$E_{cell} = E^\circ_{cell} - \frac{RT}{n\Im}\ln Q = E^\circ_{cell} - \frac{0.0592}{n}\log Q$
Charles' Law	$\frac{V}{t} = k$

Vander waal's force



For one mole of a van der Waals gas when $b = 0$ and $T = 300$ K, the plot of pV versus $1/V$ is shown below.

The value of the van der Waals constant a is

(a) 1.0 L^2 atm mol^{-2} (b) 4.5 L^2 atm mol^{-2} (c) 1.5 L^2 atm mol^{-2} (d) 3.0 L^2 atm mol^{-2}

Solution :

For one mole of a gas, the van der Waals equation is $\left(p + \frac{a}{V^2}\right)(V - b) = RT$

When $b = 0$, we have $\left(p + \frac{a}{V^2}\right)V = RT$ i.e. $pV = RT - \frac{a}{V}$

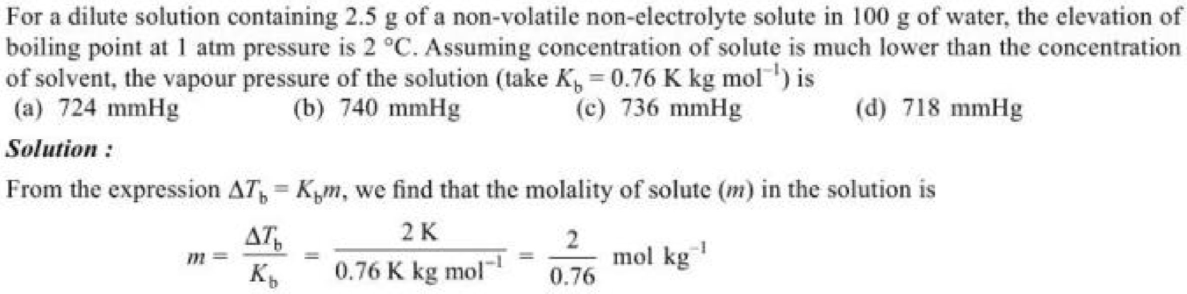
The plot of pV versus $1/V$ will be a straight line with slope equal to $-a$. Hence

Slope of the given straight line is $\frac{(20.1 - 21.6)\,\mathrm{L\,atm\,mol^{-1}}}{(3.0 - 2.0)\,\mathrm{mol\,L^{-1}}} = -1.5\ \mathrm{L^2\,atm\,mol^{-2}}$

Equating this to $-a$, we get $a = 1.5\ \mathrm{L^2\,atm\,mol^{-2}}$

Therefore, the **choice (c)** is correct.

Dilute solution containing 2.5 gm of nonvolatile



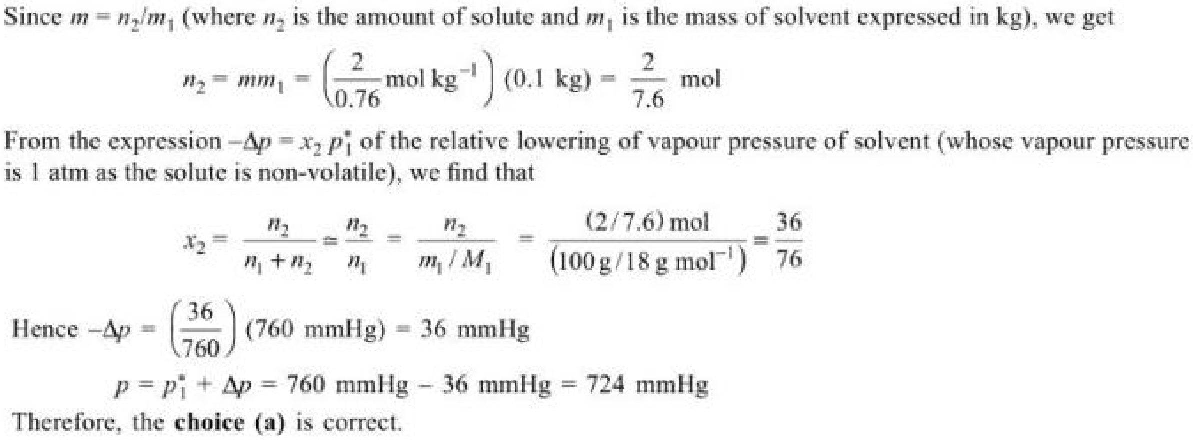
For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solute in 100 g of water, the elevation of boiling point at 1 atm pressure is 2 °C. Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure of the solution (take $K_b = 0.76$ K kg mol^{-1}) is

(a) 724 mmHg (b) 740 mmHg (c) 736 mmHg (d) 718 mmHg

Solution :

From the expression $\Delta T_b = K_b m$, we find that the molality of solute (m) in the solution is

$$m = \frac{\Delta T_b}{K_b} = \frac{2\ \mathrm{K}}{0.76\ \mathrm{K\ kg\ mol^{-1}}} = \frac{2}{0.76}\ \mathrm{mol\ kg^{-1}}$$



Since $m = n_2/m_1$ (where n_2 is the amount of solute and m_1 is the mass of solvent expressed in kg), we get

$$n_2 = mm_1 = \left(\frac{2}{0.76}\text{mol kg}^{-1}\right)(0.1\text{ kg}) = \frac{2}{7.6}\text{ mol}$$

From the expression $-\Delta p = x_2 p_1^*$ of the relative lowering of vapour pressure of solvent (whose vapour pressure is 1 atm as the solute is non-volatile), we find that

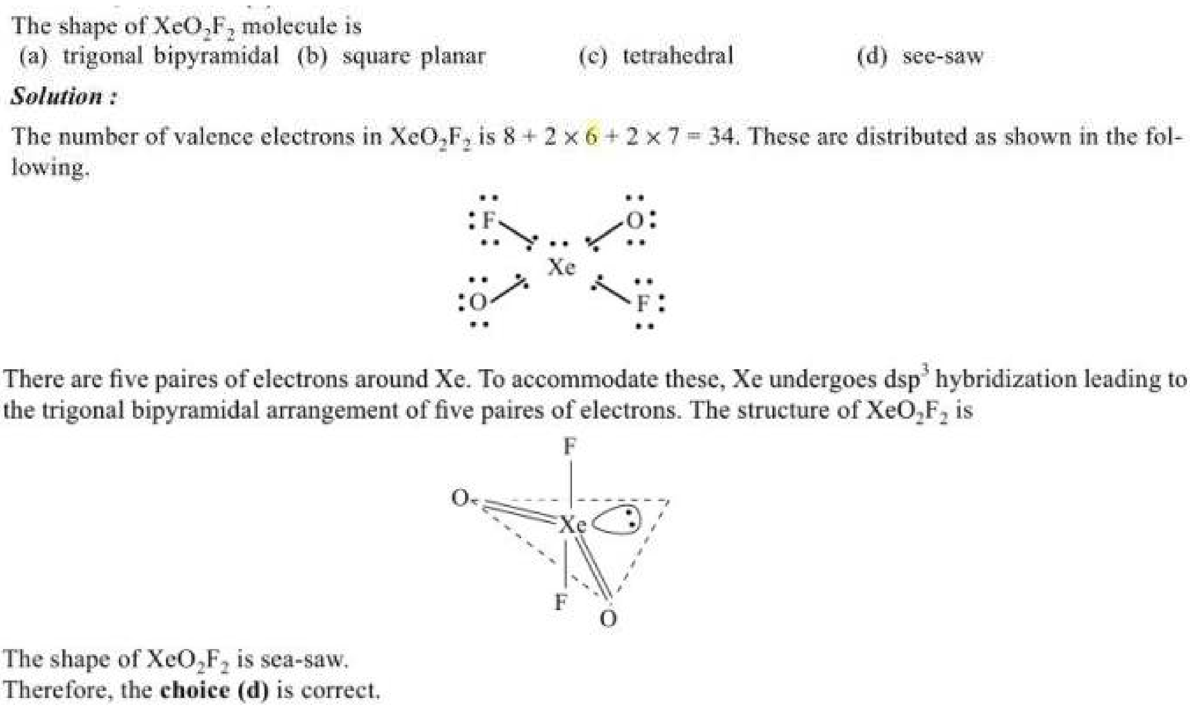
$$x_2 = \frac{n_2}{n_1 + n_2} \simeq \frac{n_2}{n_1} = \frac{n_2}{m_1/M_1} = \frac{(2/7.6)\text{ mol}}{(100\text{ g}/18\text{ g mol}^{-1})} = \frac{36}{76}$$

Hence $-\Delta p = \left(\frac{36}{760}\right)(760\text{ mmHg}) = 36\text{ mmHg}$

$$p = p_1^* + \Delta p = 760\text{ mmHg} - 36\text{ mmHg} = 724\text{ mmHg}$$

Therefore, the **choice (a)** is correct.

Shape of XeO2F2 molecule is seesaw



The shape of XeO_2F_2 molecule is
(a) trigonal bipyramidal (b) square planar (c) tetrahedral (d) see-saw

Solution :

The number of valence electrons in XeO_2F_2 is $8 + 2 \times 6 + 2 \times 7 = 34$. These are distributed as shown in the following.

There are five paires of electrons around Xe. To accommodate these, Xe undergoes dsp^3 hybridization leading to the trigonal bipyramidal arrangement of five paires of electrons. The structure of XeO_2F_2 is

The shape of XeO_2F_2 is sea-saw.
Therefore, the **choice (d)** is correct.

Various increasing and Decreasing properties

Decreasing order of reactivity towards S_N2 displacement:

n-Butyl bromide, isobutyl bromide, *sec*-butyl bromide, *tert*-butyl bromide

Increasing order of reactivity towards S_N1 displacement:

1-bromopentane, 2-bromopentane, 2-bromo-2-methylbutane

Increasing reactivity sequence of S_N1 displacement of halogen: CH_3X, 1° X, 2° X, 3° X,
Inceasing reactivity sequence of S_N2 displacement of halogen: CH_3X, 1° X, 2° X, 3° X.
Increasing reactivity of alcohols towards gaseous HBr:

2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol

Increasing order or reactivity towards E2 dehydrohalogenation of the bromides:

ethyl bromide, *n*-proyl bromide, isobutyl bromide, neopentyl bromide

Increasing stability of alkenes: $R_2C{=}CR_2$, $R_2C{=}CHR$, $R_2C{=}CH_2$, $RCH{=}CH_2$, $CH_2{=}CH_2$
Increasing dehydration of alcohol in the presence of H_2SO_4:

ethyl alcohol, isopropyl alcohol, *tert*-butyl alcohol

Decreasing order of reactivity towards E2 dehydrohalogenation:

2-bromo-2-methylbutane, 1-bromopentane, 2-bromopentane, 3-bromopentane

Increasing order of dehydrohalogenation

1-bromo-3-methylbutane, 2-bromo-2-methylbutane, 3-bromo-2-methylbutane

calculate multiple bond energy of a C triple bond

Using the data provided, calculate the multiple bond energy of a C≡C bond in C_2H_2.

$$2C(s) + H_2(g) \rightarrow C_2H_2(g) \qquad \Delta H_1 = 225\ \text{kJ mol}^{-1}$$

$$2C(s) \rightarrow 2C(g) \qquad \Delta H_2 = 1410\ \text{kJ mol}^{-1}$$

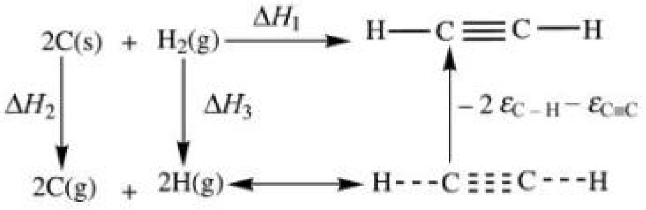
$$H_2(g) \rightarrow 2H(g) \qquad \Delta H_3 = 330\ \text{kJ mol}^{-1}$$

Take the bond energy of C—H bond equal to 350 kJ mol^{-1}.

(a) 1165 kJ mol^{-1} (b) 837 kJ mol^{-1} (c) 865 kJ mol^{-1} (d) 815 kJ mol^{-1}

Solution:

Consider the following transformations.



According to Hess's law $\Delta H_1 = \Delta H_2 + \Delta H_3 - 2\varepsilon_{C-H} - \varepsilon_{C\equiv C}$

This gives

$$\varepsilon_{C\equiv C} = \Delta H_2 + \Delta H_3 - \Delta H_1 - 2\varepsilon_{C-H} = (1410 + 330 - 225 - 2 \times 350)\ \text{kJ mol}^{-1} = 815\ \text{kJ mol}^{-1}$$

Therefore, the **choice (d)** is correct.

Some facts student must know

Largest Anion - At $^{-}$

Metals having highest b.pt and m.pt. = mercury and tungsten

Most reactive solid element - Li

Most reactive liquid element - Cs

total no. of gaseous element in periodic table - 11 (H , He , N , O , F , Ne , Cl , Ar , Kr , Xe , Ra)

TOTAL NO. OF LIQUID elements - 6 (Ga , Br , Cs , Hg , Fr , EKa)

Liquid radioactive element - Francium

N.metal wid highest M.Pt - Carbon

Metal wid highest valency = Plutonium

highest tensile strength - Boron

Most ionic compound = CsF

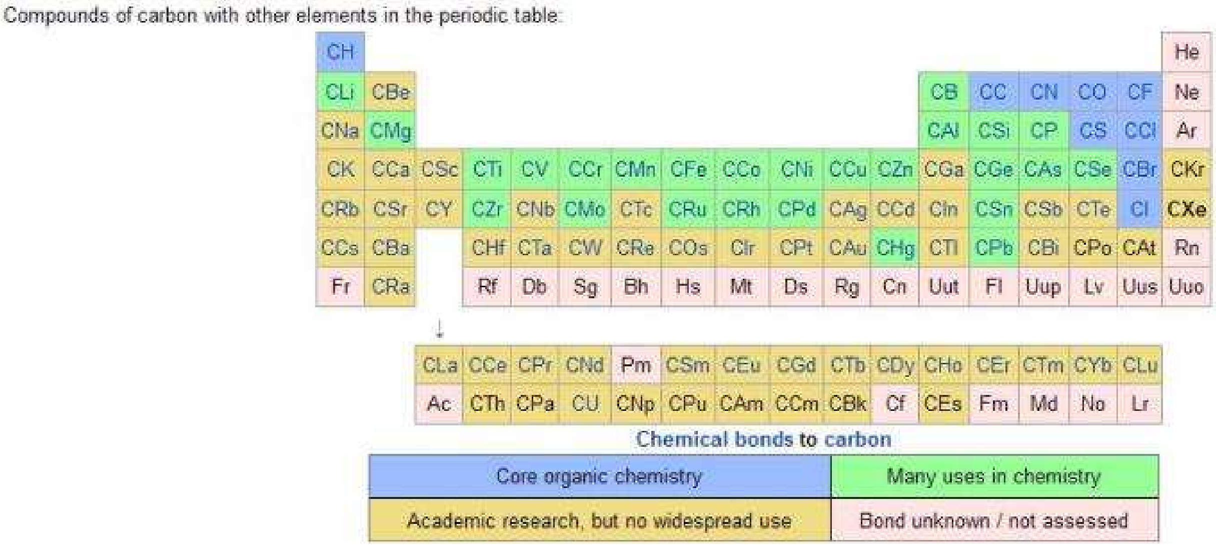
Strongest base = Cs (OH)

Strongest basic oxide = Cs_2O

Most conducting metal = Ag

-

Topic wise grouping of information kind of Dictionary of Organic Chemistry



Compounds of carbon with other elements in the periodic table:

CH																	He
CLi	CBe											CB	CC	CN	CO	CF	Ne
CNa	CMg											CAl	CSi	CP	CS	CCl	Ar
CK	CCa	CSc	CTi	CV	CCr	CMn	CFe	CCo	CNi	CCu	CZn	CGa	CGe	CAs	CSe	CBr	CKr
CRb	CSr	CY	CZr	CNb	CMo	CTc	CRu	CRh	CPd	CAg	CCd	CIn	CSn	CSb	CTe	CI	CXe
CCs	CBa		CHf	CTa	CW	CRe	COs	CIr	CPt	CAu	CHg	CTl	CPb	CBi	CPo	CAt	Rn
Fr	CRa		Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

↓

CLa	CCe	CPr	CNd	Pm	CSm	CEu	CGd	CTb	CDy	CHo	CEr	CTm	CYb	CLu
Ac	CTh	CPa	CU	CNp	CPu	CAm	CCm	CBk	Cf	CEs	Fm	Md	No	Lr

Chemical bonds to carbon

🟦 Core organic chemistry	🟩 Many uses in chemistry
🟨 Academic research, but no widespread use	🟥 Bond unknown / not assessed

Abscisic acid (ABA) - A PLANT HORMONE once thought to be responsible for the shedding (abscission) of flowers and fruit and for the onset of dormancy in buds (hence its early name, dormin). The compound is associated with the closing of pores (stoma) in the leaves of plants deprived of water.

Absolute configuration - A particular molecular configuration of a CHIRAL molecule, as denoted by comparison with a reference molecule or by some sequence rule.There are two systems for expressing absolute configuration in common use: theD-L convention and the R-S convention.

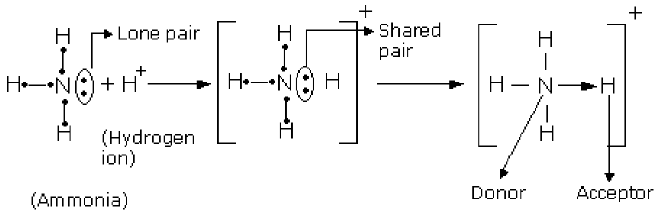
Absorption

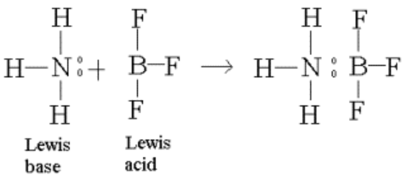
1. A process in which a gas is taken up by a liquid or solid, or in which a liquid is taken up by a solid. In absorption, the substance absorbed goes into the bulk of the material. Solids that absorb gases or liquids often have a porous structure. The absorption of gases in solids is sometimes called sorption. There is a distinction between absorption (in which one substance is assimilated into the bulk of another) and ADSORPTION (which involves attachment to the surface). Sometimes it is not obvious which process is occurring. For example, a porous solid, such as activated CHARCOAL may be said to absorb a large volume of gas, but the process may actually be adsorption on the high surface area of internal pores in the material.

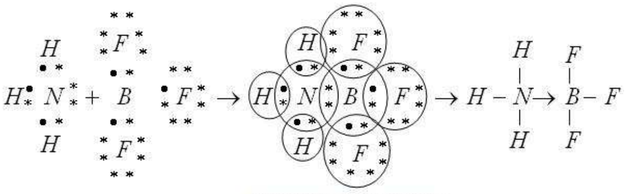
2. The process in which electromagnetic radiation, particles, or sound waves lose energy in passing through a medium. Absorption involves conversion of one form of energy into another.

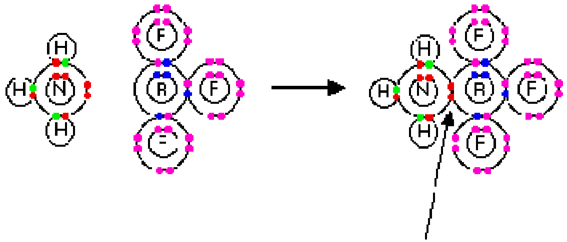
Accelerator - A substance that increases the rate of a chemical reaction. In this sense the term is synonymous with CATALYST. It is common to refer to catalysts as ‘accelerators’ in certain industrial applications. For example, accelerators are used in the VULCANIZATION of rubber and in the polymerization of adhesives. Also, in the production of composite materials using polyester resins a distinction is sometimes made between the catalyst (which initiates the polymerization reaction) and the accelerator (which is an additional substance making the catalyst more effective). The terms promoter and activator are used in a similar way.

Acceptor - The atom or group to which a pair of electrons is donated in forming a COORDINATE BOND.

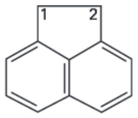





Formation of a co-ordinate bond between NH_3 and

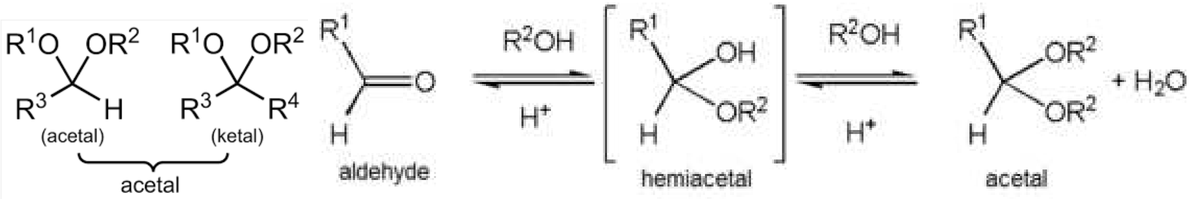


Acenaphthene - (C_{12} H_{10}) A colorless crystalline derivative of naphthalene, used in producing some dyes.



Acenaphthene

Acetal - A type of compound formed by reaction of an alcohol with either an aldehyde or a ketone. The first step in formation of an acetal is the formation of an intermediate, known as a hemiacetal. For example, ethanal (acetaldehyde; CH3CHO) reacts with ethanol (C2H5OH) as follows: $CH_3CHO + C_2H_5OH$ <==> $CH(OH)(CH_3)(C_2H_5O)$ The hemiacetal has a central carbon atom (from the aldehyde) attached to a hydrogen, a hydroxyl group, a hydrocarbon group (methyl - CH_3), and an alkoxy group (C_2H_5O). If a ketone is used rather than an aldehyde, the resulting hemiacetal contains two hydrocarbon groups. For example, reaction of the ketone R1COR2with the alcohol R3OH is:
R1COR2 + R3OH < == >CR1R2(OH)(OR3)

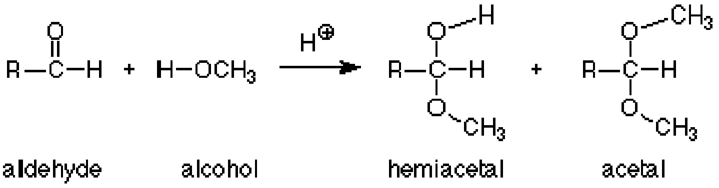


The formation of a hemiacetal is an example of NUCLEOPHILIC ADDITION to the carbonyl group of the aldehyde or ketone. The first step is attack of the lone pair on the O of the alcohol on the (positively charged) C of the carbonyl group. This is catalyzed by both acids and bases. Acid catalysis occurs by protonation of the O on the carbonyl, making the C more negative and more susceptible to nucleophilic attack. In base catalysis the OH^- ions from the base affect the -OH group of the alcohol, making it a more effective nucleophile.

In general, hemiacetals exist only in solution and cannot be isolated because they easily decompose back to the component alcohol and aldehyde or ketone. However, some cyclic hemiacetals are more stable. For example, cyclic forms of SUGAR molecules are hemiacetals.

Further reaction of hemiactals with another molecule of alcohol leads to a full acetal. For example:

CH(OH)(CH3)(OC_2H_5) + C_2H_5OH <==>CH(CH3)$(OC_2H_5)_2$

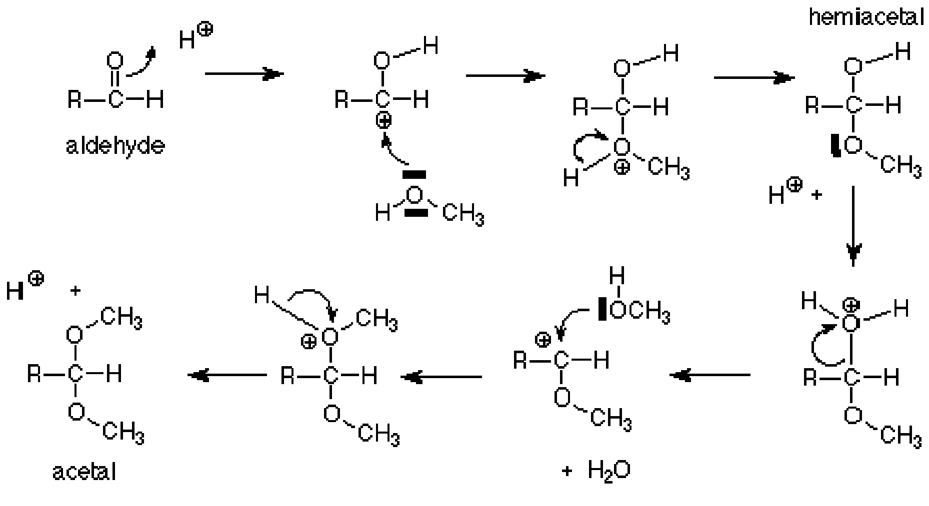


The overall reaction of an aldehyde or ketone with an alcohol to give an acetal can be written: R1COR2 + R3OH < == > CR1R2(OR3)2

It is also possible to have ‘mixed’ acetals with the general formula CR1R2(OR3)-(OR4). Note that if the acetal is derived from an aldehyde, then R1 and/or R2

May be a hydrogen atom. The mechanism of formation of an acetal from a hemiacetal is acid catalyzed. It involves protonation of the –OH group of the hemiacetal followed by loss of water to form an oxonium ion, which is attacked by the alcohol molecule.

Formerly it was conventional to use the terms ‘hemiacetal’ and ‘acetal’ for compounds formed by reaction between aldehydes and alcohols. Similar reactions between ketones and alcohols gave rise to compounds called hemiketals and ketals. Current nomenclature uses ‘hemiacetal’ and ‘acetal’ for compounds derived from either an aldehyde or a ketone, but reserves ‘hemiketal’ and ‘ketal’ for those derived from ketones. In other words, the ketals are a subclass of the acetals and the hemiketals are a subclass of the hemiacetals.

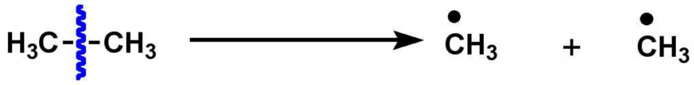


Achiral - Describing a molecule that does not have chiral properties; i.e. one that does not exhibit OPTICAL ACTIVITY.

Bond fission

A covalent bond is formed when electrons are shared between two atoms in the classical sense. A single bond (sigma bond) is thus made up of two electrons. Now a chemical reaction takes place when old bonds are broken and new ones are created. So how can one break a single bond—there are plainly two ways to go about breaking a bond as shown below.

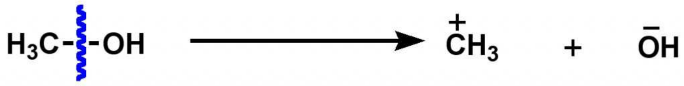
Homolytic fission



Homolysis

Homolytic fission is where each atom of the bond keeps an electron each resulting in species called free radicals. Radicals are important intermediates in organic chemistry and we will talk about them later. As the bond breaks to give two similar species each keeping an electron this form of bond breaking is called *Homolytic Fission*.

Heterolytic fission



Heterolysis

In this case we can see that one of the atoms carry a negative charge after bond cleavage indicating that it has both the electrons of the bond and the other has no electrons at all. Hence it is electron deficient thus positively charged. As the electrons are not divided equally after bond cleavage this is called *Heterolytic Fission*. In a case the C atom carries a positive charge it is called a carbocation and in the case it carries both the electrons of the broken bond and is negatively charged, it is called a Carbanion. Carbocation and Carbanions are the most important carbon intermediates in organic chemistry. Please note that both types of fissions are applicable to both homoatomic and heteroatomic bonds (bonds between two different atoms say C-N or C-O).

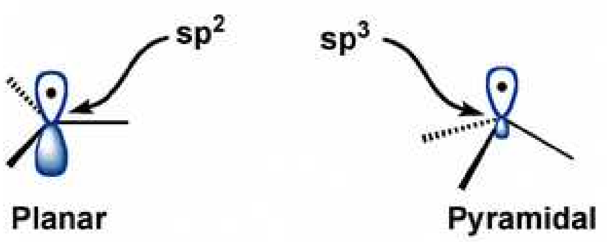
Free radicals

These are neutral intermediates, formed due to homolytic cleavage of a single bond. Some common bonds which cleave to give free radicals in organic chemistry are shown: C-O, C-Cl, C-Br, C-I, C-C, C-H. Carbon free radicals are mainly generated by:

i. Photolysis (action of light) like acetone alpha cleavage
ii. Other radical initiator like allylic bromination by N-Bromosuccinimide (NBS)

There has been a certain degree of debate as to what the shape and geometry of a free radical is like. Revisiting the theory of hybridization, there can be two basic shapes of these radicals.

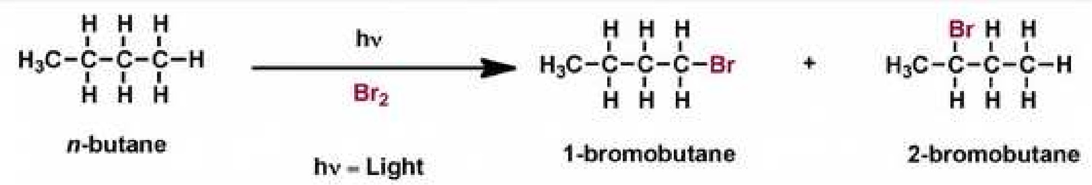
If the centre carbon atom of the radical is sp^3 hybridized (remember the one which was made of one s and three orbitals as in CH_4), the geometry will be tetrahedral.[1] But in the case of a radical there are only three groups attached to the sp^3 hybridized carbon atom so they we will have a shape of what resembles a pyramid—it's a tetrahedron with its head cut off. So sp^3 hybridized radicals are pyramidal in shape. The single electron of the radical would then be housed in a sp^3 orbital. The other option is sp^2 hybridization. In that case the C atom is sp^2 hybridized, so as discussed previously the shape would be planar with the single electron in the unhybridized p-orbital with the three substituents having sp^2 hybridized bonds.



Two different geometries of free radicals. The single electrons are shown as black dots.

So to summarize free radicals:

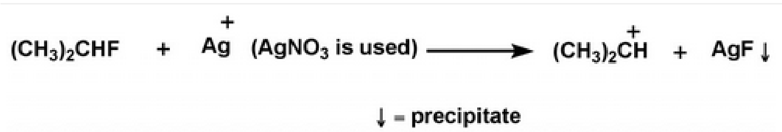
- Formed under activation by light or use of additional compounds called Radical Initiators.
- They are very reactive, because they have an unpaired electron which wants to get paired up.
- They are either pyramidal or planar with the lone electron in their sp^3 or p orbitals respectively.
- Because of their high reactivity, they tend to be less selective. In simple terms it means that it sometimes difficult to predict what products are formed in reactions which involve free radicals and we actually get several products from a single reaction.



This reaction shows the formation of two products with the Br atom attached to different carbons.

Carbocations

Carbocations are formed from the heterolytic cleavage of a carbon-heteroatom (meaning a non carbon atom in general) bond where the other atom is more electronegative than carbon like a C-O, C-N, C-X (X can be Cl, Br, I, etc) bond. This is quite logical as after the cleavage if a carbocation is to be formed the two electrons of the bond must go to the other atom. And this is favoured if that other atom is electronegative. Carbocations can be made in difficult conditions by using so-called superacids, developed by George Olah (Nobel Prize, 1994), which helps stabilize these intermediates substantially to be analyzed. Formation of carbocations can be assisted by using cations like Ag^+, with alkyl halides as substrates.



$$(CH_3)_2CHF + \overset{+}{Ag}\ (AgNO_3 \text{ is used}) \longrightarrow (CH_3)_2\overset{+}{C}H + AgF\downarrow$$

Formation of carbocation

The precipitating out of the silver salt forces the equilibrium to shift towards the forwards reaction.

A Similar reaction is Finkelstein reaction is particularly useful for preparing iodoalkanes. The iodoalkanes are obtained by heating chloro or bromoalkanes with a concentrated solution of sodium iodide in dry acetone.

In Acetone after Reflux (Heating in enclosed container) for a long time [Refluxing is a process of heating a liquid in a flask provided with a condenser. The vapours of the liquid which rise up get condensed back into the flask.]

RX + NaI ------ > RI + NaX where X = Cl, Br, and R is an Alkyl group

Sodium chloride and sodium bromide being less soluble in acetone get precipitated from the solution and can be removed by filtration. This also prevents the backward reaction to occur according to Le Chatelier's principle. The reaction gives the best results with primary halides.

With iodide, the solvate $NaI \cdot 3\,(CH_3)_2CO$ can be formed, in which each Na^+ is coordinated by 6 acetone ligands via oxygen lone pairs, and the I− ions fill in the gaps between these octahedral units, being surrounded by the methyl groups of the acetones. I− has a larger ionic radius compared to Cl− and Br− and thus fills the gap completely, thereby minimizing empty space in the lattice and its distance to Na+, which is, however, still larger than in solvent-free sodium iodide. This larger distance between the ions decreases the lattice energy, which in turn makes the compound readily soluble in acetone. Cl− and Br− are too small to fit in these gaps, and as the cation-anion distance becomes too large, the only way to minimize the lattice energy is the formation of a solvent-free structure NaX (X = Cl−, Br−). When the lattice energy is larger than the energy released by solvation of the ions, namely that of Na+ by complexation with acetone, the compound becomes insoluble and precipitates from the solution.

The positively charged carbon atom in carbocations is sp^2 hybridized, which means it's planar as we know by now. The three substituents of the carbocation lie in a plane leaving the unhybridized empty p orbital perpendicular to them.

These intermediates react with species which are electron rich (quite obvious) and being charged are stabilized in polar solvents. (Just as Na^+ is soluble and stable in polar water). Carbocations are important intermediates in most mechanisms along with carbanions as we shall see later.

To summarize carbocations:

- Formed due to heterolysis of a C-X bond (where X is more electronegative) and thus has a positive charge.
- Planar in shape (sp^2 hybridized carbon), with empty p orbital perpendicular to the plane of the molecule.
- Reactive towards electron rich species.

Carbanions

These are intermediates also formed as a result of heterolysis, but here the electron pair from the bond is kept by the carbon atom. From what we saw earlier the more electronegative atom keeps the electrons, so in this case carbon must the more electronegative of the two atoms making up the bond. Now there are only a few atoms (non-metals; metals are not usually part of organic chemistry) which are less electronegative, so the most common bond cleavage which yields carbanions is the C-H bond. The ease of breaking this bond and creating a carbanion is also a measure of the compound's acidity, because a H^+ is also generated with the carbanion, which makes the molecule an acid in the Bronsted sense.

Carbanions have three groups attached to each other and a lone pair of electrons which gives it its negative charge (similar to the ammonia molecule where the central N has 3 Hs and a lone pair of electrons). So its geometry is pyramidal (tetrahedral but since there is no fourth group again it's like a tetrahedral with head cut off) and the carbon atom is sp^3 hybridized.

Carbanions are also stable in polar solution (electrostatic stabilization).

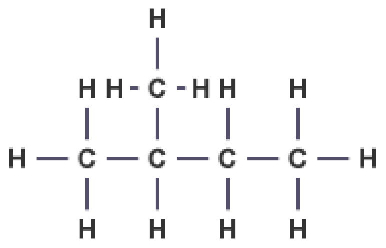
To summarize carbanions:

- Formed due to heterolysis of a C-X bond (where X is less electronegative) and thus has a negative charge.
- Pyramidal is shape (sp^3 hybridized) with the excess electrons placed in one sp^3 hybrid orbital.
- Reactive towards positively charged (electron deficient species).

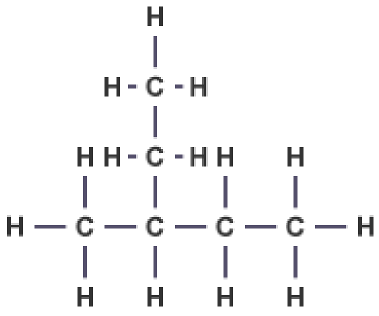
Stability of intermediates

Most organic reactions take place via formation of intermediates. So the study of different intermediates would help us predict the course of the reaction and the main aspect to look at would be their stability. No organic mechanism has been conclusively 'PROVEN', all the mechanism we see are the most plausible ones derived from many experiments, a major component of which is isolating and studying the intermediates. It is difficult to say that a certain mechanism is absolutely correct, but it is quite simple to point out an incorrect mechanism. One of the ways a chemist would confirm an incorrect mechanism is if it involves a very unstable intermediate. The good thing about this is that with a few empirical rules and principles in mind, it is quite simple to assign relative stability of intermediates like radicals, carbocations and carbanions. And what is even better is that we have already discussed these principles.

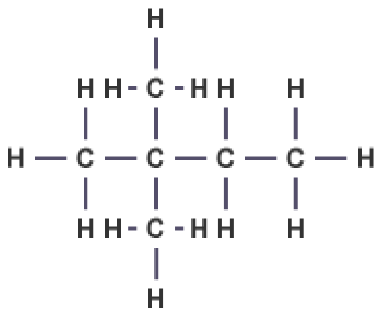
For carbocations and free radicals (both electron poor species), any group which donates electron density to the carbon centre would stabilize it and inversely electron withdrawing groups would increase electron deficiency on the carbon centre leading to destabilization. (Remember charge is not desirable, the most stable species are usually neutral). So following the same logic the effect should just be opposite in the case of carbanions as they are electron rich (negatively charged) instead of being electron deficient like the above two. So groups which pull away electrons from the charged carbon atom would have a stabilizing effect whereas electron donation would destabilize the intermediate as it loads more negative charge on an already negatively charged atom.



2-methylbutane

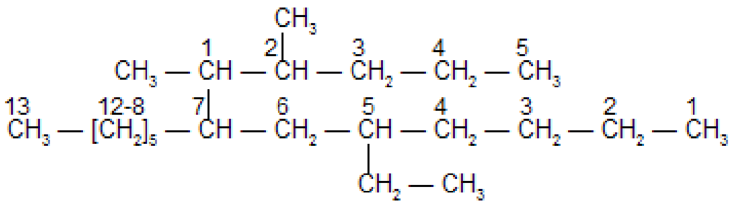


3-methylpentane (not 2-ethylbutane)



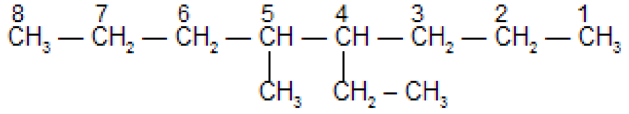
2,2-dimethylbutane

The name of a complex radical is considered to start with the first letter of its complete name.



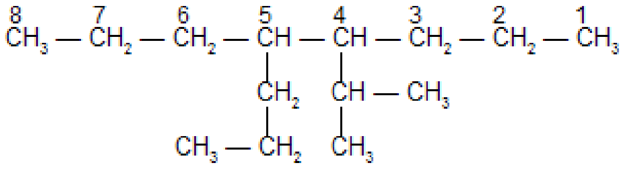
dimethylpentyl (as a complete single substituent) is alphabetized under " d ", thus 7-(1,2-Dimethylpentyl)-5-ethyltridecane

In cases where names of complex radicals are composed of identical words, preference for citation is given to that radical which contains the lowest locant at the first cited point of difference in the radical.



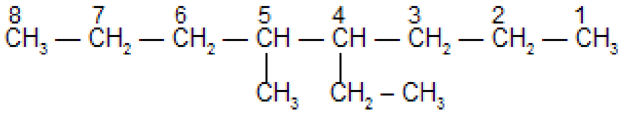
$CH_3-CH_2-CH_2-CH(CH_3)-CH(CH_2-CH_3)-CH_2-CH_2-CH_3$

4-Ethyl-5-methyloctane



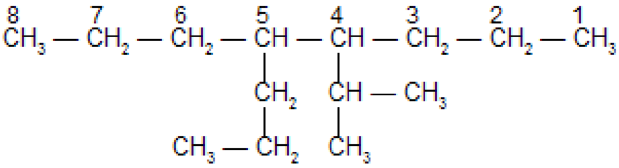
4-Isopropyl-5-propyloctane

If two or more side chains are in equivalent positions the one to be assigned the lower number is that cited first in the name.



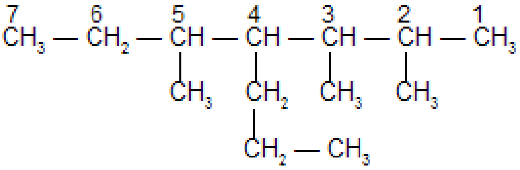
$\overset{8}{C}H_3-\overset{7}{C}H_2-\overset{6}{C}H_2-\overset{5}{C}H(CH_3)-\overset{4}{C}H(CH_2-CH_3)-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}H_3$

4-Ethyl-5-methyloctane

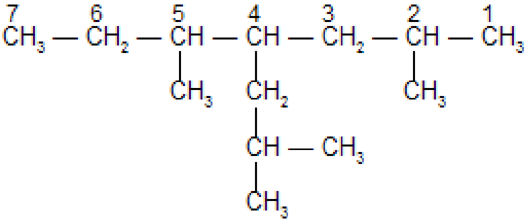


4-Isopropyl-5-propyloctane

The lowestsum rule.

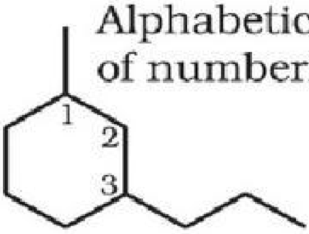


2,3,5-Trimethyl-4-propylheptane (not 3,5,6-Trimethyl-4-propylheptane)



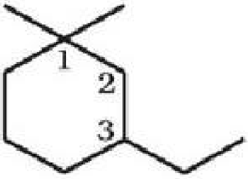
4-Isobutyl-2,5-dimethylheptane (not 4-Isobatyl-2, 6-dimethylheptane

Cyclopentane



Alphabetical order of numbering

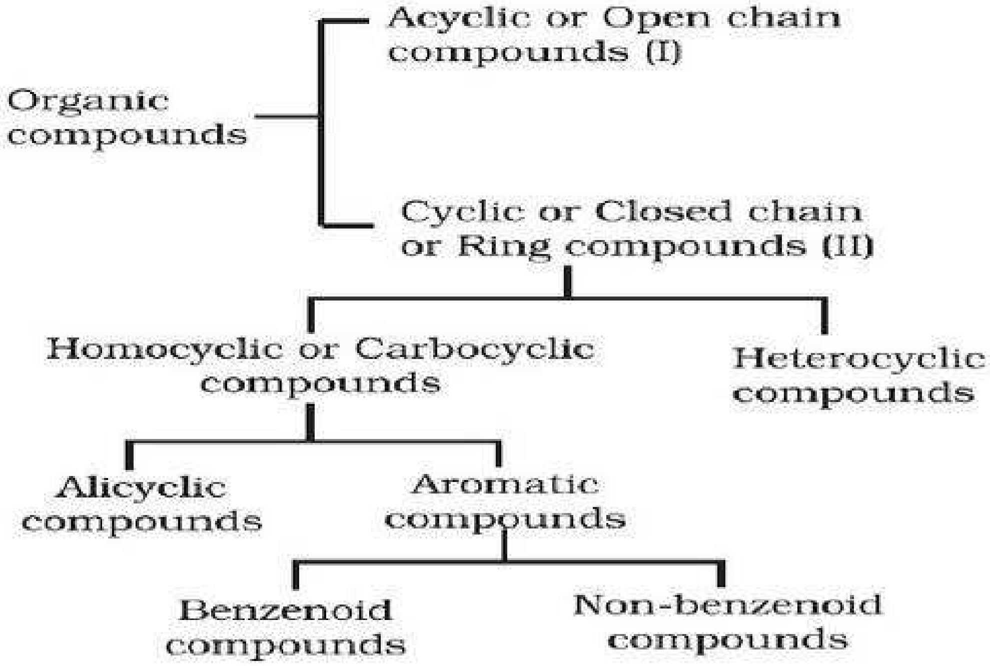
1-Methyl-3-propylcyclohexane



More branched carbon gets lower number

3-Ethyl-1,1-dimethylcyclohexane (not 1-ethyl-3,3-dimethylcyclohexane)

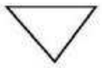
CLASSIFICATION OF ORGANIC COMPOUNDS



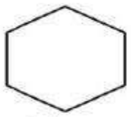
Alicyclic or closed chain or ring compounds

Alicyclic (aliphatic cyclic) compounds contain carbon atoms joined in the form of a ring (homocyclic). Sometimes atoms other than carbon are also present in the ring (heterocylic).

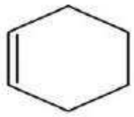
Some examples are



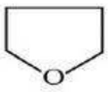
Cyclopropane



Cyclohexane



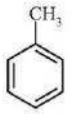
Cyclohexene



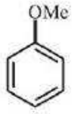
Tetrahydrofuran

Nomenclature of Substituted Benzene Compounds

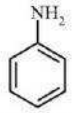
For IUPAC nomenclature of substituted benzene compounds, the substituent is placed as prefix to the word *benzene as* shown in the following examples.



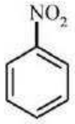
Methylbenzene
(Toluene)



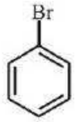
Methoxybenzene
(Anisole)



Aminobenzene
(Aniline)



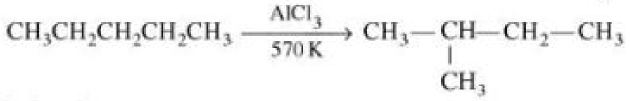
Nitrobenzene



Bromobenzene

How Isomers are made ?

(a) *Normal to branched chain in alkane* *n*-Alkane is heated with $AlCl_3$ at 570 K to give branched chain



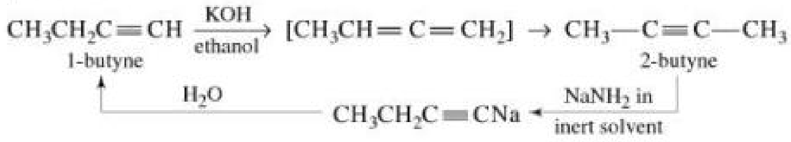
$$CH_3CH_2CH_2CH_2CH_3 \xrightarrow[570\,K]{AlCl_3} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$$

(b) *Shift of double bond*

In the presence of catalyst like $Al_2(SO_4)_3$, alkene undergo isomerization at high temperature (770 – 970 K).

$$CH_3CH_2CH_2CH{=}CH_2 \rightarrow CH_3CH_2CH{=}CHCH_3$$

(c) *Shift of triple bond*



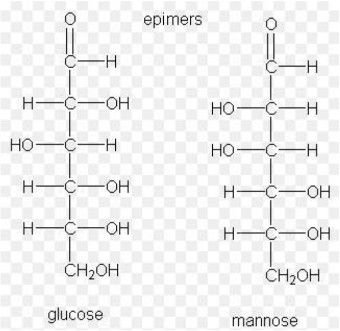
$$\underset{\text{1-butyne}}{CH_3CH_2C{\equiv}CH} \xrightarrow[\text{ethanol}]{KOH} [CH_3CH{=}C{=}CH_2] \rightarrow \underset{\text{2-butyne}}{CH_3-C{\equiv}C-CH_3}$$

$$\text{2-butyne} \xrightarrow[\text{inert solvent}]{NaNH_2\text{ in}} CH_3CH_2C{\equiv}CNa \xrightarrow{H_2O} \text{1-butyne}$$

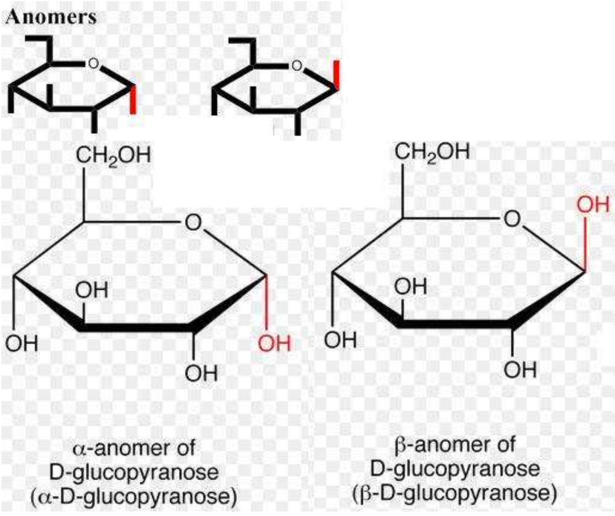
Heating with ethanolic potassium hydroxide shifts the triple bond towards the centre of the chain whereas heating with sodamide in an inert solvent shifts the bond towards the end of chain.

The choice of principal functional group is made on the basis of order of preference. **The order of decreasing priority for some functional groups is: -COOH, –SO3H, -COOR (R=alkyl group), COCl, -CONH2, -CN,-HC=O, >C=O, -OH, -NH2, >C=C<, -C≡C- .**

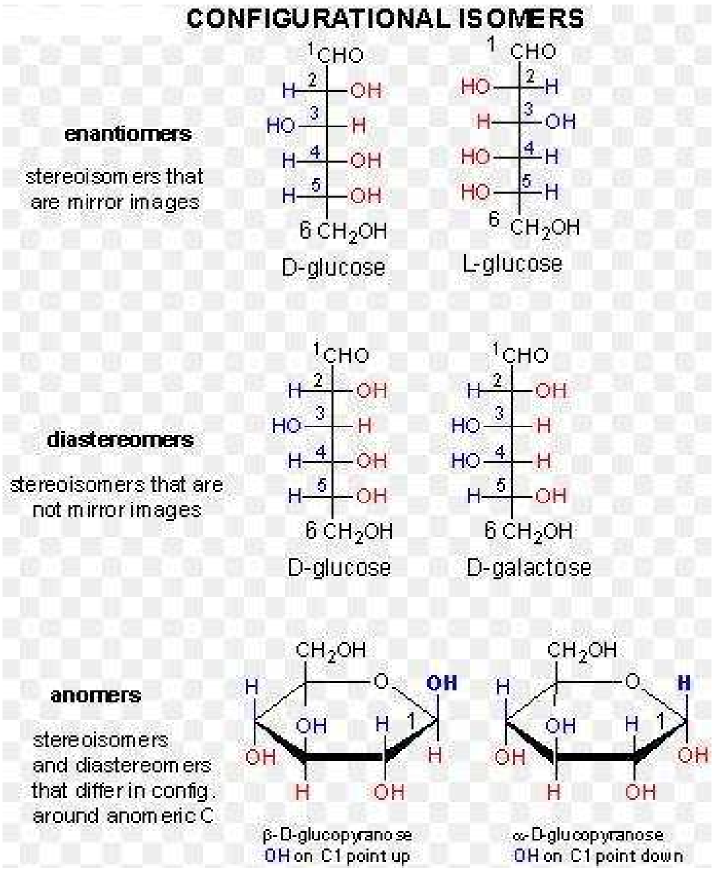
Epimers

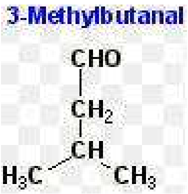


Anomers



Epimer Anomer comparison

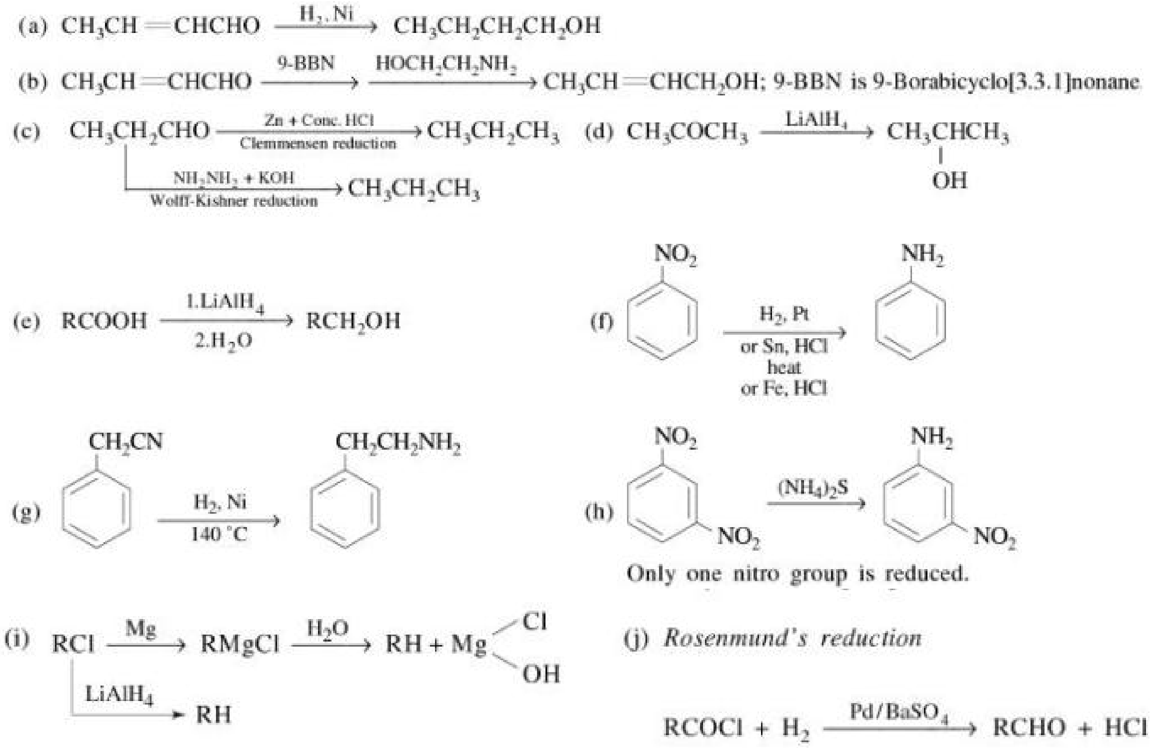




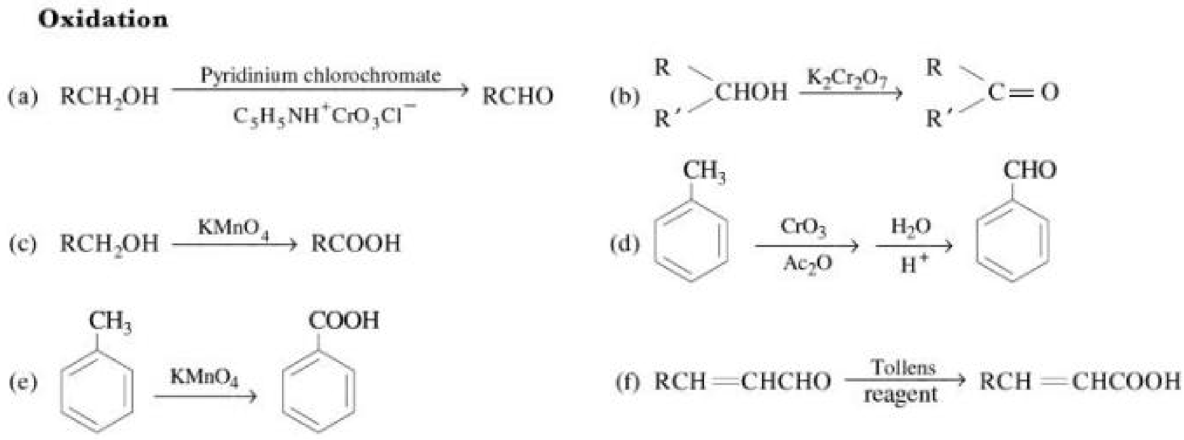
Epimers are monosaccharides that differ in chirality at only one carbon. In the straight-chain format, epimers will have H and OH-substituents switched at one backbone carbon, but not at any others.

Anomers are special epimers; in cyclic forms of one single monosaccharide, anomers differ in chirality at the anomeric (hemiacetal) carbon only. In the straight-chain format, anomers will have the same configuation.

Various Methods of Reduction used in Organic Chemistry

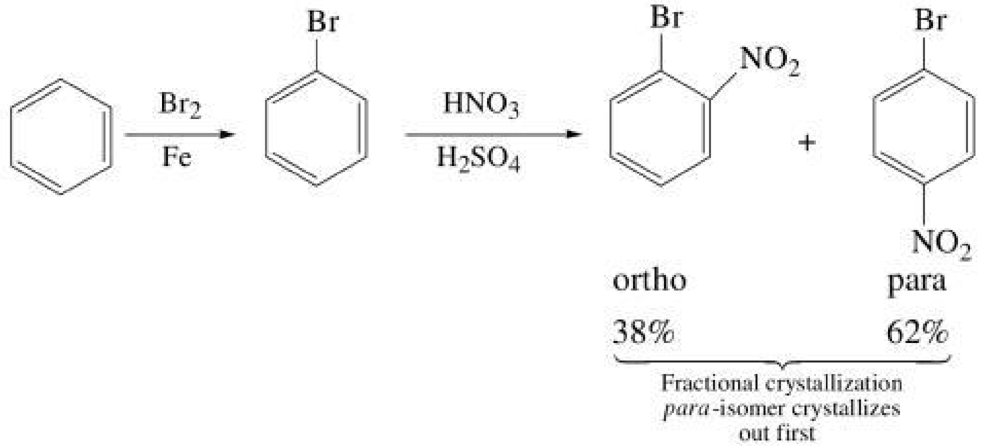


Various methods of Oxidation



Synthesis of p-bromonitrobenzene in 2 steps

a synthesis of *p*-bromonitrobenzene from benzene in two steps.

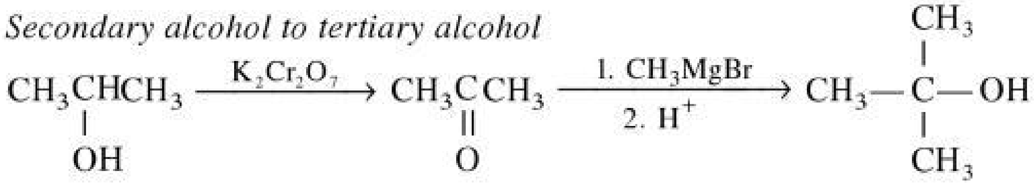


ortho 38%

para 62%

Fractional crystallization
para-isomer crystallizes
out first

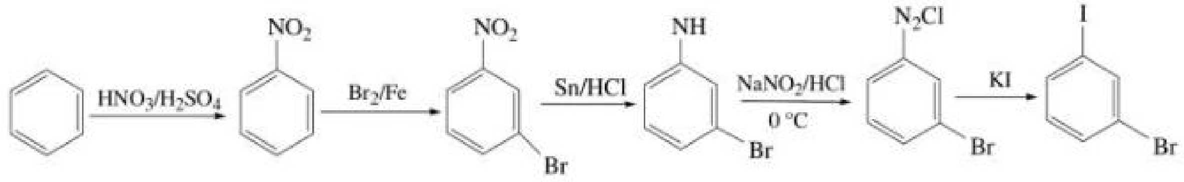
Secondary alcohol to tertiary alcohol



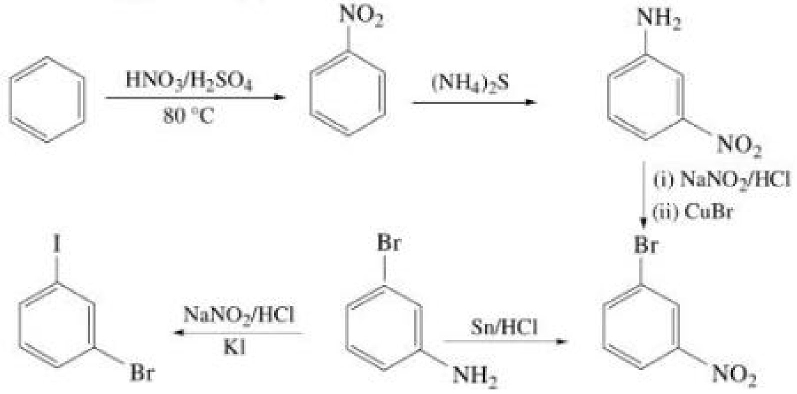
$$CH_3\underset{OH}{\underset{|}{C}}HCH_3 \xrightarrow{K_2Cr_2O_7} CH_3\underset{O}{\underset{||}{C}}CH_3 \xrightarrow[2.\ H^+]{1.\ CH_3MgBr} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$$

Prepare m-bromoiodobenzene from benzene

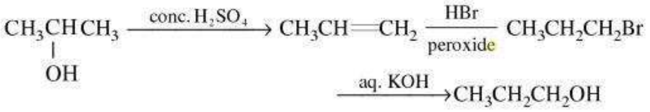
prepare *m*-bromoiodobenzene from benzene (in not more than 5-7 steps)?



Alternatively, we may proceed as follows:



Secondary alcohol to Primary alcohol

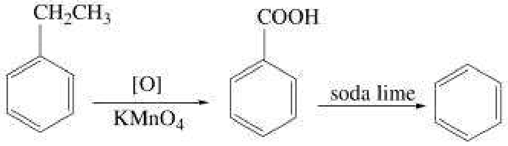


$$CH_3\underset{\underset{OH}{|}}{C}HCH_3 \xrightarrow{conc.\ H_2SO_4} CH_3CH{=}CH_2 \xrightarrow[peroxide]{HBr} CH_3CH_2CH_2Br \xrightarrow{aq.\ KOH} CH_3CH_2CH_2OH$$

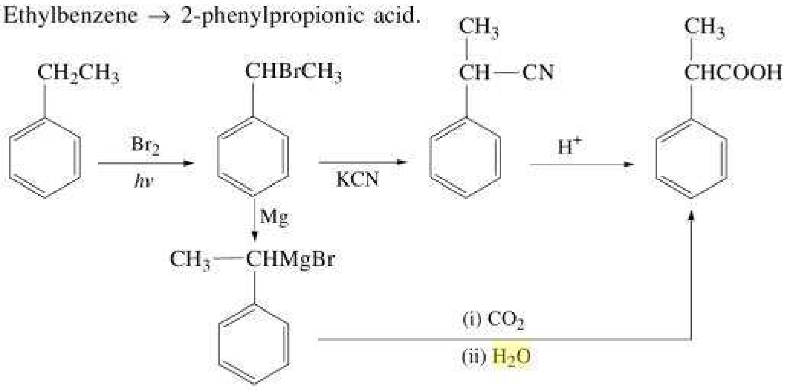
To convert Ethylebenzene to Benzene   and Ethylebenzene to phenylpropionic acid

Show the steps to carry out the following transformations.

(i) Ethylbenzene → benzene



(ii) Ethylbenzene → 2-phenylpropionic acid.

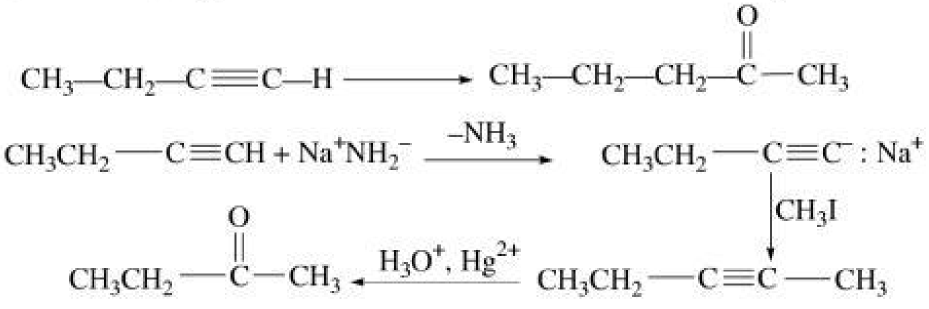


Alcohol to alcohol with one carbon more

$$CH_3OH \xrightarrow{PBr_3} CH_3Br \xrightarrow{KCN} CH_3CN \xrightarrow{[H]} CH_3CH_2NH_2 \xrightarrow{HNO_2} CH_3CH_2OH$$

Carryout the transformations 1-Butyne to ketone

Carry out the following transformation in not more than three steps.



$$CH_3-CH_2-C\equiv C-H \longrightarrow CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$

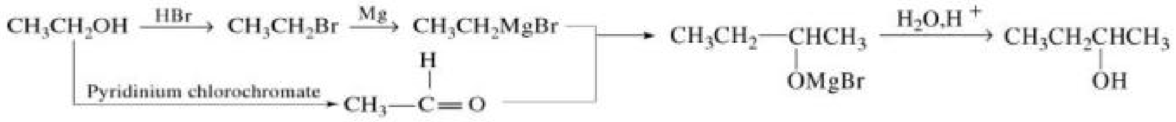
$$CH_3CH_2-C\equiv CH + Na^+NH_2^- \xrightarrow{-NH_3} CH_3CH_2-C\equiv C^- : Na^+$$

$$\xrightarrow{CH_3I} CH_3CH_2-C\equiv C-CH_3 \xrightarrow{H_3O^+,\ Hg^{2+}} CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH_3$$

Alcohol to alcohol with one carbon less

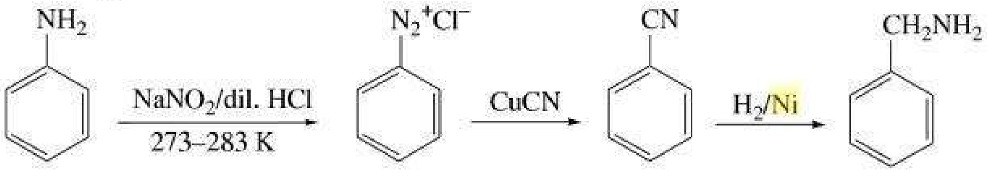
$$CH_3CH_2OH \xrightarrow[K_2Cr_2O_7]{[O]} CH_3COOH \xrightarrow{soda\ lime} CH_4 \xrightarrow[hv]{Cl_2} CH_3Cl \xrightarrow{aq.\ KOH} CH_3OH$$

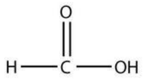
Simple alcohol to complicated alcohol



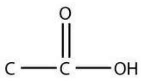
Conversion of Aniline to Benzylamine

How would you bring about the following conversion (in 3 steps)?
Aniline → Benzylamine

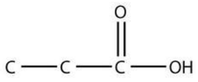




Methanoic acid



Ethanoic acid

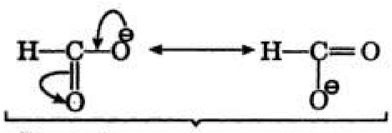


Propanoic acid

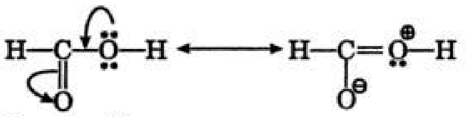
(i) Carbon-oxygen bond lengths in formic acid are different but are the same in sodium formate. Justify.

(ii) Phenate ion has more number of contributing structures than benzoate ion: but still benzoic acid is a stronger acid. Explain.

Solution. (*i*) In sodium formate, the contributing structures for the anion are equivalent while these are not the same in formic acid.



Formate ion



Formate acid

Thus, carbon-oxygen bond length in formate ion is the same for both the bonds while these are different in formic acid.

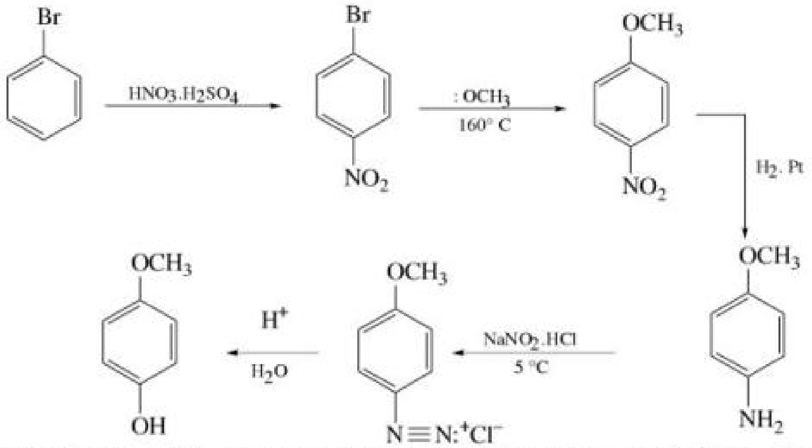
(*ii*) In phenate ion, the negative charge is dispersed only one electronegative oxygen atoms while there are two available oxygen atoms in benzoate ion to disperse the negative charge.

Amine to amine containing one carbon more

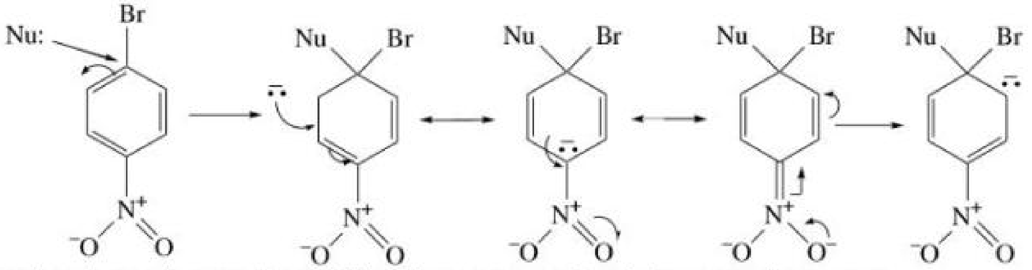
$$RCH_2NH_2 \xrightarrow[0\,^\circ C]{HNO_2} RCH_2OH \xrightarrow{PBr_3} RCH_2Br \xrightarrow{NaCN} RCH_2CN \xrightarrow{H_2/Ni} RCH_2CH_2NH_2$$

Synthesis of 4-methoxyphenol from bromobenzene

How would you synthesise 4-methoxyphenol from bromobenzene is NOT more than five steps? State clearly the reagents used in each step and show the structure of the intermediate compounds in your synthetic scheme.



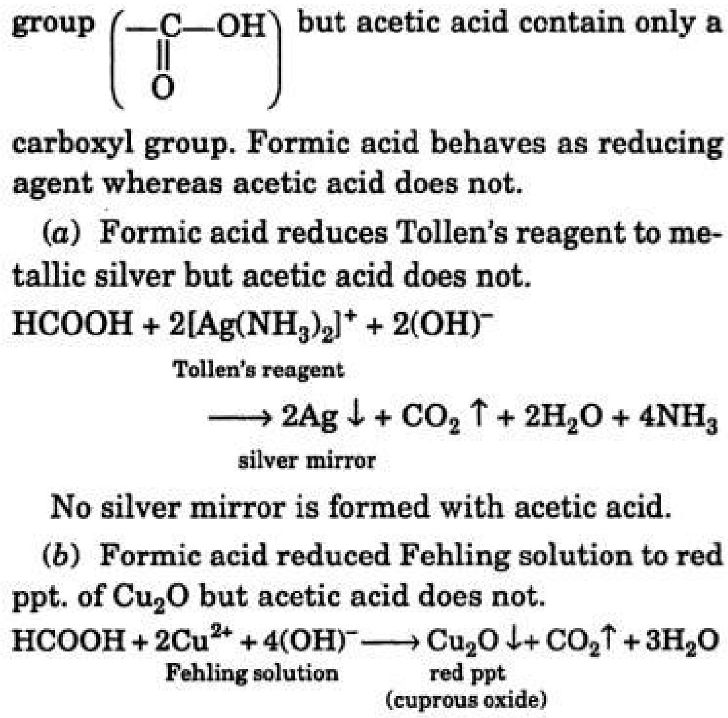
The introduction of —NO_2 group at *para* position in bromobenzene facilitates the nucleophilic replacement of —Br by —OCH_3.



The negative charge is strongly stabilised by resonance involving *para*-nitro group.

Write chemical tests to distinguish between:

Solution. Formic acid $\left(\mathrm{H-\overset{\overset{\displaystyle O}{\|}}{C}-OH}\right)$ contains both an aldehyde $\left(\mathrm{\overset{\overset{\displaystyle H}{|}}{-C}=O}\right)$ as well as carboxyl



group $\left(-\underset{\underset{O}{\|}}{C}-OH\right)$ but acetic acid contain only a carboxyl group. Formic acid behaves as reducing agent whereas acetic acid does not.

(*a*) Formic acid reduces Tollen's reagent to metallic silver but acetic acid does not.

$$\underset{\text{Tollen's reagent}}{HCOOH + 2[Ag(NH_3)_2]^+ + 2(OH)^-} \longrightarrow \underset{\text{silver mirror}}{2Ag\downarrow} + CO_2\uparrow + 2H_2O + 4NH_3$$

No silver mirror is formed with acetic acid.

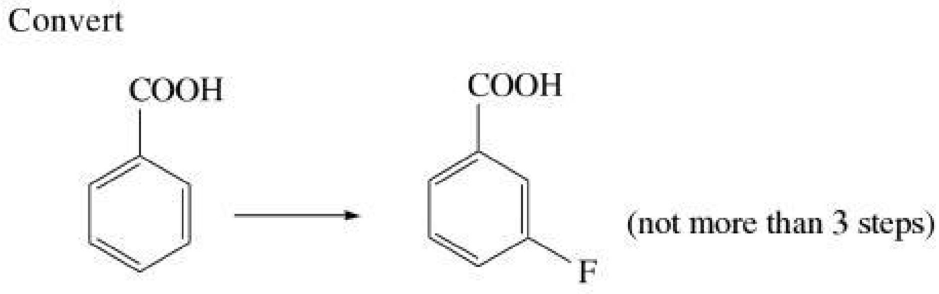
(*b*) Formic acid reduced Fehling solution to red ppt. of Cu_2O but acetic acid does not.

$$HCOOH + \underset{\text{Fehling solution}}{2Cu^{2+}} + 4(OH)^- \longrightarrow \underset{\substack{\text{red ppt}\\\text{(cuprous oxide)}}}{Cu_2O\downarrow} + CO_2\uparrow + 3H_2O$$

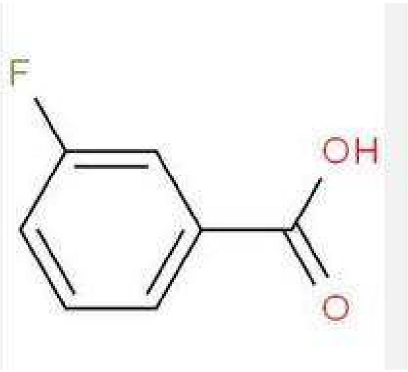
Amine to amine containing one carbon less

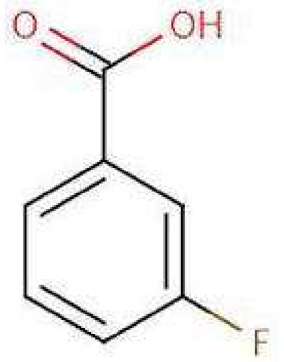
$$RCH_2NH_2 \xrightarrow[0°C]{HNO_2} RCH_2OH \xrightarrow[KMnO_4]{[O]} RCOOH \xrightarrow{SOCl_2} RCOCl \xrightarrow{NH_3} RCONH_2 \xrightarrow{OBr^-} RNH_2$$

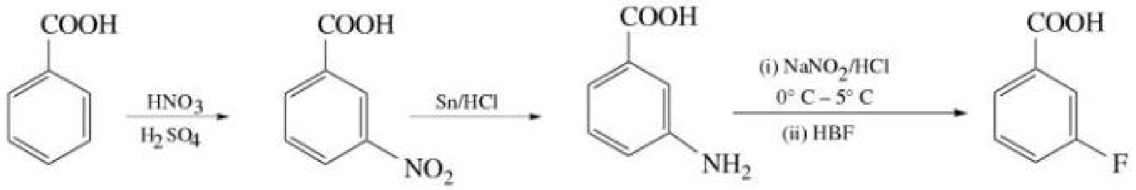
Convert Benzoic acid to meta fluorobenzoic acid (2-fluorobenzoic acid)



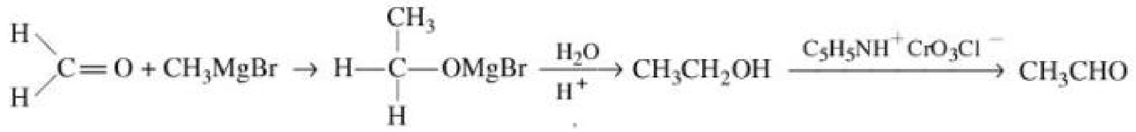
metafluoro benzoicacid







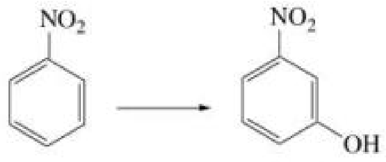
Aldehyde to aldehyde containing one carbon more



$$\mathrm{H_2C{=}O} + \mathrm{CH_3MgBr} \rightarrow \mathrm{H-\underset{H}{\overset{CH_3}{C}}-OMgBr} \xrightarrow[H^+]{H_2O} \mathrm{CH_3CH_2OH} \xrightarrow{C_5H_5NH^+CrO_3Cl^-} \mathrm{CH_3CHO}$$

Convert Nitrobenzene to meta hydroxynitrobenzene (or 4-nitrophenol)

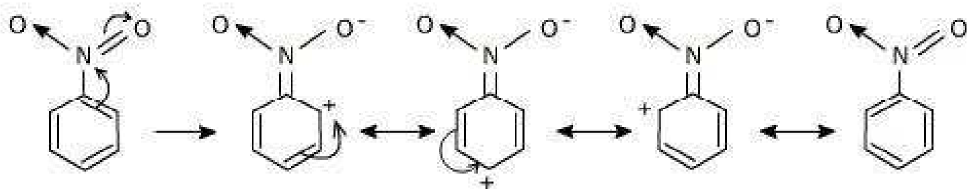
Convert



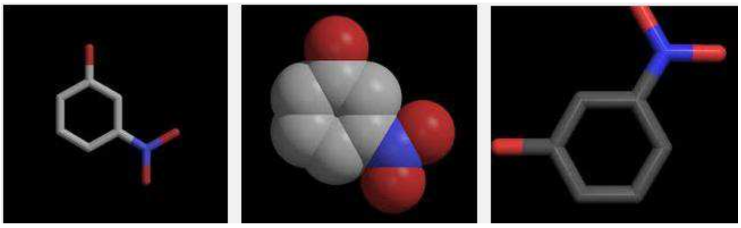
in not more than 4 steps mentioning the reagents, reaction conditions and intermediates in the above conversion.

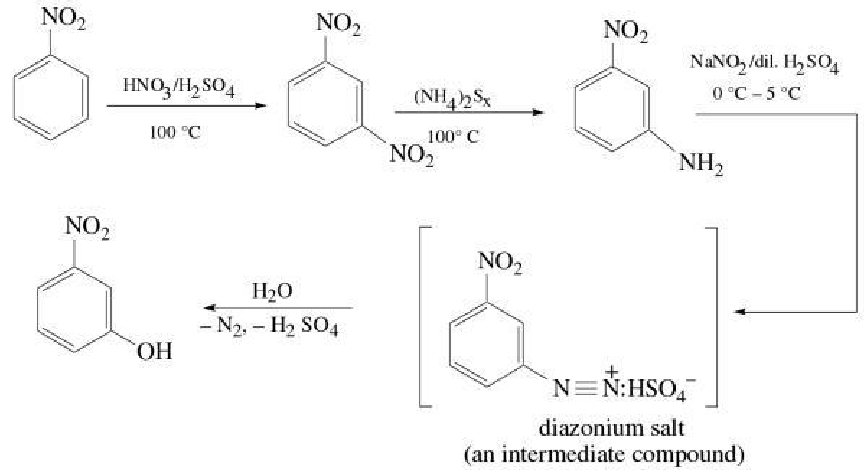
The given conversion can be carried out as follows.

Nitrobenzene resonance structure

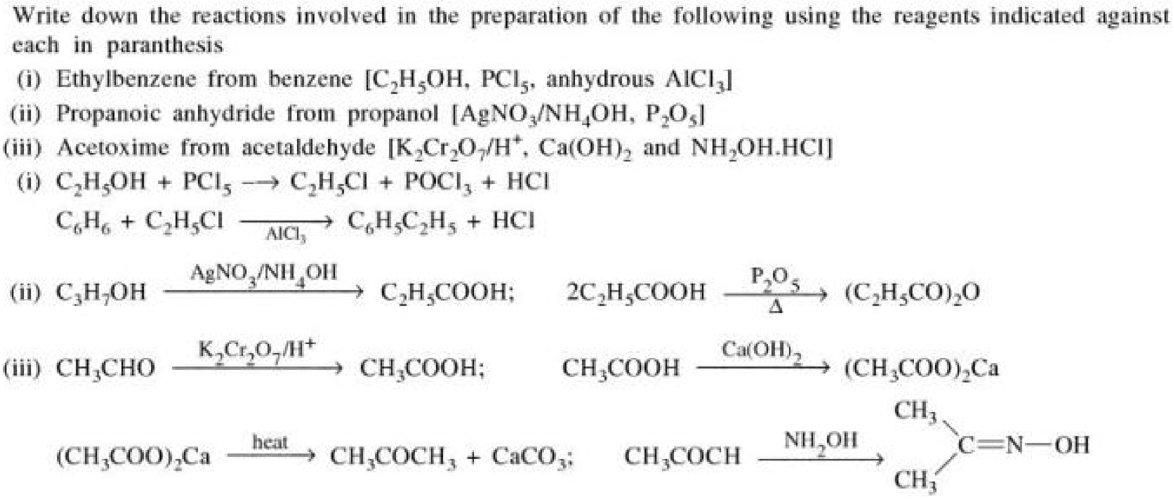


4 nitrophenol or metahydroxynitrobenzene





Many conversions or preparations



Write down the reactions involved in the preparation of the following using the reagents indicated against each in paranthesis

(i) Ethylbenzene from benzene [C_2H_5OH, PCl_5, anhydrous $AlCl_3$]

(ii) Propanoic anhydride from propanol [$AgNO_3/NH_4OH$, P_2O_5]

(iii) Acetoxime from acetaldehyde [$K_2Cr_2O_7/H^+$, $Ca(OH)_2$ and $NH_2OH.HCl$]

(i) $C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl + POCl_3 + HCl$

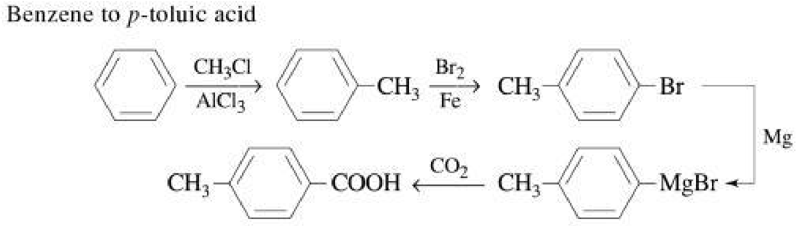
$C_6H_6 + C_2H_5Cl \xrightarrow[AlCl_3]{} C_6H_5C_2H_5 + HCl$

(ii) $C_3H_7OH \xrightarrow{AgNO_3/NH_4OH} C_2H_5COOH$; $2C_2H_5COOH \xrightarrow[\Delta]{P_2O_5} (C_2H_5CO)_2O$

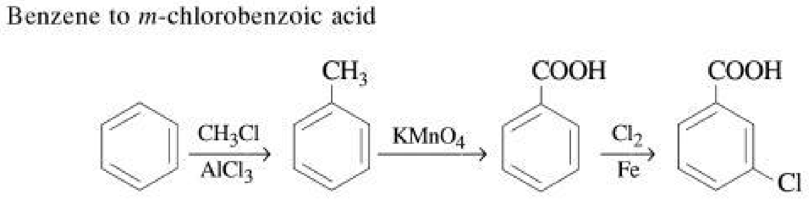
(iii) $CH_3CHO \xrightarrow{K_2Cr_2O_7/H^+} CH_3COOH$; $CH_3COOH \xrightarrow{Ca(OH)_2} (CH_3COO)_2Ca$

$(CH_3COO)_2Ca \xrightarrow{heat} CH_3COCH_3 + CaCO_3$; $CH_3COCH \xrightarrow{NH_2OH} \begin{matrix}CH_3\\ \\ CH_3\end{matrix}\!\!>C{=}N{-}OH$

Benzene to p-toluic acid

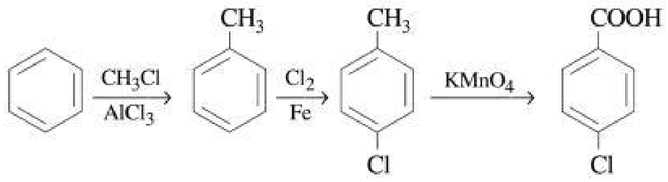


Benzene to m-chlorobenzoic acid



Benzene to p-chlorobenzoic acid

Benzene to *p*-chlorobenzoic acid



Acetic acid to Malonic acid

Acetic acid to malonic acid

$$CH_3COOH \xrightarrow{Br_2,\ P} BrCH_2COOH \xrightarrow{KCN} CNCH_2COOH \xrightarrow[H^+]{H_2O} HOOCCH_2COOH$$

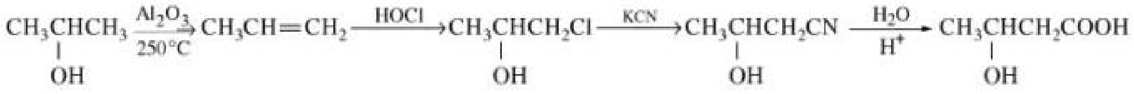
Ethyne to propanoic acid

Ethyne to propanoic acid

$$HC{\equiv}CH \xrightarrow[\text{catalyst}]{\text{Lindlar}} H_2C{=}CH_2 \xrightarrow{HCl} CH_3CH_2Cl \xrightarrow{KCN} C_2H_5CN \xrightarrow[H^+]{H_2O} C_2H_5COOH$$

Isopropyl alcohol to β-hydroxybutyric acid

Isopropyl alcohol to β-hydroxybutyric acid



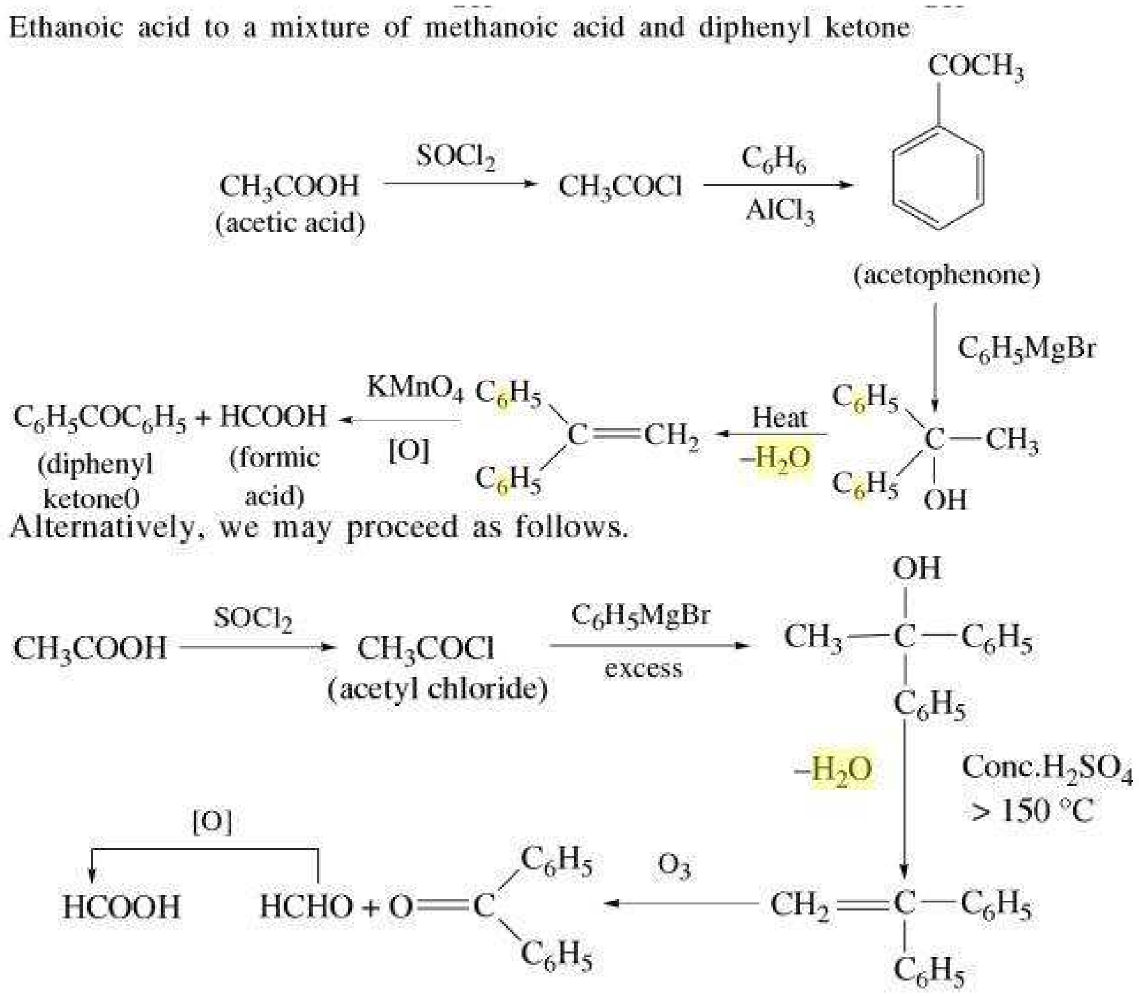
$$\underset{OH}{CH_3\overset{}{C}HCH_3} \xrightarrow[250°C]{Al_2O_3} CH_3CH{=}CH_2 \xrightarrow{HOCl} CH_3\underset{OH}{C}HCH_2Cl \xrightarrow{KCN} CH_3\underset{OH}{C}HCH_2CN \xrightarrow[H^+]{H_2O} CH_3\underset{OH}{C}HCH_2COOH$$

Acetic acid to Propanoic acid

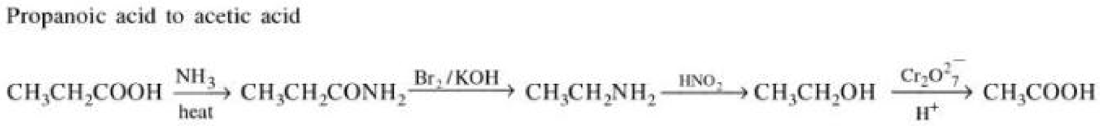
Acetic acid to propanoic acid

$$CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH \xrightarrow{PCl_3} CH_3CH_2Cl \xrightarrow{KCN} CH_3CH_2CN \xrightarrow[H^+]{H_2O} CH_3CH_2COOH$$

Ethanoic acid to a mixture of methanoic acid and diphenyl ketone

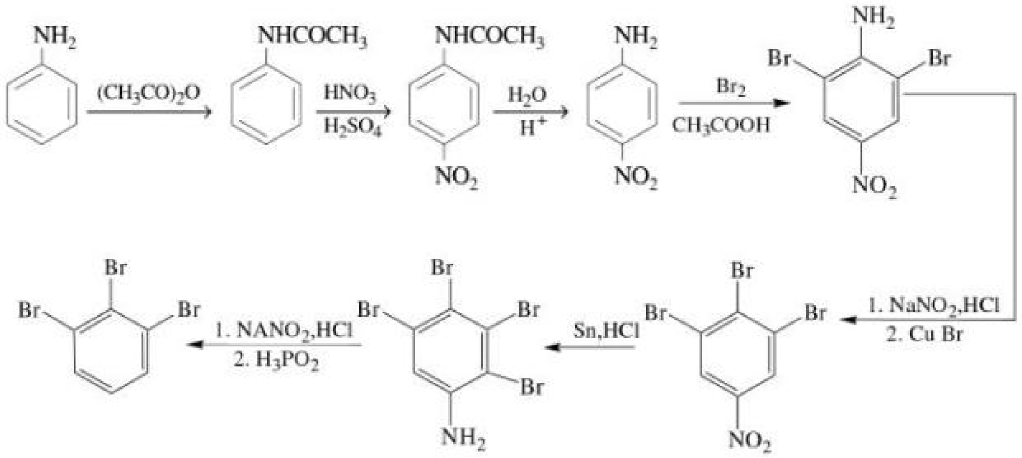


Propanoic acid to acetic acid


Propanoic acid to acetic acid

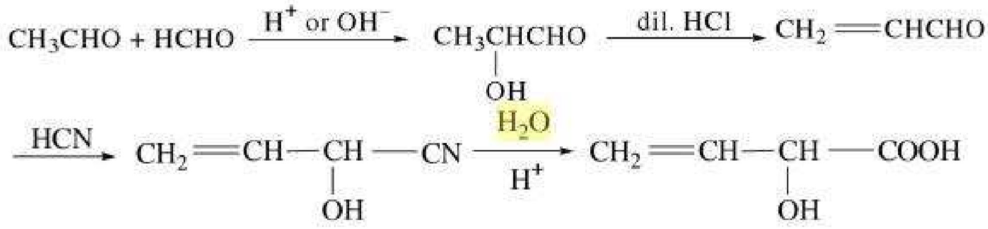
$$CH_3CH_2COOH \xrightarrow[heat]{NH_3} CH_3CH_2CONH_2 \xrightarrow{Br_2/KOH} CH_3CH_2NH_2 \xrightarrow{HNO_2} CH_3CH_2OH \xrightarrow[H^+]{Cr_2O_7^{2-}} CH_3COOH$$

Aniline to 1, 2, 3-tribromobenzene



Ethanal to 2-hydroxy-3-butenoic acid

Ethanal to 2-hydroxy-3-butenoic acid

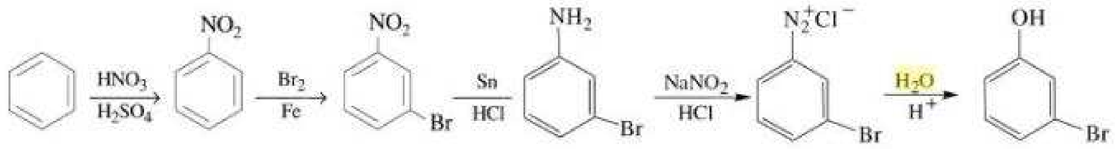


$$CH_3CHO + HCHO \xrightarrow{H^+ \text{ or } OH^-} \underset{\displaystyle OH}{CH_3\overset{}{C}HCHO} \xrightarrow{\text{dil. HCl}} CH_2{=}CHCHO$$

$$\xrightarrow{HCN} CH_2{=}CH{-}\underset{\displaystyle OH}{CH}{-}CN \xrightarrow[H^+]{H_2O} CH_2{=}CH{-}\underset{\displaystyle OH}{CH}{-}COOH$$

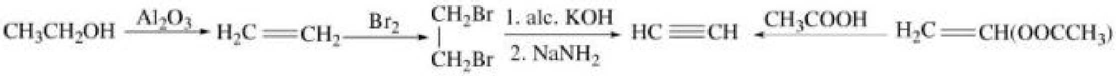
Benzene to m-bromophenol

Benzene to *m*-bromophenol



Ethyl alcohol to Vinyl alcohol

Ethyl alcohol to vinyl acetate



$$CH_3CH_2OH \xrightarrow{Al_2O_3} H_2C{=}CH_2 \xrightarrow{Br_2} \begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix} \xrightarrow[\text{2. NaNH}_2]{\text{1. alc. KOH}} HC{\equiv}CH \xrightarrow{CH_3COOH} H_2C{=}CH(OOCCH_3)$$

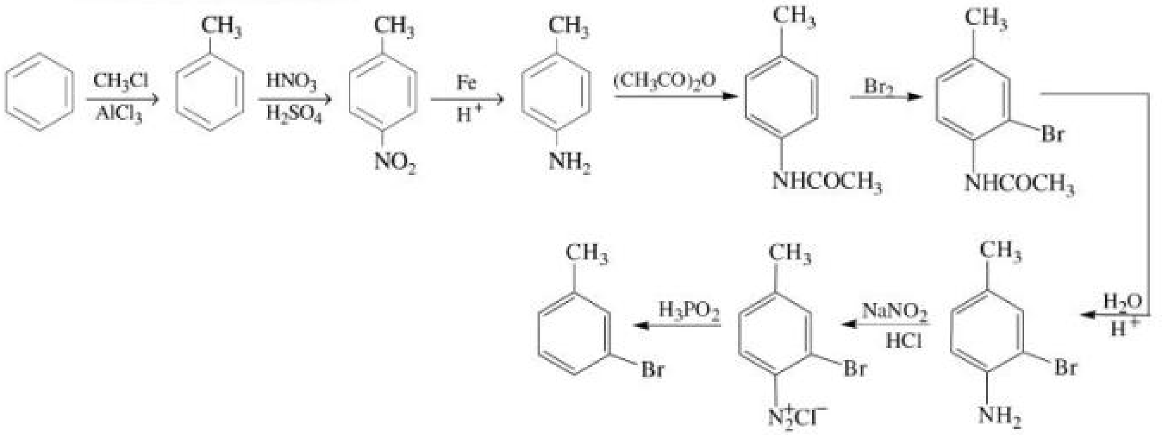
Methylamine to ethylamine

Methylamine to ethylamine

$$CH_3NH_2 \xrightarrow{HNO_2} CH_3OH \xrightarrow{PCl_3} CH_3Cl \xrightarrow{KCN} CH_3CN \xrightarrow{Sn/HCl} CH_3CH_2NH_2$$

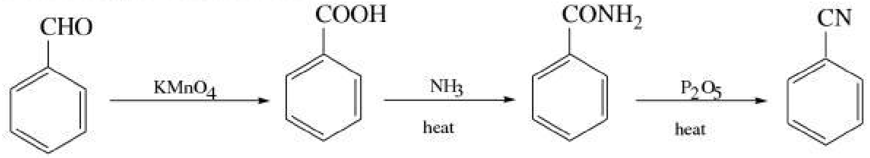
Benzene to m-bromotoluene

Benzene to *m*-bromotoluene



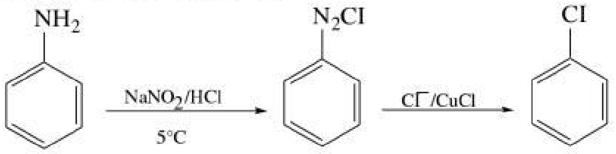
Benzaldehyde to cyanobenzene

Benzaldehyde to cyanobenzene



Aniline to Chlorobenzene

Aniline to Chlorobenzene

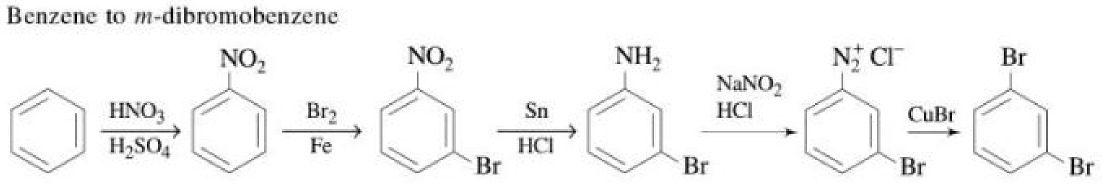


Ethylamine to Methylamine

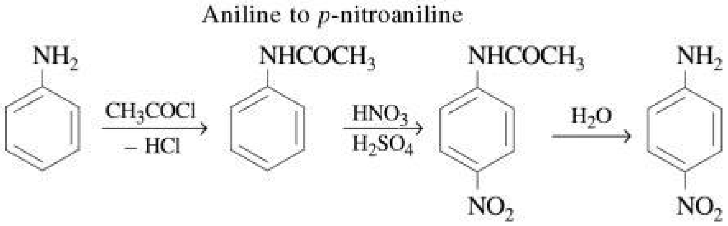
Ethylamine to methylamine

$$CH_3CH_2NH_2 \xrightarrow{HNO_2} CH_3CH_2OH \xrightarrow[H^+]{Cr_2O_7^{2-}} CH_3COOH \xrightarrow[heat]{NH_3} CH_3CONH_2 \xrightarrow{Br_2/KOH} CH_3NH_2$$

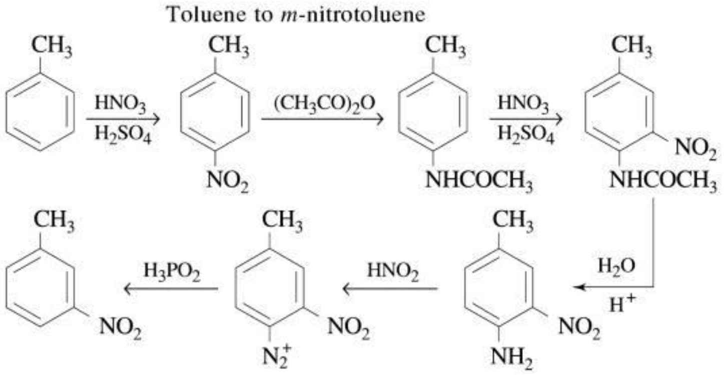
Benzene to m-dibromobenzene



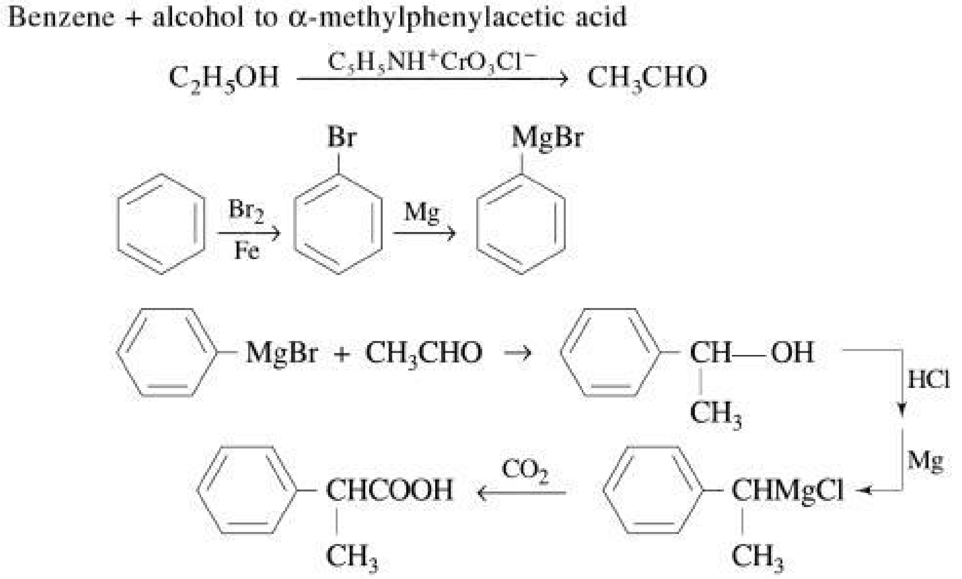
Aniline to p-nitroaniline

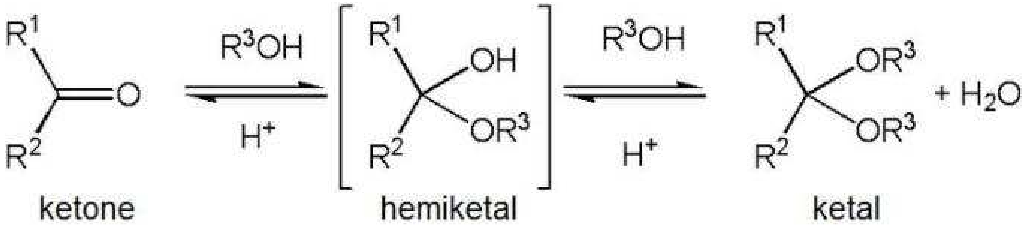


Toluene to m-nitrotoluene

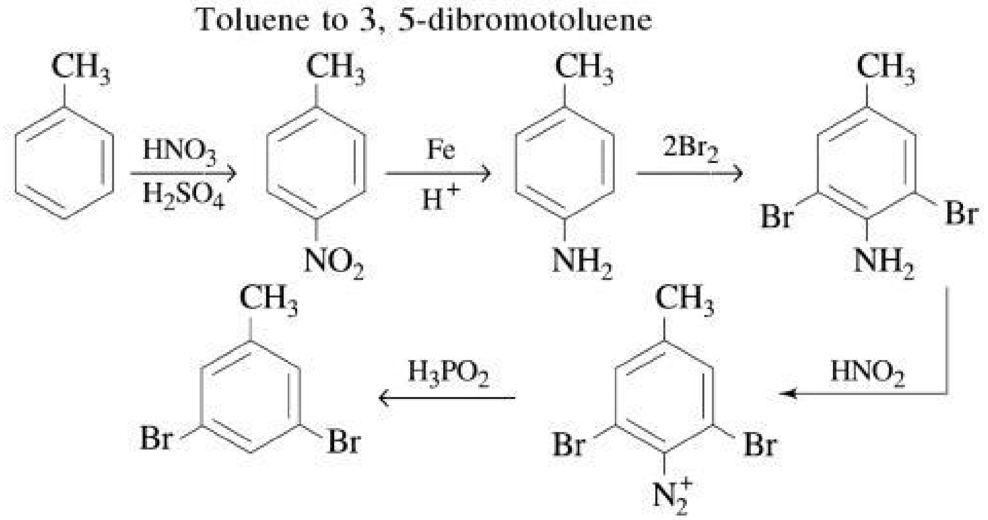


Convert Benzene + Alcohol to α-methylphenylacetic acid

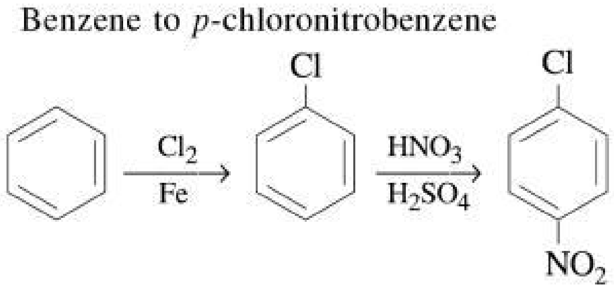




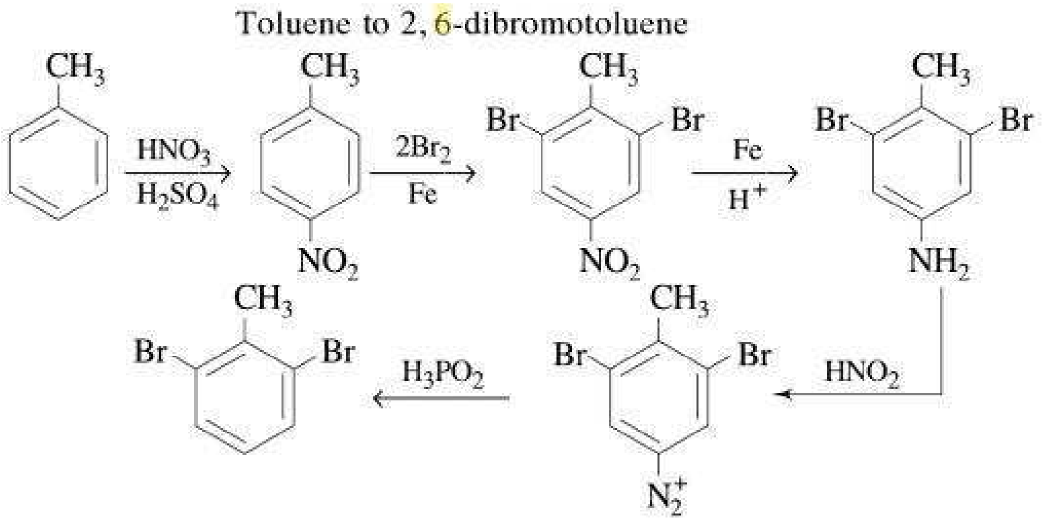
Toluene to 3,5 dibromotoluene



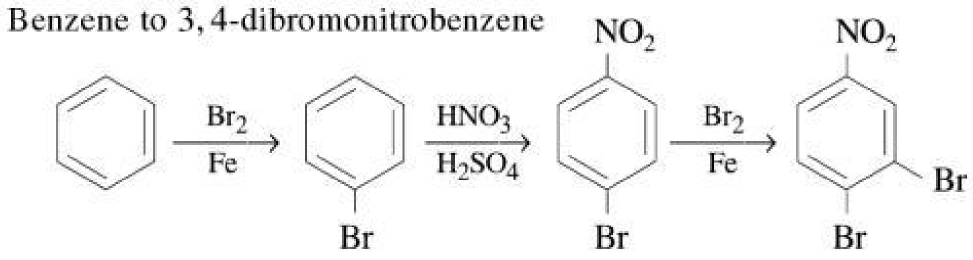
Benzene to p-chloronitrobenzene



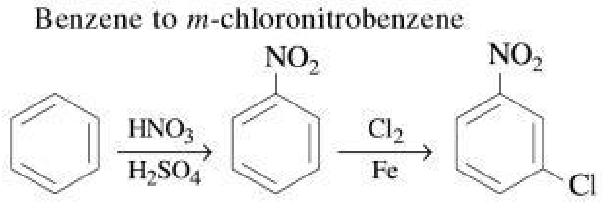
Toluene to 2,6 dibromotoluene



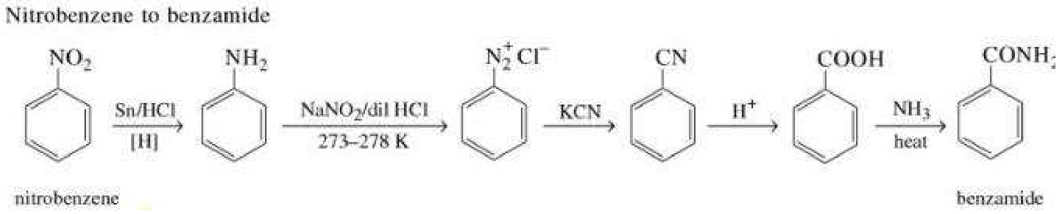
Benzene to 3,4-dibromonitrobenzene



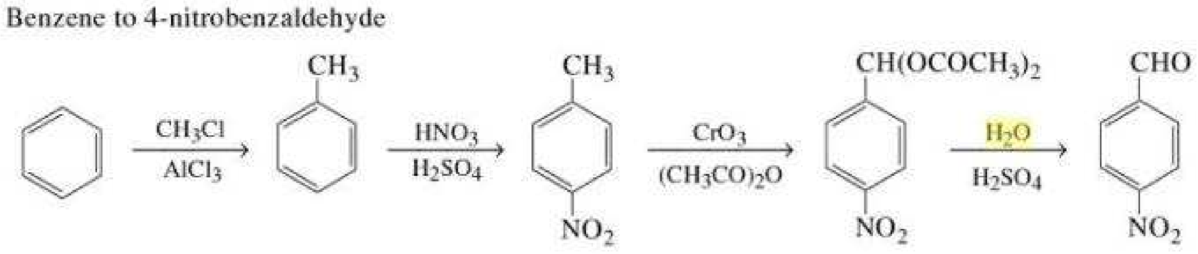
Benzene to m-chloronitrobenzene



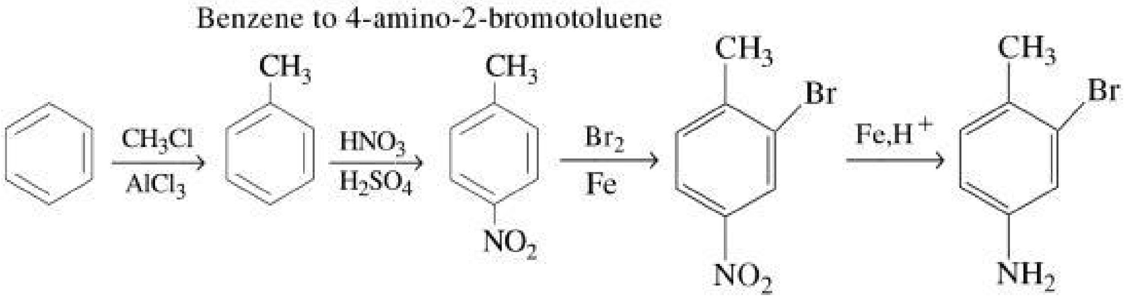
Nitrobenzene to benzamide

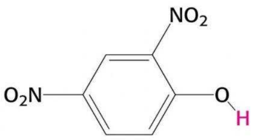


Benzene to 4-nitrobenzaldehyde



Benzene to 4-amino-2-bromotoluene

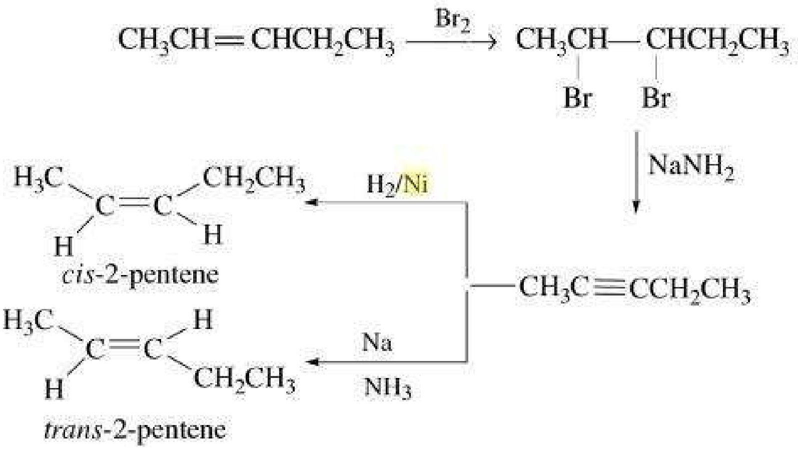


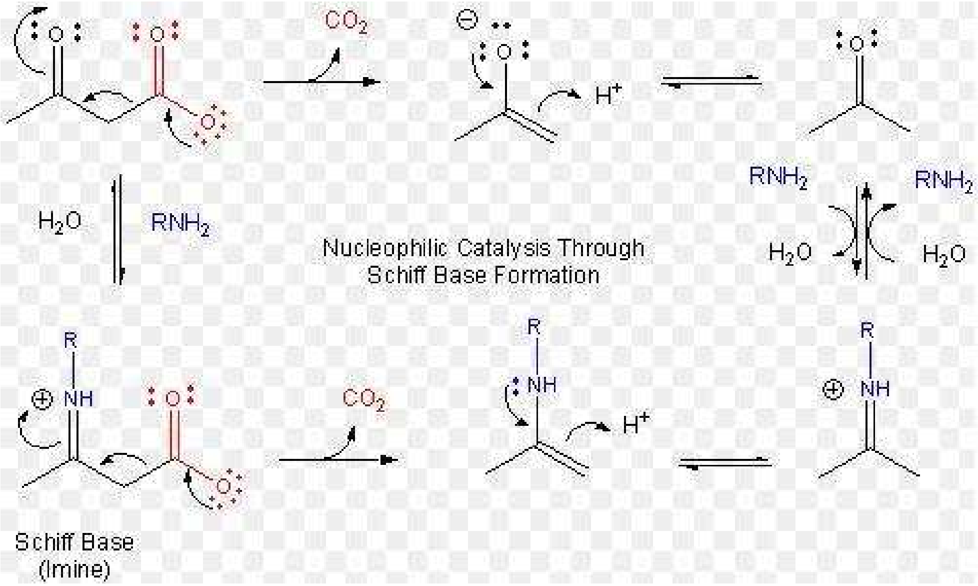


2,4-Dinitrophenol (DNP)

Convert a mixture of cis-2-pentene and trans-2-pentene into cis-2-pentene or trans-2-pentene

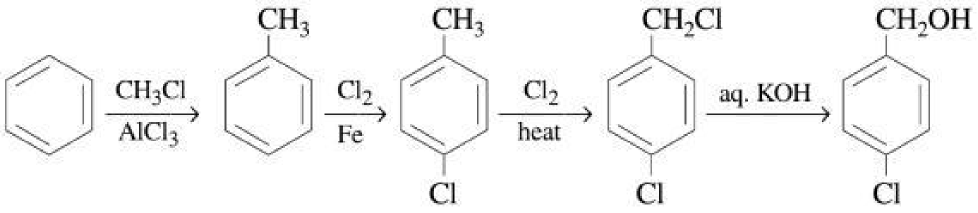
A mixture of *cis*-2-pentene and *trans*-2-pentene into *cis*-2-pentene or *trans*-2-pentene



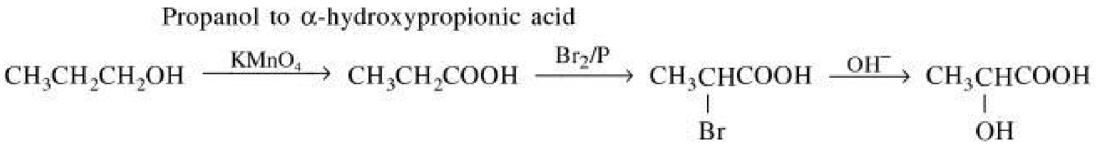


Benzene to p-chlorobenzylalcohol

Benzene to *p*-chlorobenzylalcohol

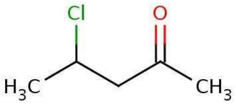


Convert Propanol to α-hydroxypropanoic acid

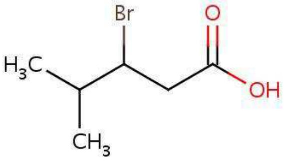

Propanol to α-hydroxypropionic acid

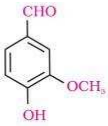
$$CH_3CH_2CH_2OH \xrightarrow{KMnO_4} CH_3CH_2COOH \xrightarrow{Br_2/P} \underset{\substack{| \\ Br}}{CH_3CHCOOH} \xrightarrow{OH^-} \underset{\substack{| \\ OH}}{CH_3CHCOOH}$$

4-chloropentane-2-one

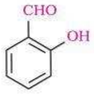


3-Bromo-4-methylpentanoic acid

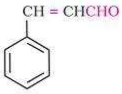




Vanillin

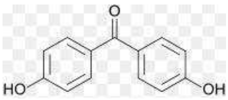


Salicylaldehyde

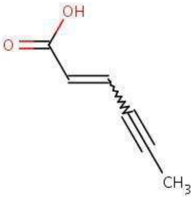


Cinnamaldehyde

p,p’- dihydroxybenzophenone

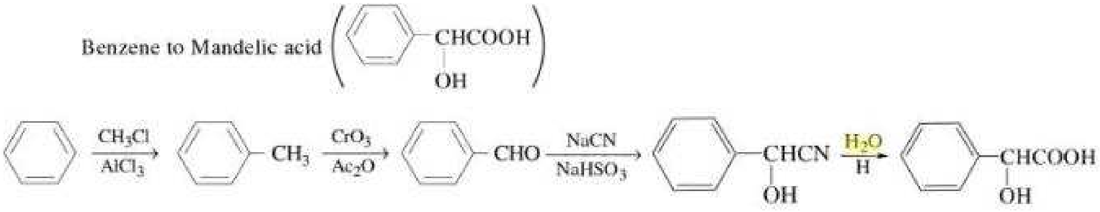


Hex-2-ene-4-ynoicacid

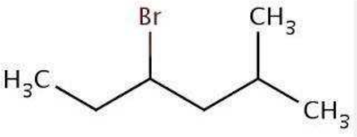


Heptan-2-one

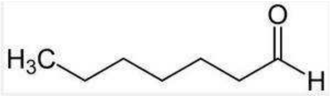
Benzene to Mandelic Acid



4-Bromo-2-methylhexane

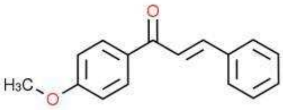


Heptanal

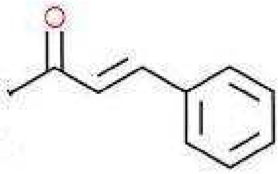


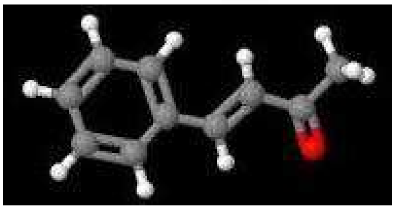
1-(4-Methoxyphenyl)-3-phenylprop-2-en-1-one

1-(4-Methoxyphenyl)-3-phenylprop-2-en-1-one

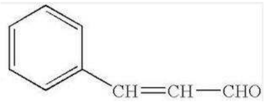


4-phenylprop-3-ene-2-one

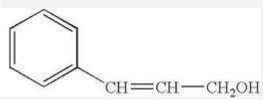




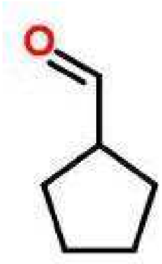
3-phenylprop-2-ene-1-al



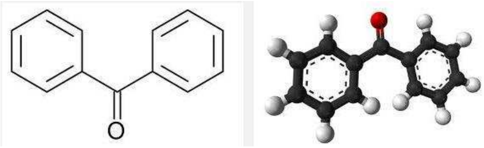
3-phenyl-prop-2-ene-1-ol



cyclopentancarbaldehyde

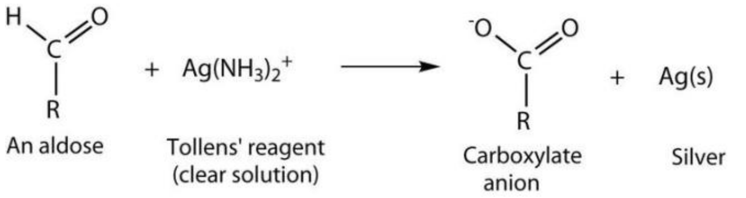


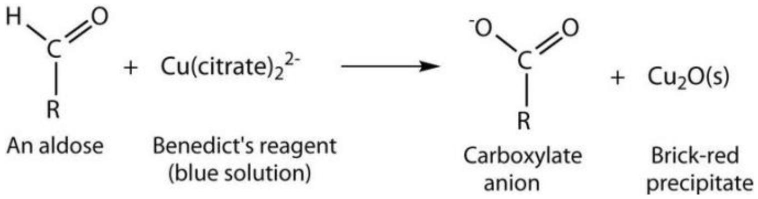
Benzophenone also diphenylmethanone



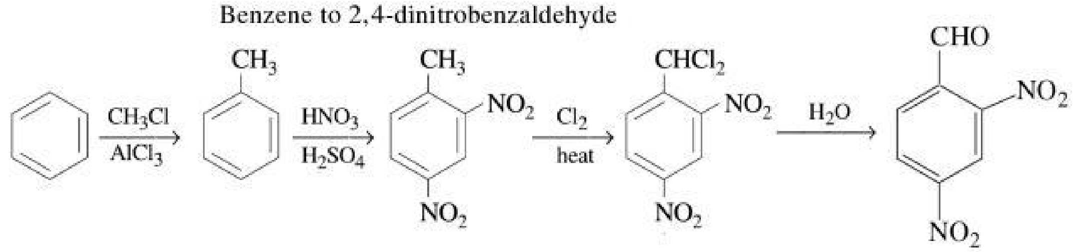
Tollen's Reagent

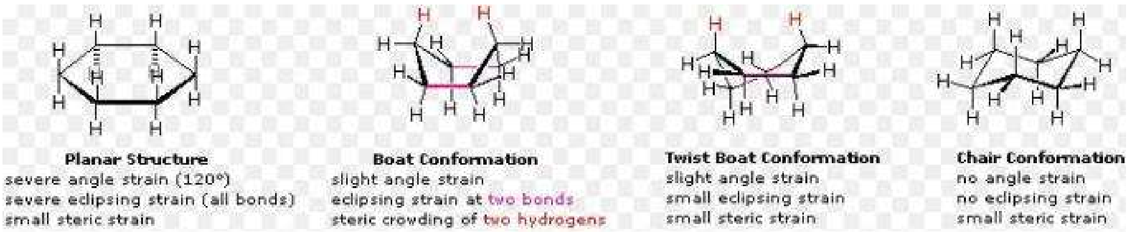
$$\underset{\text{An aldehyde}}{RCHO(aq)} + 2Ag(NH_3)_2^+(aq) + 3OH^-(aq) \longrightarrow RCOO^-(aq) + \underset{\text{Free silver}}{2Ag(s)} + 4NH_3(aq) + 2H_2O$$



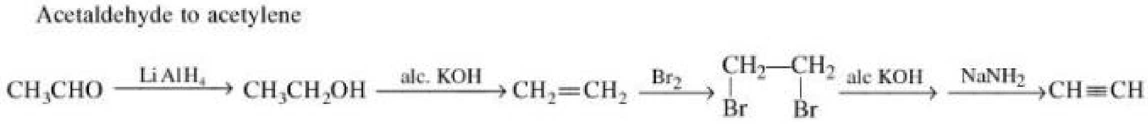


Benzene to 2,4-dinitrobenzaldehyde

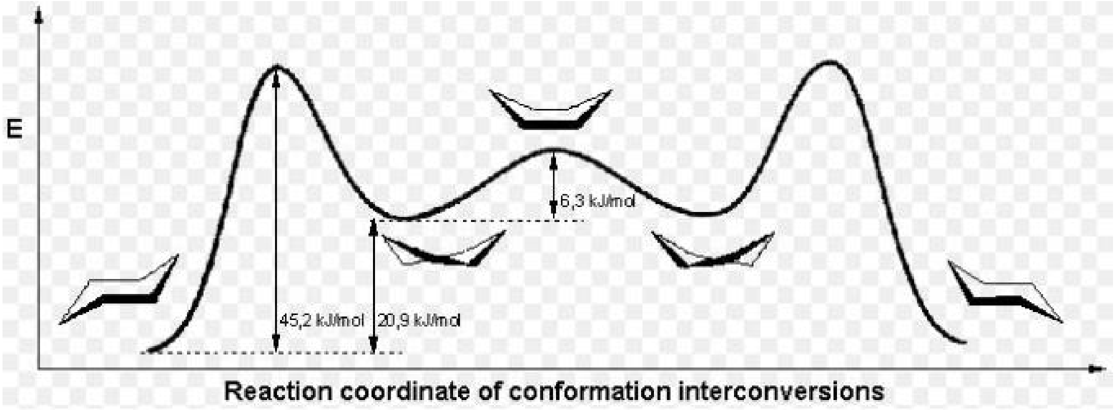




Acetaldehyde to Acetylene

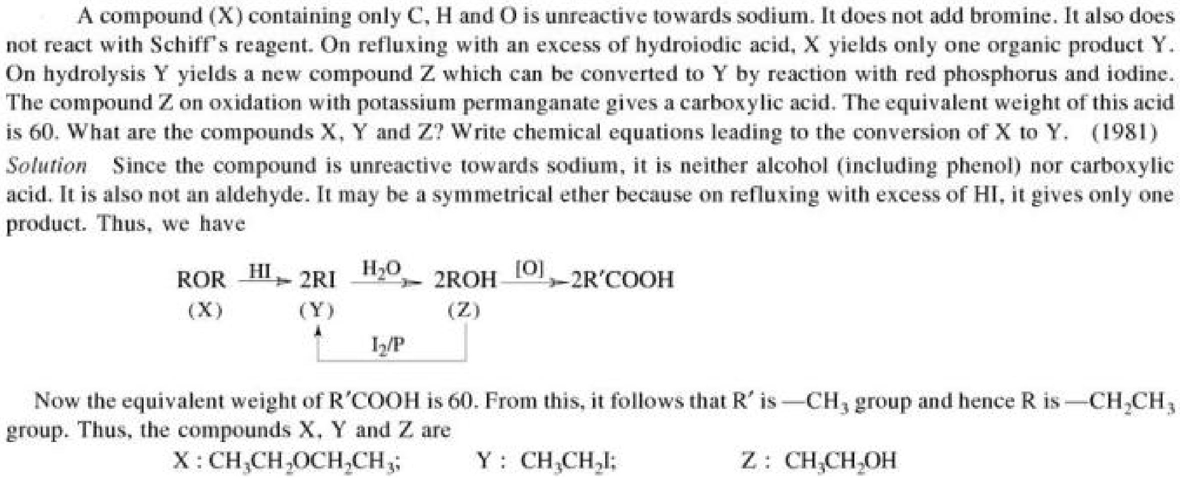


$$CH_3CHO \xrightarrow{LiAlH_4} CH_3CH_2OH \xrightarrow{alc.\ KOH} CH_2{=}CH_2 \xrightarrow{Br_2} \underset{Br}{CH_2}-\underset{Br}{CH_2} \xrightarrow{alc\ KOH} \xrightarrow{NaNH_2} CH{\equiv}CH$$



Identify the compounds

compound contains C, H and O unreactive towards Na (Sodium)



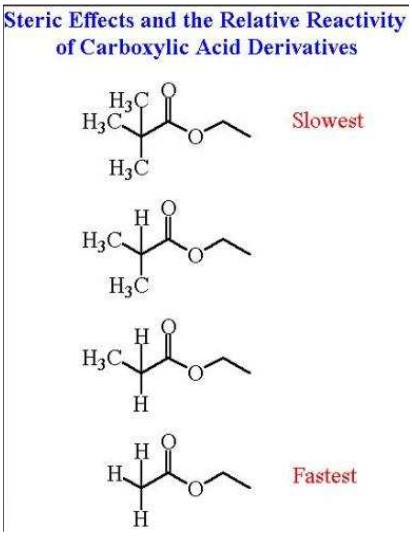
A compound (X) containing only C, H and O is unreactive towards sodium. It does not add bromine. It also does not react with Schiff's reagent. On refluxing with an excess of hydroiodic acid, X yields only one organic product Y. On hydrolysis Y yields a new compound Z which can be converted to Y by reaction with red phosphorus and iodine. The compound Z on oxidation with potassium permanganate gives a carboxylic acid. The equivalent weight of this acid is 60. What are the compounds X, Y and Z? Write chemical equations leading to the conversion of X to Y. (1981)

Solution Since the compound is unreactive towards sodium, it is neither alcohol (including phenol) nor carboxylic acid. It is also not an aldehyde. It may be a symmetrical ether because on refluxing with excess of HI, it gives only one product. Thus, we have

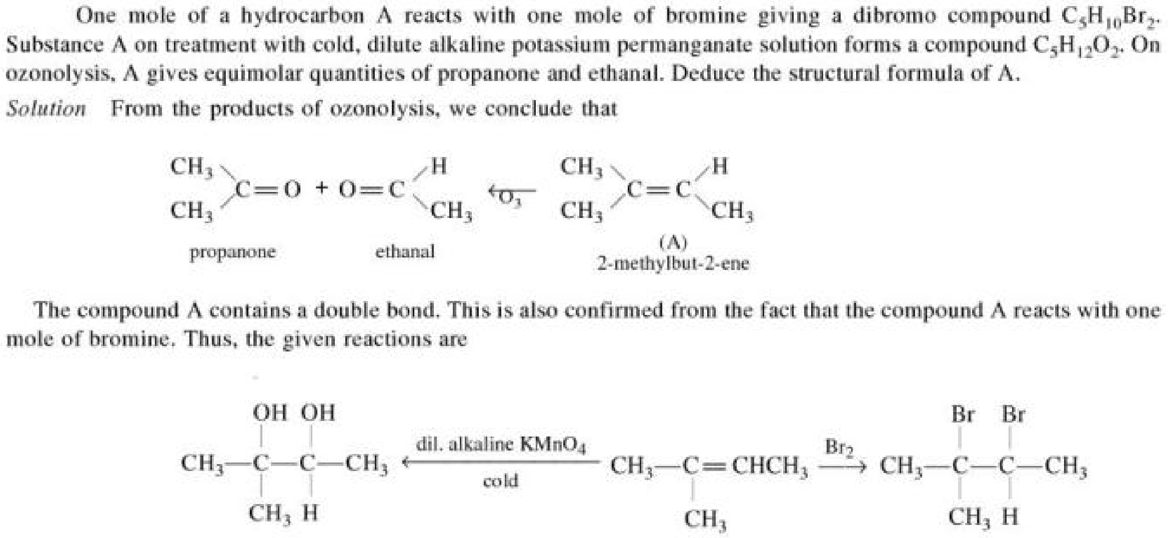
$$\begin{tikzcd}
\underset{(X)}{\mathrm{ROR}} \arrow[r, "\mathrm{HI}"] & \underset{(Y)}{2\mathrm{RI}} \arrow[r, "\mathrm{H_2O}"] & \underset{(Z)}{2\mathrm{ROH}} \arrow[r, "{[O]}"] \arrow[l, bend left, "\mathrm{I_2/P}"] & 2\mathrm{R'COOH}
\end{tikzcd}$$

Now the equivalent weight of R′COOH is 60. From this, it follows that R′ is —CH_3 group and hence R is —CH_2CH_3 group. Thus, the compounds X, Y and Z are

X : $CH_3CH_2OCH_2CH_3$; Y : CH_3CH_2I; Z : CH_3CH_2OH



Identify the compound
A hydrocarbon reacts with Bromine to give dibromo compound



One mole of a hydrocarbon A reacts with one mole of bromine giving a dibromo compound $C_5H_{10}Br_2$. Substance A on treatment with cold, dilute alkaline potassium permanganate solution forms a compound $C_5H_{12}O_2$. On ozonolysis, A gives equimolar quantities of propanone and ethanal. Deduce the structural formula of A.

Solution From the products of ozonolysis, we conclude that

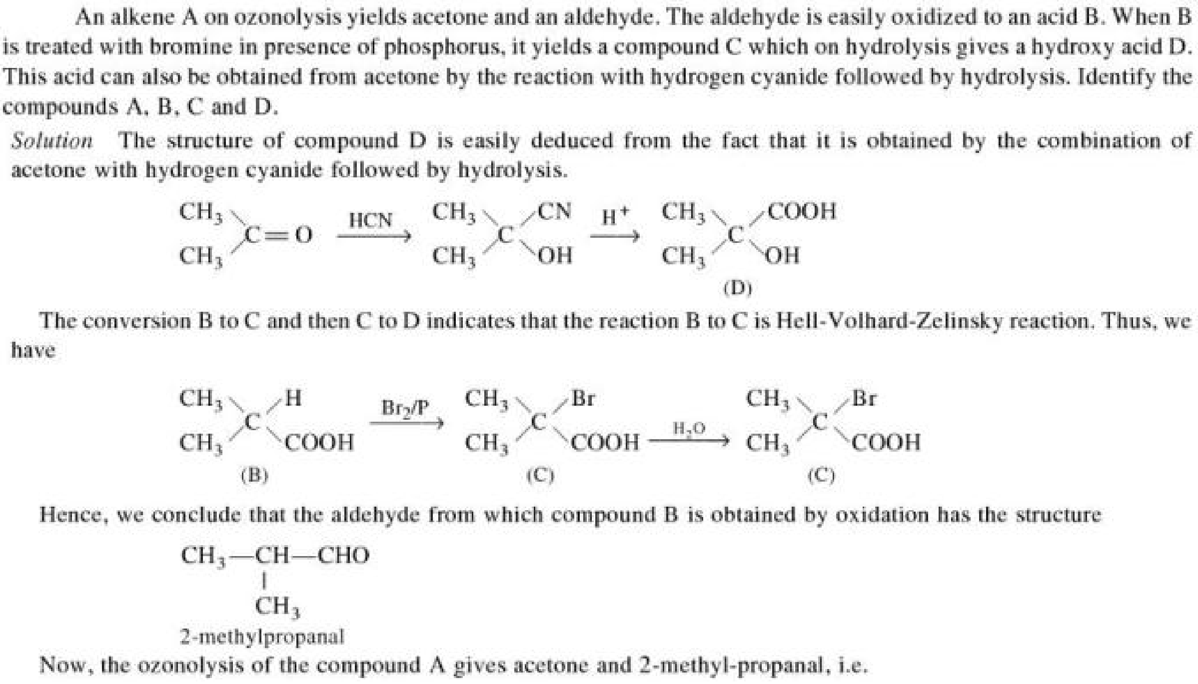
$$\underset{\text{propanone}}{(CH_3)_2C{=}O} + \underset{\text{ethanal}}{O{=}C(H)CH_3} \xleftarrow{O_3} \underset{\text{2-methylbut-2-ene}}{\underset{(A)}{(CH_3)_2C{=}C(H)CH_3}}$$

The compound A contains a double bond. This is also confirmed from the fact that the compound A reacts with one mole of bromine. Thus, the given reactions are

$$CH_3{-}C(OH)(CH_3){-}CH(OH){-}CH_3 \xleftarrow[\text{cold}]{\text{dil. alkaline } KMnO_4} CH_3{-}C(CH_3){=}CHCH_3 \xrightarrow{Br_2} CH_3{-}C(Br)(CH_3){-}CH(Br){-}CH_3$$

Identify the compound

An alkene A on ozonolysis yields acetone and an aldehyde



An alkene A on ozonolysis yields acetone and an aldehyde. The aldehyde is easily oxidized to an acid B. When B is treated with bromine in presence of phosphorus, it yields a compound C which on hydrolysis gives a hydroxy acid D. This acid can also be obtained from acetone by the reaction with hydrogen cyanide followed by hydrolysis. Identify the compounds A, B, C and D.

Solution The structure of compound D is easily deduced from the fact that it is obtained by the combination of acetone with hydrogen cyanide followed by hydrolysis.

$$(CH_3)_2C{=}O \xrightarrow{HCN} (CH_3)_2C(CN)(OH) \xrightarrow{H^+} \underset{(D)}{(CH_3)_2C(COOH)(OH)}$$

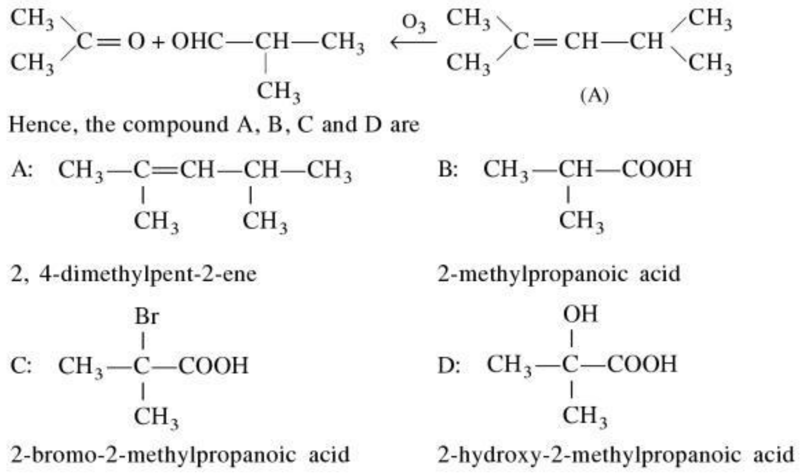
The conversion B to C and then C to D indicates that the reaction B to C is Hell-Volhard-Zelinsky reaction. Thus, we have

$$\underset{(B)}{(CH_3)_2C(H)(COOH)} \xrightarrow{Br_2/P} \underset{(C)}{(CH_3)_2C(Br)(COOH)} \xrightarrow{H_2O} \underset{(C)}{(CH_3)_2C(Br)(COOH)}$$

Hence, we conclude that the aldehyde from which compound B is obtained by oxidation has the structure

$$\underset{\text{2-methylpropanal}}{CH_3{-}CH(CH_3){-}CHO}$$

Now, the ozonolysis of the compound A gives acetone and 2-methyl-propanal, i.e.



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C{=}O + OHC\text{—}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{—}CH_3 \xleftarrow{O_3} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C{=}CH\text{—}CH\!<\!\!\begin{matrix}CH_3\\CH_3\end{matrix}$$

(A)

Hence, the compound A, B, C and D are

A: $CH_3\text{—}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH\text{—}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{—}CH_3$

2, 4-dimethylpent-2-ene

B: $CH_3\text{—}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{—}COOH$

2-methylpropanoic acid

C: $CH_3\text{—}\overset{\displaystyle Br}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}\text{—}COOH$

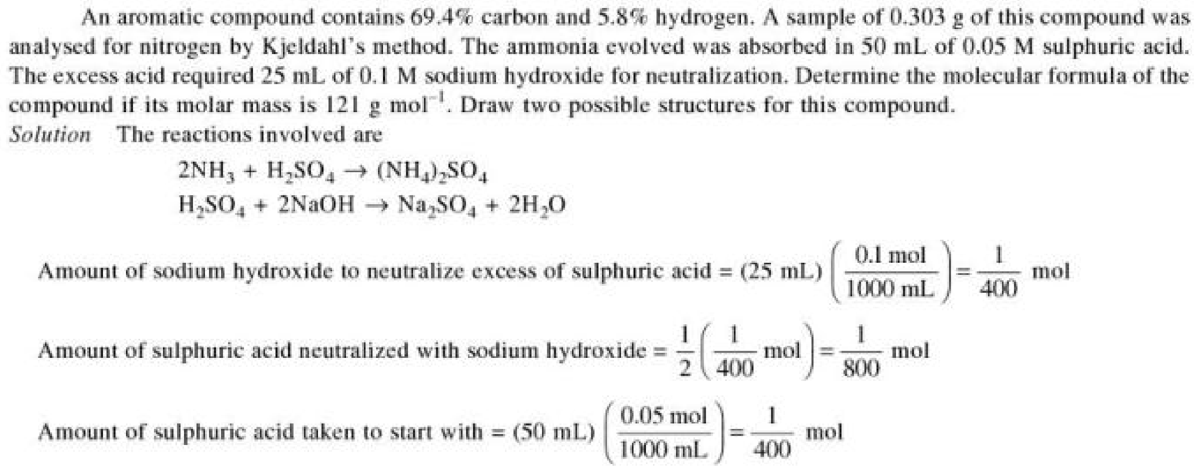
2-bromo-2-methylpropanoic acid

D: $CH_3\text{—}\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}\text{—}COOH$

2-hydroxy-2-methylpropanoic acid

Identify the compound

An aromatic comound contains 69.4% carbon, 5.8% hydrogen



An aromatic compound contains 69.4% carbon and 5.8% hydrogen. A sample of 0.303 g of this compound was analysed for nitrogen by Kjeldahl's method. The ammonia evolved was absorbed in 50 mL of 0.05 M sulphuric acid. The excess acid required 25 mL of 0.1 M sodium hydroxide for neutralization. Determine the molecular formula of the compound if its molar mass is 121 g mol^{-1}. Draw two possible structures for this compound.

Solution The reactions involved are

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$
$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$

Amount of sodium hydroxide to neutralize excess of sulphuric acid $= (25\ \text{mL})\left(\dfrac{0.1\ \text{mol}}{1000\ \text{mL}}\right) = \dfrac{1}{400}\ \text{mol}$

Amount of sulphuric acid neutralized with sodium hydroxide $= \dfrac{1}{2}\left(\dfrac{1}{400}\ \text{mol}\right) = \dfrac{1}{800}\ \text{mol}$

Amount of sulphuric acid taken to start with $= (50\ \text{mL})\left(\dfrac{0.05\ \text{mol}}{1000\ \text{mL}}\right) = \dfrac{1}{400}\ \text{mol}$

Amount of sulphuric acid neutralized by ammonia = $\left(\frac{1}{400} - \frac{1}{800}\right)$ mol = $\frac{1}{800}$ mol

Amount of ammonia evolved = $2\left(\frac{1}{800}\text{ mol}\right) = \frac{1}{400}$ mol

Mass of nitrogen in the evolved ammonia = $\left(\frac{1}{400}\text{ mol}\right)(14\text{ g mol}^{-1}) = \frac{7}{200}$ g

Per cent of nitrogen in the given aromatic compound = $\frac{(7/200)\text{ g}}{0.303\text{ g}} \times 100 = 11.6$

Per cent of oxygen in the given aromatic compound = 100 − (69.4 + 5.8 + 11.6) = 13.2
The ratios of atoms present in the given compound are

$$\text{C : H : N : O} \;::\; \frac{69.4}{12} : \frac{5.8}{1} : \frac{11.6}{14} : \frac{13.2}{16} \;::\; 5.8 : 5.8 : 0.83 : 0.83 :: 7 : 7 : 1 : 1$$

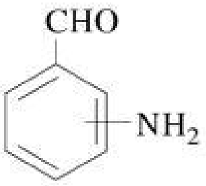
Hence, for the given compound, we have

Empirical formula = C_7H_7NO Empirical molar mass = 121 g mol^{-1}

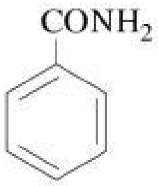
It is given that 121 g mol^{-1} is also the molar mass. Hence,

Molecular formula = C_7H_7NO

Since, the given compound is aromatic, the two possible structures are



and



Identify the compound

An Organic compound CxH2yOy was burnt with twice the amount of Oxygen

An organic compound $C_xH_{2y}O_y$ was burnt with twice the amount of oxygen needed for complete combustion to CO_2 and H_2O. The hot gases, when cooled to 0 °C and 1 atm pressure, measured 2.24 L. The water collected during cooling weighed 0.9 g. The vapour pressure of pure water at 20 °C is 17.5 mmHg and is lowered by 0.104 mmHg when 50 g of the organic compound is dissolved in 1000 g of water. Give the molecular formula of the organic compound.

Solution The combustion reaction is $C_xH_{2y}O_y + x\,O_2 \rightarrow x\,CO_2 + y\,H_2O$

To start with, the amount of O_2 taken is $2x$. Hence, after the combustion reaction, we will be left with the following amounts.

Amount of oxygen left unreacted = x; Amount of carbon dioxide = x; Amount of water = y

When this mixture is cooled to 0 °C and 1 atm, we will be left with oxygen and carbon dioxide. Hence, the amount $2x$ occupies the given volume of 2.24 L at STP. Hence,

$$\text{Amount } x = \frac{(2.24/2)\text{ L}}{22.4\text{ L mol}^{-1}} = 0.05\text{ mol}$$

Now, Mass of water collected = 0.9 g Amount of water collected, $y = \frac{0.9\text{ g}}{18\text{ g mol}^{-1}} = 0.05$ mol

Thus, the empirical formula of the compound is $C_{0.05}H_{2\times0.05}O_{0.05}$, i.e. CH_2O. Now, according to Raoult's law

$$-\frac{\Delta p}{p^*} = x_2 \quad \text{i.e.} \quad \frac{0.104\text{ mmHg}}{17.5\text{ mmHg}} = \frac{(50\text{ g}/M)}{(50\text{ g}/M) + (1000\text{ g}/18\text{ g mol}^{-1})}$$

Solving for M, we get $M = 150.5 \text{ g mol}^{-1}$

$$\text{Number of repeating units of } CH_2O \text{ in the molecular formula} = \frac{150.5}{12+2+16} \simeq 5$$

Hence, Molecular formula of the compound is $C_5H_{10}O_5$.

Identify the Compound

Alcohol when heated with concentrated H2SO4

An alcohol A, when heated with concentrated H_2SO_4 gives an alkene B. When B is bubbled through bromine water and the product obtained is dehydrohalogenated with excess of sodamide, a new compound C is obtained. The compound C gives D when treated with warm dilute H_2SO_4 in presence of $HgSO_4$. D can also be obtained either by oxidizing A with $KMnO_4$ or from acetic acid through its calcium salt. Identify A, B, C and D.

Solution The given reactions are as follows.

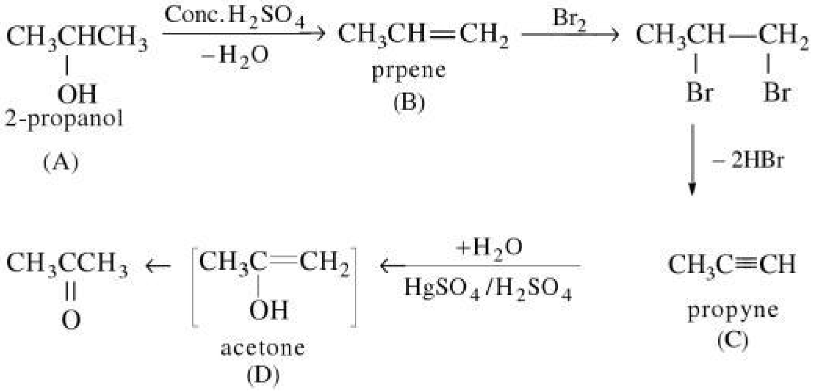
The reaction of obtaining D from calcium acetate is

$$\underset{}{(CH_3COO)_2Ca} \rightarrow \underset{(D)}{CH_3COCH_3} + CaCO_3$$

Hence, D is acetone. Since the latter is also obtained from the oxidation of alcohol A, compound A will be

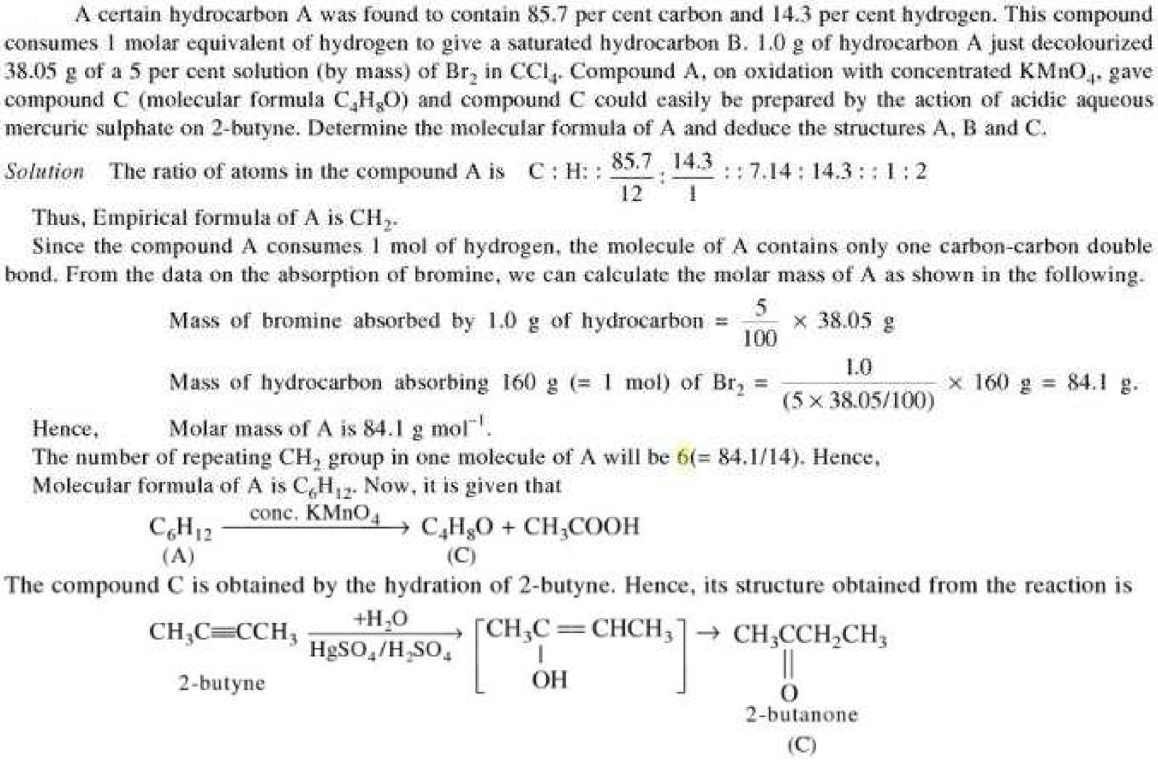
$\underset{\displaystyle OH}{CH_3\overset{}{C}HCH_3}$.

Hence, the reactions depicted above are as follows.



Identify the compound

Certain hydrocarbon was found to contain 85.7% carbon



A certain hydrocarbon A was found to contain 85.7 per cent carbon and 14.3 per cent hydrogen. This compound consumes 1 molar equivalent of hydrogen to give a saturated hydrocarbon B. 1.0 g of hydrocarbon A just decolourized 38.05 g of a 5 per cent solution (by mass) of Br_2 in CCl_4. Compound A, on oxidation with concentrated $KMnO_4$, gave compound C (molecular formula C_4H_8O) and compound C could easily be prepared by the action of acidic aqueous mercuric sulphate on 2-butyne. Determine the molecular formula of A and deduce the structures A, B and C.

Solution The ratio of atoms in the compound A is $C : H :: \frac{85.7}{12} : \frac{14.3}{1} :: 7.14 : 14.3 :: 1 : 2$

Thus, Empirical formula of A is CH_2.

Since the compound A consumes 1 mol of hydrogen, the molecule of A contains only one carbon-carbon double bond. From the data on the absorption of bromine, we can calculate the molar mass of A as shown in the following.

$$\text{Mass of bromine absorbed by 1.0 g of hydrocarbon} = \frac{5}{100} \times 38.05 \text{ g}$$

$$\text{Mass of hydrocarbon absorbing 160 g (= 1 mol) of } Br_2 = \frac{1.0}{(5 \times 38.05/100)} \times 160 \text{ g} = 84.1 \text{ g.}$$

Hence, Molar mass of A is 84.1 g mol^{-1}.

The number of repeating CH_2 group in one molecule of A will be 6(= 84.1/14). Hence,

Molecular formula of A is C_6H_{12}. Now, it is given that

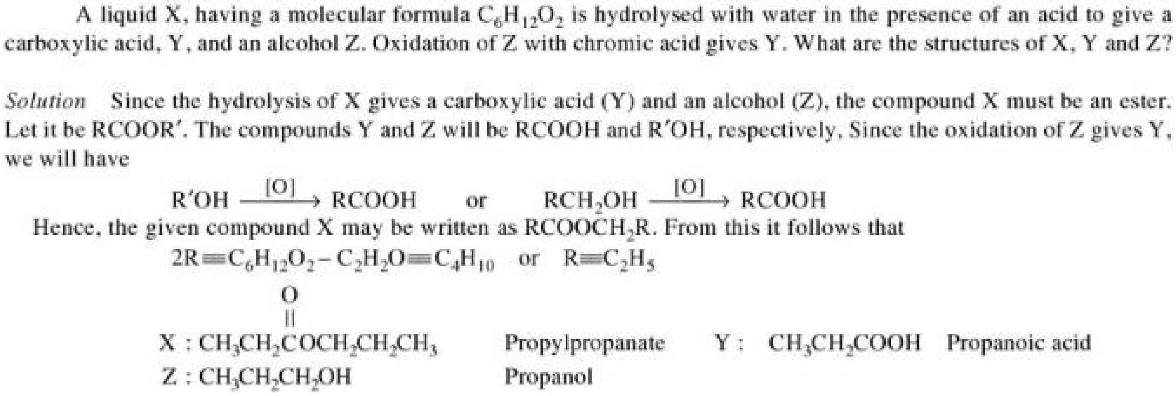
$$\underset{(A)}{C_6H_{12}} \xrightarrow{\text{conc. } KMnO_4} \underset{(C)}{C_4H_8O} + CH_3COOH$$

The compound C is obtained by the hydration of 2-butyne. Hence, its structure obtained from the reaction is

$$\underset{\text{2-butyne}}{CH_3C{\equiv}CCH_3} \xrightarrow[HgSO_4/H_2SO_4]{+H_2O} \left[\begin{array}{c} CH_3\underset{\substack{|\\ OH}}{C}{=}CHCH_3 \end{array}\right] \rightarrow \underset{\substack{\text{2-butanone}\\ \text{(C)}}}{CH_3\underset{\substack{\|\\ O}}{C}CH_2CH_3}$$

Identify the compound

A liquid X having a molecular formula C6H12O2 is hydrolyzed with water



A liquid X, having a molecular formula $C_6H_{12}O_2$ is hydrolysed with water in the presence of an acid to give a carboxylic acid, Y, and an alcohol Z. Oxidation of Z with chromic acid gives Y. What are the structures of X, Y and Z?

Solution Since the hydrolysis of X gives a carboxylic acid (Y) and an alcohol (Z), the compound X must be an ester. Let it be RCOOR′. The compounds Y and Z will be RCOOH and R′OH, respectively. Since the oxidation of Z gives Y, we will have

$$R'OH \xrightarrow{[O]} RCOOH \quad \text{or} \quad RCH_2OH \xrightarrow{[O]} RCOOH$$

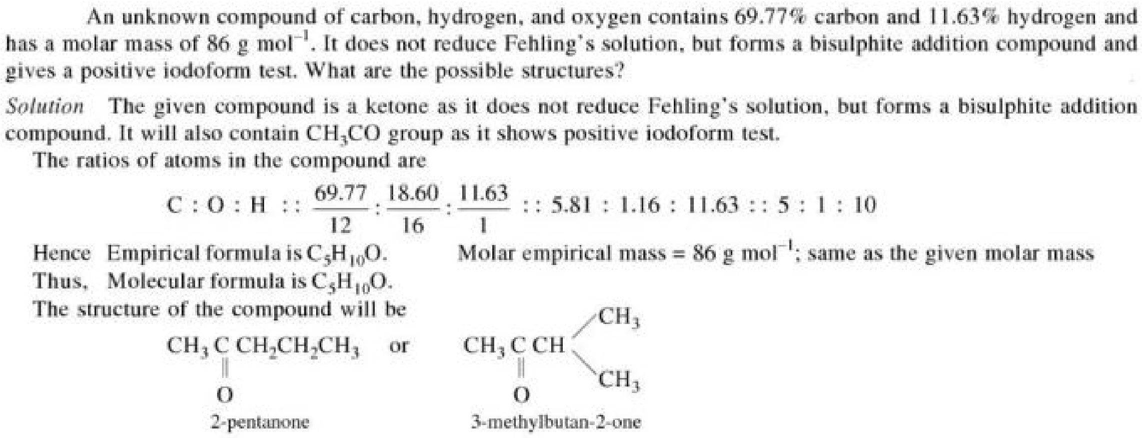
Hence, the given compound X may be written as $RCOOCH_2R$. From this it follows that

$$2R \equiv C_6H_{12}O_2 - C_2H_2O \equiv C_4H_{10} \quad \text{or} \quad R \equiv C_2H_5$$

X : $CH_3CH_2\overset{\substack{O\\ \|}}{C}OCH_2CH_2CH_3$ Propylpropanate Y : CH_3CH_2COOH Propanoic acid

Z : $CH_3CH_2CH_2OH$ Propanol

Identify the compound



An unknown compound of carbon, hydrogen, and oxygen contains 69.77% carbon and 11.63% hydrogen and has a molar mass of 86 g mol^{-1}. It does not reduce Fehling's solution, but forms a bisulphite addition compound and gives a positive iodoform test. What are the possible structures?

Solution The given compound is a ketone as it does not reduce Fehling's solution, but forms a bisulphite addition compound. It will also contain CH_3CO group as it shows positive iodoform test.

The ratios of atoms in the compound are

$$C : O : H :: \frac{69.77}{12} : \frac{18.60}{16} : \frac{11.63}{1} :: 5.81 : 1.16 : 11.63 :: 5 : 1 : 10$$

Hence Empirical formula is $C_5H_{10}O$. Molar empirical mass = 86 g mol^{-1}; same as the given molar mass

Thus, Molecular formula is $C_5H_{10}O$.

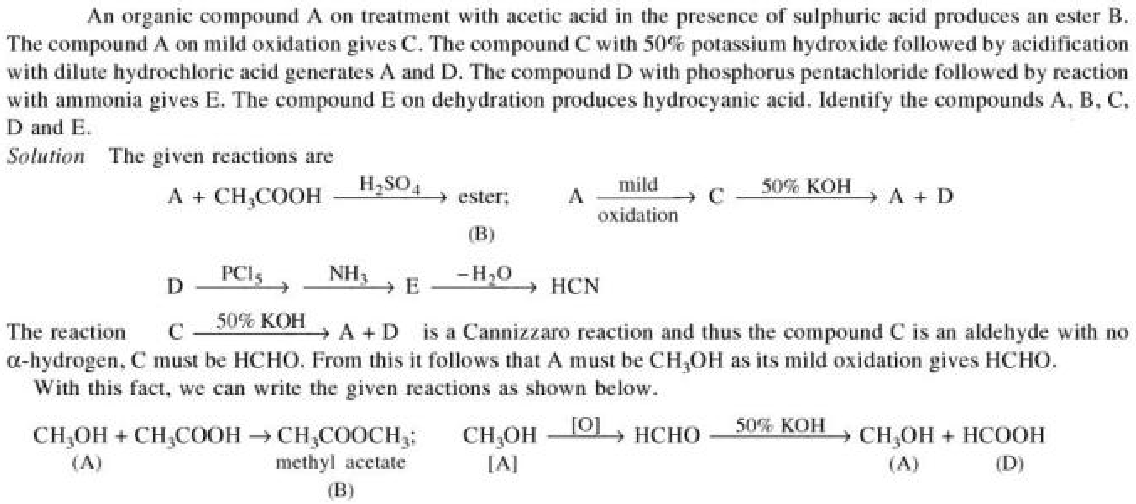
The structure of the compound will be

$CH_3\underset{\underset{O}{\|}}{C}CH_2CH_2CH_3$ or $CH_3\underset{\underset{O}{\|}}{C}CH(CH_3)_2$

2-pentanone 3-methylbutan-2-one

Identify the compound

An organic compound A on treatment with acetic acid in the presence of Sulphuric acid



An organic compound A on treatment with acetic acid in the presence of sulphuric acid produces an ester B. The compound A on mild oxidation gives C. The compound C with 50% potassium hydroxide followed by acidification with dilute hydrochloric acid generates A and D. The compound D with phosphorus pentachloride followed by reaction with ammonia gives E. The compound E on dehydration produces hydrocyanic acid. Identify the compounds A, B, C, D and E.

Solution The given reactions are

$$A + CH_3COOH \xrightarrow{H_2SO_4} \underset{(B)}{\text{ester}}; \quad A \xrightarrow[\text{oxidation}]{\text{mild}} C \xrightarrow{50\%\ KOH} A + D$$

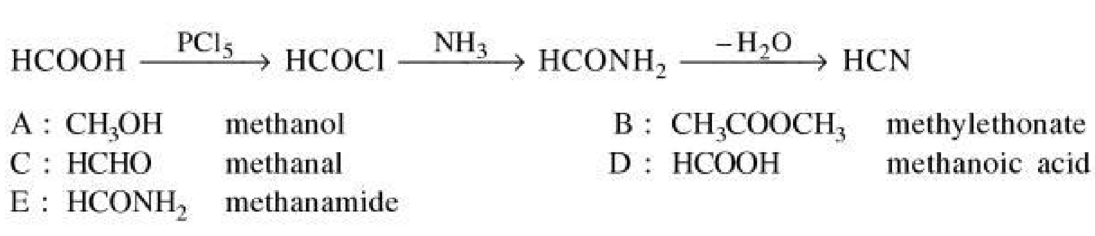
$$D \xrightarrow{PCl_5} \xrightarrow{NH_3} E \xrightarrow{-H_2O} HCN$$

The reaction $C \xrightarrow{50\%\ KOH} A + D$ is a Cannizzaro reaction and thus the compound C is an aldehyde with no α-hydrogen, C must be HCHO. From this it follows that A must be CH_3OH as its mild oxidation gives HCHO.

With this fact, we can write the given reactions as shown below.

$$\underset{(A)}{CH_3OH} + CH_3COOH \rightarrow \underset{\underset{(B)}{\text{methyl acetate}}}{CH_3COOCH_3}; \quad \underset{[A]}{CH_3OH} \xrightarrow{[O]} HCHO \xrightarrow{50\%\ KOH} \underset{(A)}{CH_3OH} + \underset{(D)}{HCOOH}$$

Hence



$$HCOOH \xrightarrow{PCl_5} HCOCl \xrightarrow{NH_3} HCONH_2 \xrightarrow{-H_2O} HCN$$

A : CH_3OH methanol

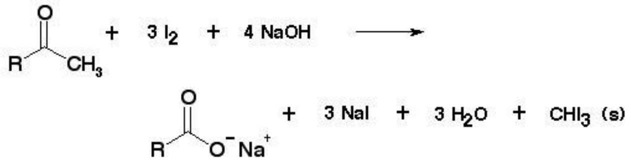
B : CH_3COOCH_3 methylethonate

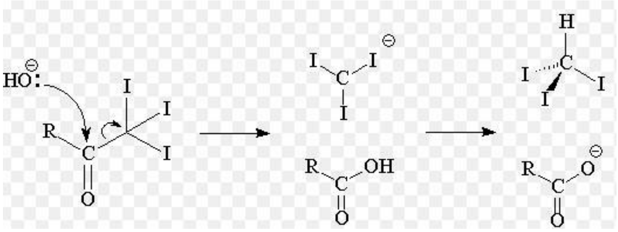
C : HCHO methanal

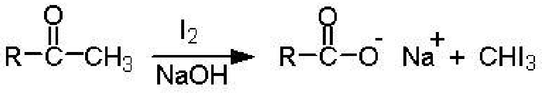
D : HCOOH methanoic acid

E : $HCONH_2$ methanamide

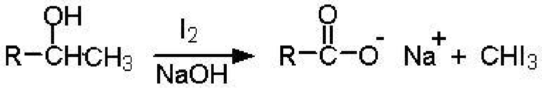
Iodoform Test



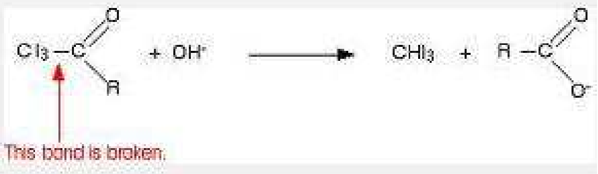




$$R-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[NaOH]{I_2} R-\overset{O}{\overset{\|}{C}}-O^- \; Na^+ + CHI_3$$



$$R-\overset{OH}{\overset{|}{C}H}CH_3 \xrightarrow[NaOH]{I_2} R-\overset{O}{\overset{\|}{C}}-O^- \; Na^+ + CHI_3$$



Identify the compound

An organic compound X, on analysis gives 24.24 per cent carbon and 4.04 per cent hydrogen. Further, sodium extract of 1.0 g of X gives 2.90 g of silver chloride with acidified silver nitrate solution. The compound X may be represented by two isomeric structures, Y and Z. The compound Y on treatment with aqueous potassium hydroxide solution gives a dihydroxy compound, while Z on similar treatment gives ethanal. Find out the molecular formula of X and give the structures of Y and Z.

Solution Mass per cent of chlorine in the organic compound X

$$= \frac{M_{Cl}}{M_{AgCl}} \frac{m_{AgCl}}{m_{compound}} \times 100 = \frac{35.5}{143.5} \times \frac{2.90}{1.0} \times 100 = 71.21$$

The ratios of atoms in the molecule of X are

$$C:H:Cl::\frac{24.24}{12}:\frac{4.04}{1}:\frac{71.72}{35.5}::2:4:2::1:2:1$$

Empirical formula of X is CH_2Cl

Since the isomer Y of the compound gives a dihydroxy compound on treating with aqueous KOH, it follows that the compound must contain two Cl atoms. Hence,

Molecular formula of X is $C_2H_4Cl_2$.

Its two isomers are $\underset{(Z)}{CH_3CHCl_2}$ and $\underset{(Y)}{ClCH_2CH_2Cl}$.

The reaction are

$$\underset{(Z)}{CH_3CHCl_2} \xrightarrow{\text{aq. KOH}} [CH_3CH(OH)_2] \rightarrow \underset{\text{ethanal}}{CH_3CHO}$$

$$ClCH_2CH_2Cl \xrightarrow{\text{aq. KOH}} \underset{\text{ethylene glycol}}{HOCH_2CH_2OH}$$

Match the entries given on the left with those given on the right.

(a) Cyclopropane, chlorine and light	(p) Electrophilic substitution
(b) Propanone and sodium bisulphite	(q) Homologous pair
(c) Ethanal and Methanal	(r) Homolytic addition
(d) Benzene, nitric acid and sulphuric acid	(s) Free radical substitution
(e) Propene, hydrogen bromide and a peroxide catalyst	(t) nucleophilic addition

Ans :

(a) – (s); (b) – (t); (c) – (q); (d) – (p); (e) – (r)

https://zookeepersblog.wordpress.com/science-tuition-chemistry-physics-mathematics-for-iit-jee-aieee-std-11-12-pu-isc-cbse/

Match the entries given on the left with those given on the right.

(a) Pyrolysis of alkanes
(b) Benzene + Chloroethane (+ anhydrous $AlCl_3$)
(c) $CH_3COOC_2H_5$ + NaOH
(d) Preparation of alkanes
(e) Phenol + $CHCl_3$ (NaOH)
(f) C_2H_5Br + alcKOH

(p) Elimination reaction
(q) Saponification
(r) Wurtz reaction
(s) Friedel-craft reaction
(t) Reimer-Tiemann reaction
(u) Cracking

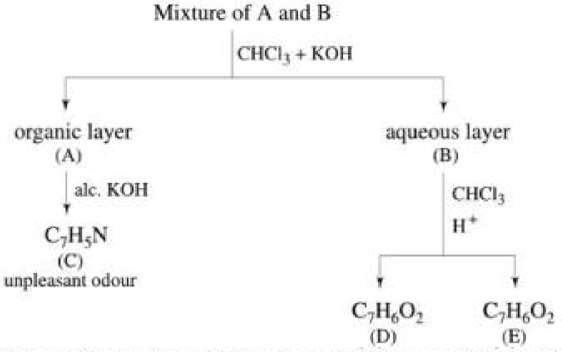
Ans :

(a) – (u); (b) – (s); (c) – (q); (d) – (r); (e) – (t);
(f) – (p)

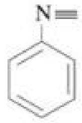
Identify the compound

A mixture of two aromatic compounds A and B was separated by dissolving in chloroform followed by extraction with aqueous KOH solution. The organic layer containing compound A, when heated with alcoholic solution of KOH produced a compound C (C_7H_5N) associated with an unpleasant odour. The alkaline aqueous layer on the other hand, when heated with chloroform and then acidified gave a mixture of two isomeric compounds D and E of molecular formula $C_7H_6O_2$. Identify the compounds A, B, C, D, and E and write their structures.

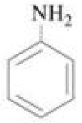
Solution We have



The compound C is an isocyanide which is produced from a primary amine. Hence, the structures of C and A are

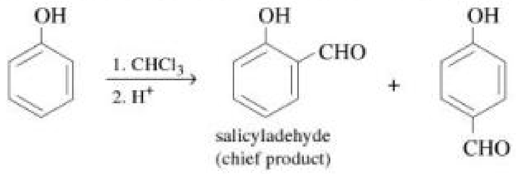


(C)



(A)

The compound B exhibits Reimer-Tiemann reaction. Thus, the compound B must be phenol. The reaction is

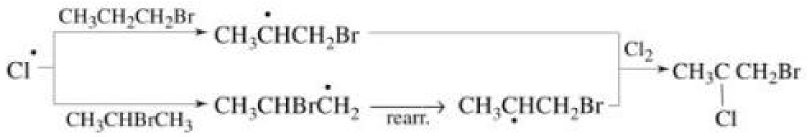


salicyladehyde
(chief product)

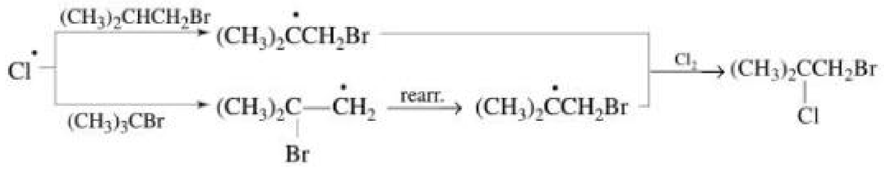
Rearrangement by migration of Bromine

Rearrangement, by migration of Br, of initially formed 1° radical into more stable 2° or 3° radical.

Chlorination of either *n*-propyl or isopropyl bromide gives 1-bromo-2-chloropropane.



Chlorination of either isobutyl or *tert*-butyl bromide gives 1-bromo-2-chloro-2-methylpropane.



Identify the Compound

An organic compound containing C, H and O exists in two isomeric forms A and B. A mass of 0.108 g of one of the isomers gives on combustion 0.308 g of CO_2 and 0.072 g of H_2O. A is insoluble NaOH and $NaHCO_3$ while B is soluble in NaOH. A reacts with concentrated HI to give compounds C and D. C can be separated from D by the ethanolic $AgNO_3$ solution and D is soluble in NaOH. B reacts readily with bromine to give compound E of molecular formula, $C_7H_5OBr_3$. Identify A, B, C, D and E with justification and give their structures.

Solution We have

$$\text{Per cent of carbon in the compound} = \frac{M_C}{M_{CO_2}}\,\frac{m_{CO_2}}{m_{\text{compound}}}\times 100 = \left(\frac{12}{44}\right)\left(\frac{0.308}{0.108}\right)(100) = 77.78$$

$$\text{Per cent of hydrogen in the compound} = \frac{2M_H}{M_{H_2O}}\,\frac{m_{H_2O}}{m_{\text{compound}}}\times 100 = \left(\frac{2}{18}\right)\left(\frac{0.072}{0.108}\right)(100) = 7.41$$

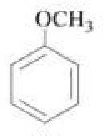
Per cent of oxygen in the compound = 100 − (77.78 + 7.41) = 14.81.

The ratios of atoms in the compound are

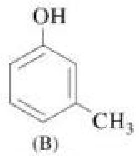
$$C : H : O :: \frac{77.78}{12} : \frac{7.41}{1} : \frac{14.81}{16} :: 6.48 : 7.41 : 0.926 :: 7 : 8 : 1$$

Hence, Empirical formula of the compound is C_7H_8O.

Since the isomer B on reacting with bromine water gives compound E ($C_7H_5OBr_3$), the molecular formula of A and B will be the same as the empirical formula derived above, since both contain the same number of carbon atoms. As E is obtained from B by the substitution of hydrogen with bromine and since there is high carbon content in B, the compounds A and B must be aromatic. Now, since compound A is insoluble in NaOH and $NaHCO_3$ and compound B is soluble in NaOH, it may be concluded that B is a phenolic compound and A is an ether. Hence, the structures of A and B are

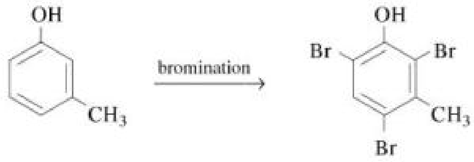


(A)
anisol

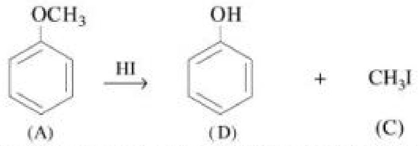


(B)
m-cresol

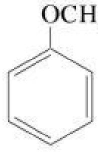
The bromination of B gives



The reaction of compound A with HI is

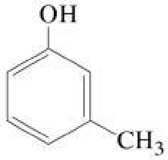


The compound C can be separated from D by use of ethanolic $AgNO_3$ solution as it is soluble in it whereas D will remain insoluble. The compound D will be soluble in NaOH as it is phenol. Hence, the structures of A, B, C, D and E are



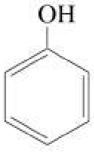
(A)
anisol

;



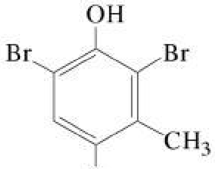
(B)
m-cresol

; CH_3I ;
(C)



(D)

;



(E)

Match the entries given on the left with those given on the right.

(a) Decarboxylation	(p) Addition reaction
(b) Ozonolysis	(q) Sodalime
(c) Williamson's synthesis	(r) Structure of alkene
(d) Dichloroethylene	(s) Ether

Ans :

(a) – (q); (b) – (r); (c) – (s); (d) – (p)

Identify the compound

Basic volatile Nitrogen compound

A basic volatile nitrogen compound gave a foul smelling gas when treated with chloroform and alcoholic potash. A 0.295 g sample of the substance, dissolved in aqueous HCl, and treated with $NaNO_2$ solution at 0 °C liberated a colourless, odourless gas whose volume corresponded to 112 mL at STP. After the evolution of the gas was complete, the aqueous solution was distilled to give an organic liquid which did not contain nitrogen and which on warming with alkali and iodine gave a yellow precipitate. Identify the original substance. Assume that it contains one N atom per molecule.

Solution Since the compound gives a foul smelling gas on treating with $CHCl_3$ and alcoholic KOH, the compound must be a primary amine.

$$RNH_2 + CHCl_3 + 3KOH \rightarrow \underset{\substack{\text{alkyl isocyanide} \\ \text{(foul smelling gas)}}}{RNC} + 3KCl + 3H_2O \qquad (1)$$

Since the compound on treating with $NaNO_2/HCl$ at 0 °C produces a colourless gas, the compound must be an aliphatic primary amine.

$$RNH_2 + HNO_2 \rightarrow ROH + N_2 + H_2O \qquad (2)$$

Thus, the gas produced is nitrogen.

$$\text{Amount of gas liberated} = \frac{112\ \text{mL}}{22400\ \text{mL mol}^{-1}} = \frac{1}{200}\ \text{mol}$$

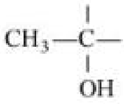
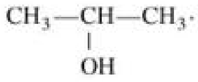
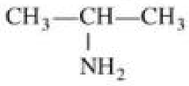
From the above equation, it is obvious that

$$\text{Amount of compound RNH}_2 = \frac{1}{200}\ \text{mol}$$

If M is the molar mass of RNH_2, then

$$\frac{2.295\ \text{g}}{M} = \frac{1}{200}\ \text{mol} \qquad \text{or} \qquad M = 0.295 \times 200\ \text{g mol}^{-1} = 59\ \text{g mol}^{-1}.$$

Thus, the molar mass of alkyl group R is (59 – 16) g mol^{-1}, i.e. 43 g mol^{-1}. Hence, R must be C_3H_7.

From Eq. (2), it is obvious that the liquid obtained after distillation is ROH. Since this gives yellow precipitate with alkali and iodine (iodoform test), it must contain  $CH_3\text{—}\underset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}\text{—}$ group. Hence, it is concluded that ROH is  $CH_3\text{—}\underset{\displaystyle OH}{\underset{|}{CH}}\text{—}CH_3$. Thus, the original compound is  $CH_3\text{—}\underset{\displaystyle NH_2}{\underset{|}{CH}}\text{—}CH_3$

isopropylamine

Match the entries given on the left with those given on the right.

(a) Lucas test	(p) Phenol
(b) Neutral $FeCl_3$	(q) Glucose
(c) Dye test	(r) Tertiary alcohol
(d) Tollens test	(s) Aniline

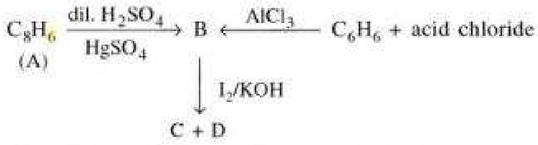
Ans :

(a) – (r); (b) – (p); (c) – (s); (d) – (q)

Identify the compound

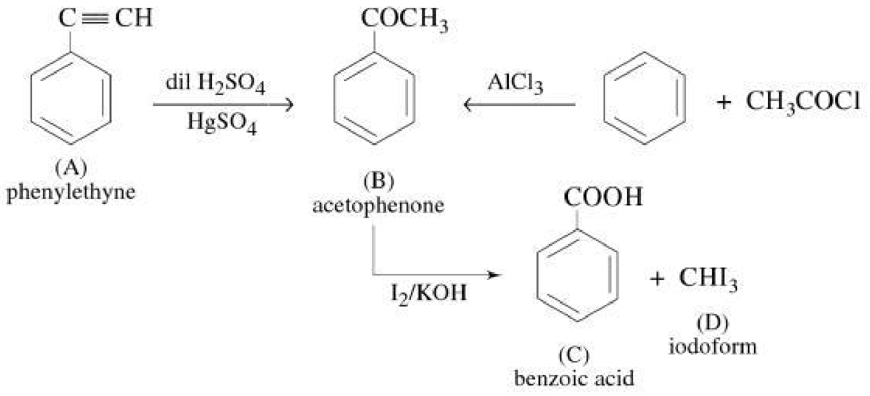
An organic compound A, C_8H_6, on treatment with dilute sulphuric acid containing mercuric sulphate gives a compound B, which can also be obtained from a reaction of benzene with an acid chloride in the presence of anhydrous aluminium chloride. The compound B, when treated with iodine in aqueous KOH, yields C and a yellow compound D. Identify A, B, C and D with justification. Show how B is formed from A.

Solution The given reactions are

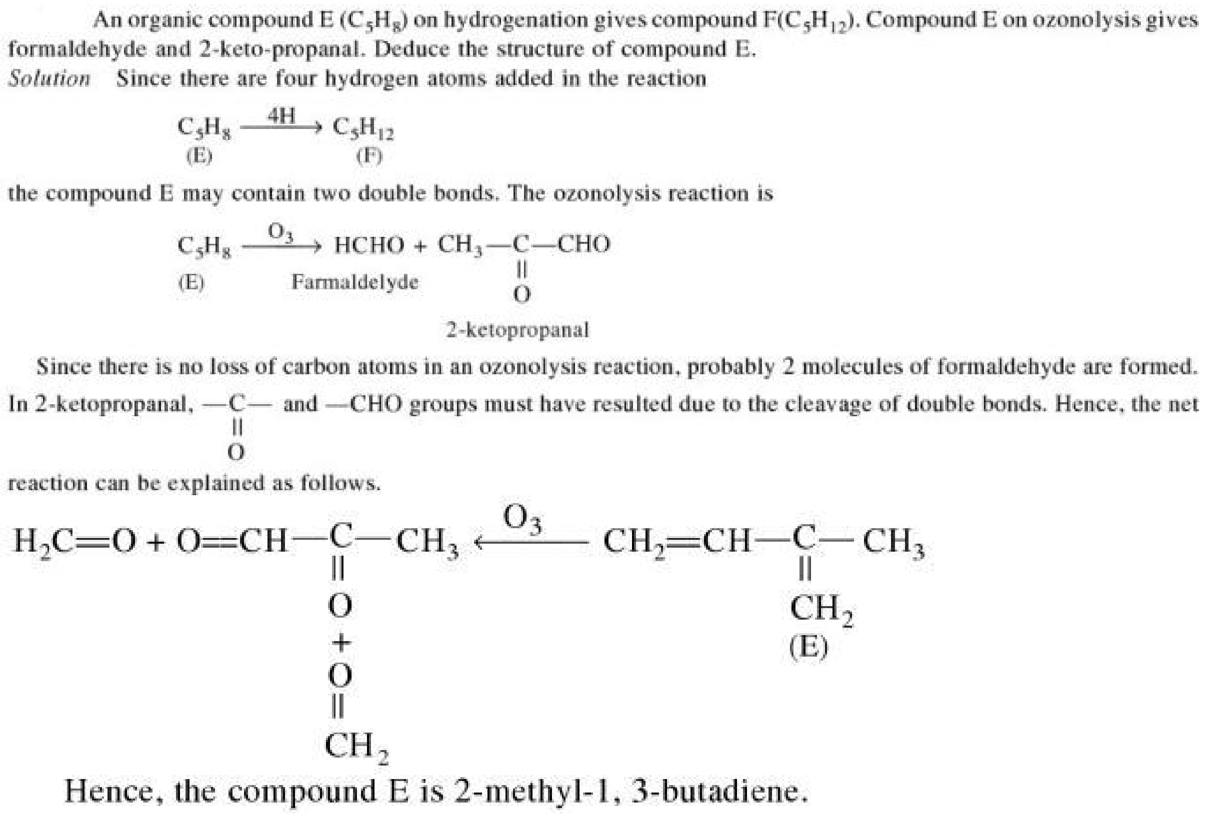


The reaction of B with I_2 in KOH is iodoform reaction. The compound D is iodoform, CHI_3. The compound B must contain —$COCH_3$ group so as to exhibit iodoform reaction. Since D is obtained from benzene by Friedel-Crafts reaction, it is an aromatic ketone ($C_6H_5COCH_3$). The compound C must be an acid.

The compound A may be represented as $C_6H_5C_2H$. Since it gives $C_6H_5COCH_3$ on treating with dilute H_2SO_4 and $HgSO_4$, it must contain a triple bond (—C≡CH) in the side chain. Hence, the given reactions may be represented as



Identify the compound



An organic compound E (C_5H_8) on hydrogenation gives compound F(C_5H_{12}). Compound E on ozonolysis gives formaldehyde and 2-keto-propanal. Deduce the structure of compound E.

Solution Since there are four hydrogen atoms added in the reaction

$$\underset{(E)}{C_5H_8} \xrightarrow{4H} \underset{(F)}{C_5H_{12}}$$

the compound E may contain two double bonds. The ozonolysis reaction is

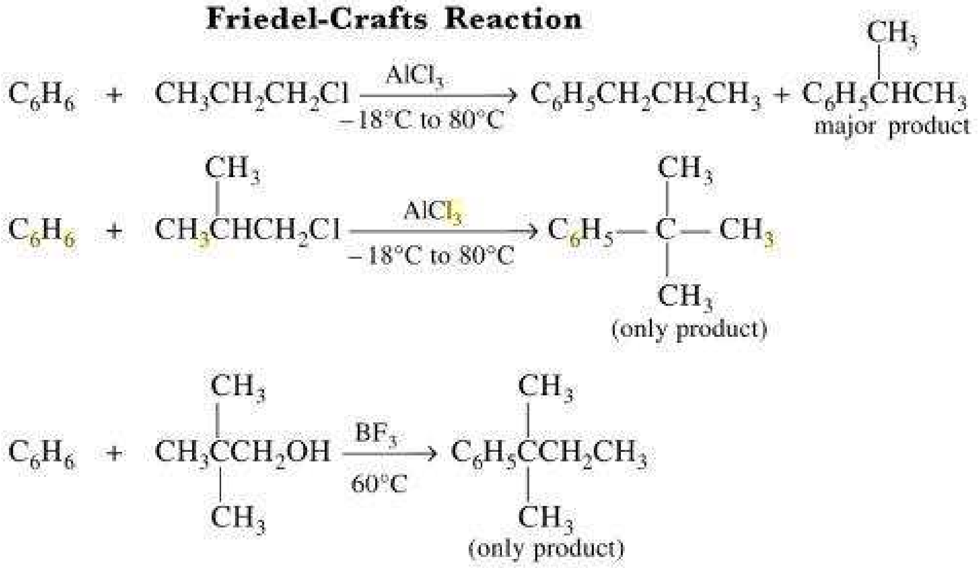
$$\underset{(E)}{C_5H_8} \xrightarrow{O_3} \underset{\text{Farmaldelyde}}{HCHO} + \underset{\text{2-ketopropanal}}{CH_3-\underset{\substack{\| \\ O}}{C}-CHO}$$

Since there is no loss of carbon atoms in an ozonolysis reaction, probably 2 molecules of formaldehyde are formed. In 2-ketopropanal, $-\underset{\substack{\| \\ O}}{C}-$ and —CHO groups must have resulted due to the cleavage of double bonds. Hence, the net reaction can be explained as follows.

$$H_2C{=}O + O{=}CH-\underset{\substack{\| \\ O \\ + \\ O \\ \| \\ CH_2}}{C}-CH_3 \xleftarrow{O_3} CH_2{=}CH-\underset{\substack{\| \\ CH_2 \\ (E)}}{C}-CH_3$$

Hence, the compound E is 2-methyl-1, 3-butadiene.

Friedel Crafts Reaction



Friedel-Crafts Reaction

$$C_6H_6 + CH_3CH_2CH_2Cl \xrightarrow[-18^\circ C \text{ to } 80^\circ C]{AlCl_3} C_6H_5CH_2CH_2CH_3 + C_6H_5\overset{\overset{\textstyle CH_3}{|}}{C}HCH_3$$

major product

$$C_6H_6 + CH_3\overset{\overset{\textstyle CH_3}{|}}{C}HCH_2Cl \xrightarrow[-18^\circ C \text{ to } 80^\circ C]{AlCl_3} C_6H_5-\underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle CH_3}{|}}{C}}-CH_3$$

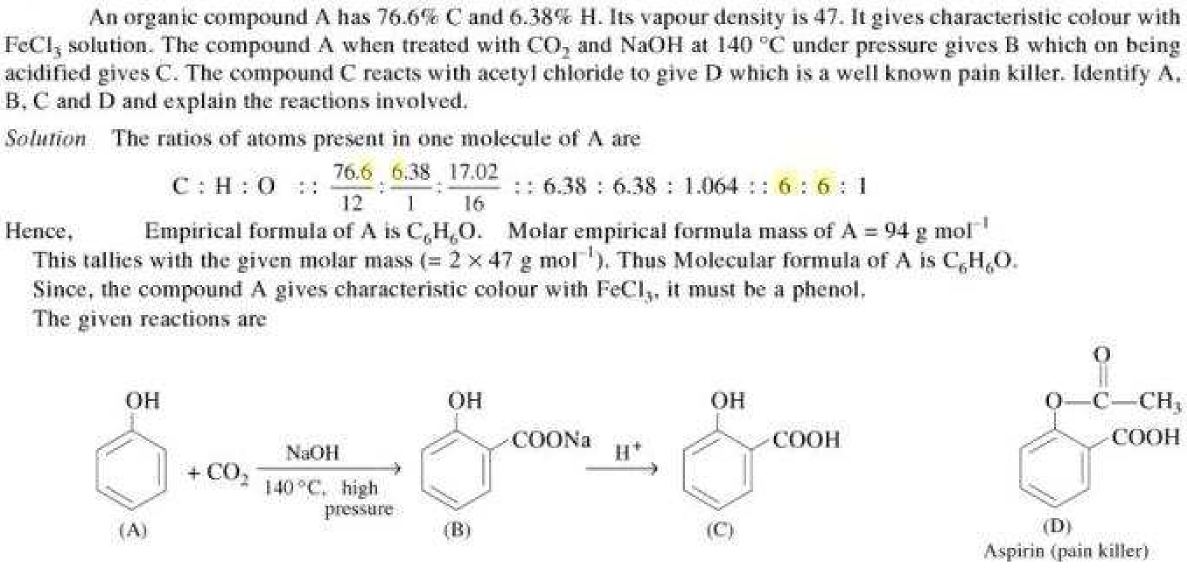
(only product)

$$C_6H_6 + CH_3\underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle CH_3}{|}}{C}}CH_2OH \xrightarrow[60^\circ C]{BF_3} C_6H_5\underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle CH_3}{|}}{C}}CH_2CH_3$$

(only product)

Identify the compound

An Organic compound A has 76.6% C and 6.38% H (Aspirin)



An organic compound A has 76.6% C and 6.38% H. Its vapour density is 47. It gives characteristic colour with $FeCl_3$ solution. The compound A when treated with CO_2 and NaOH at 140 °C under pressure gives B which on being acidified gives C. The compound C reacts with acetyl chloride to give D which is a well known pain killer. Identify A, B, C and D and explain the reactions involved.

Solution The ratios of atoms present in one molecule of A are

$$C : H : O \quad :: \quad \frac{76.6}{12} : \frac{6.38}{1} : \frac{17.02}{16} \quad :: \quad 6.38 : 6.38 : 1.064 \quad :: \quad 6 : 6 : 1$$

Hence, Empirical formula of A is C_6H_6O. Molar empirical formula mass of A = 94 g mol^{-1}

This tallies with the given molar mass (= 2 × 47 g mol^{-1}). Thus Molecular formula of A is C_6H_6O.

Since, the compound A gives characteristic colour with $FeCl_3$, it must be a phenol.

The given reactions are

(A) (B) (C) (D)

Aspirin (pain killer)

Match the entries given on the left with those given on the right.

Friedel-Crafts	oil	alkenes
Fermentation	Lewis acid	soap
Dehydrohalogenation	cuprous chloride	anhydrous $AlCl_3$
Sandmeyer	yeast	chlorobenzene
Saponification	alcoholic alkali	ethanol

Ans :

Friedel-Crafts;	Lewis acid;	anhydrous $AlCl_3$
Fermentation;	yeast;	ethanol
Dehydrohalogenation;	alcoholic alkali;	alkenes
Sandmeyer;	cuprous chloride;	chlorobenzene
Saponification;	oil;	soap

Identify the compound

An organic compound A of molar mass 140.5 gm per mole has 68.32% Hydrogen

An organic compound A of molar mass 140.5 g mol^{-1} has 68.32% C, 6.4% H and 25.26% Cl. Hydrolysis of A with dilute acid gives compound B, $C_8H_{10}O$. Compound B can be oxidized under mild conditions to compound C, C_8H_8O. Compound C forms a phenylhydrazone D with $PhNHNH_2$ and gives a positive iodoform test. Deduce the structures of compounds A to D with proper reasoning.

Solution The ratios of atoms in a molecule of A are

$$C:H:Cl :: \frac{68.32}{12} : \frac{6.4}{1} : \frac{25.26}{35.5} :: 5.69 : 6.4 : 0.71 :: 8 : 9 : 1$$

Hence, Empirical formula of A is C_8H_9Cl. Molar empirical formula mass of A = 140.5 g mol^{-1}

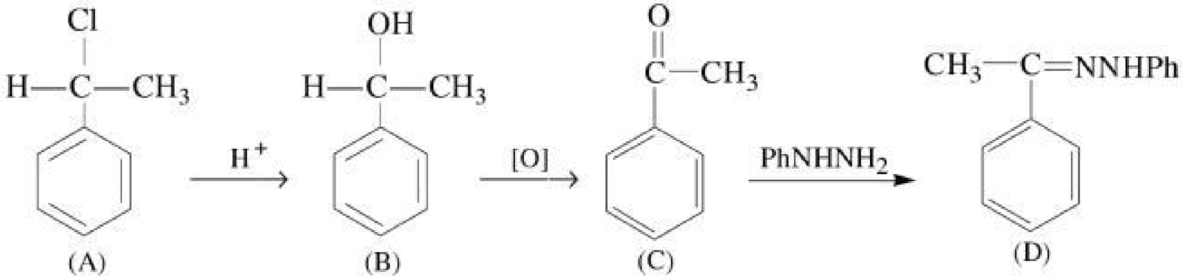
This tallies with the given molar mass. Thus Molecular formula of A is C_8H_9Cl.

The high content of carbon indicates the presence of aromatic (or benzene) ring in the molecule.

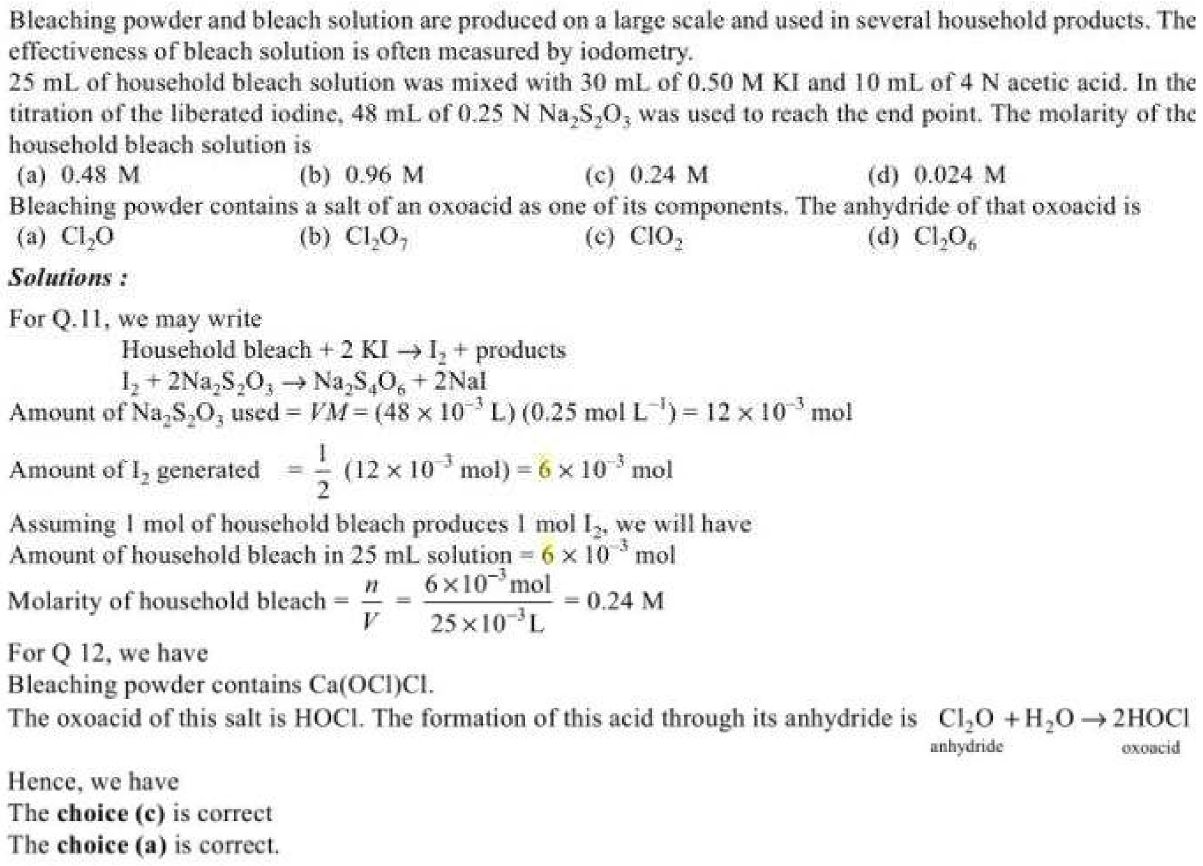
Since Cl atom in the compound A is easily replaced during hydrolysis of A with dilute acid, the Cl atom must be attached to the aliphatic portion of the molecule.

Since the compound C gives a positive iodoform test, it must contain—$COCH_3$ group.

Since the compound C is obtained by mild oxidation of B, the latter must be a secondary alcohol. Hence, the compound A also contains secondary chlorine atom. Consistent with this, the given reactions are as follows.



Question



Bleaching powder and bleach solution are produced on a large scale and used in several household products. The effectiveness of bleach solution is often measured by iodometry.

25 mL of household bleach solution was mixed with 30 mL of 0.50 M KI and 10 mL of 4 N acetic acid. In the titration of the liberated iodine, 48 mL of 0.25 N $Na_2S_2O_3$ was used to reach the end point. The molarity of the household bleach solution is

(a) 0.48 M (b) 0.96 M (c) 0.24 M (d) 0.024 M

Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is

(a) Cl_2O (b) Cl_2O_7 (c) ClO_2 (d) Cl_2O_6

Solutions :

For Q.11, we may write

$$\text{Household bleach} + 2\,KI \rightarrow I_2 + \text{products}$$

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$$

Amount of $Na_2S_2O_3$ used $= VM = (48 \times 10^{-3}\ L)\,(0.25\ mol\ L^{-1}) = 12 \times 10^{-3}$ mol

Amount of I_2 generated $= \frac{1}{2}\,(12 \times 10^{-3}\ mol) = 6 \times 10^{-3}$ mol

Assuming 1 mol of household bleach produces 1 mol I_2, we will have

Amount of household bleach in 25 mL solution $= 6 \times 10^{-3}$ mol

Molarity of household bleach $= \frac{n}{V} = \frac{6 \times 10^{-3}\,mol}{25 \times 10^{-3}\,L} = 0.24$ M

For Q 12, we have

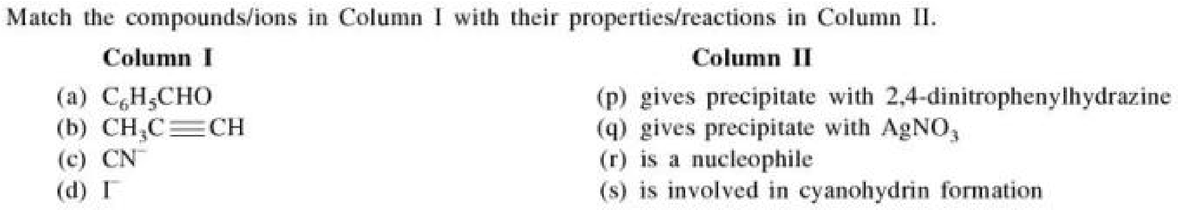
Bleaching powder contains Ca(OCl)Cl.

The oxoacid of this salt is HOCl. The formation of this acid through its anhydride is $\underset{\text{anhydride}}{Cl_2O} + H_2O \rightarrow \underset{\text{oxoacid}}{2HOCl}$

Hence, we have

The **choice (c)** is correct

The **choice (a)** is correct.



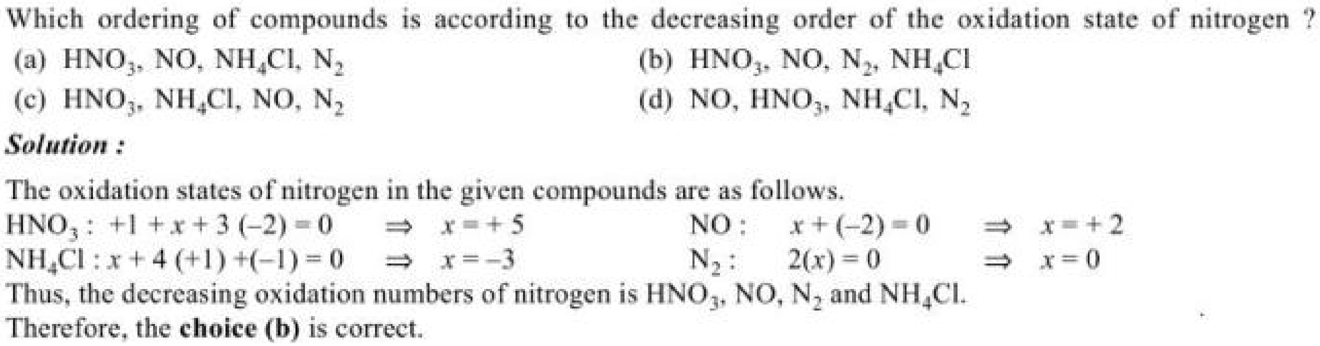
Match the compounds/ions in Column I with their properties/reactions in Column II.

Column I	Column II
(a) C_6H_5CHO	(p) gives precipitate with 2,4-dinitrophenylhydrazine
(b) $CH_3C{\equiv}CH$	(q) gives precipitate with $AgNO_3$
(c) CN^-	(r) is a nucleophile
(d) I^-	(s) is involved in cyanohydrin formation

Ans :

(a) – (p), (q), (s); (b) – (q); (c) – (q), (r), (s); (d) – (q)

In decreasing order of Oxidation state of Nitrogen



Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen ?

(a) HNO_3, NO, NH_4Cl, N_2 (b) HNO_3, NO, N_2, NH_4Cl

(c) HNO_3, NH_4Cl, NO, N_2 (d) NO, HNO_3, NH_4Cl, N_2

Solution :

The oxidation states of nitrogen in the given compounds are as follows.

HNO_3 : $+1 + x + 3(-2) = 0 \Rightarrow x = +5$ NO : $x + (-2) = 0 \Rightarrow x = +2$

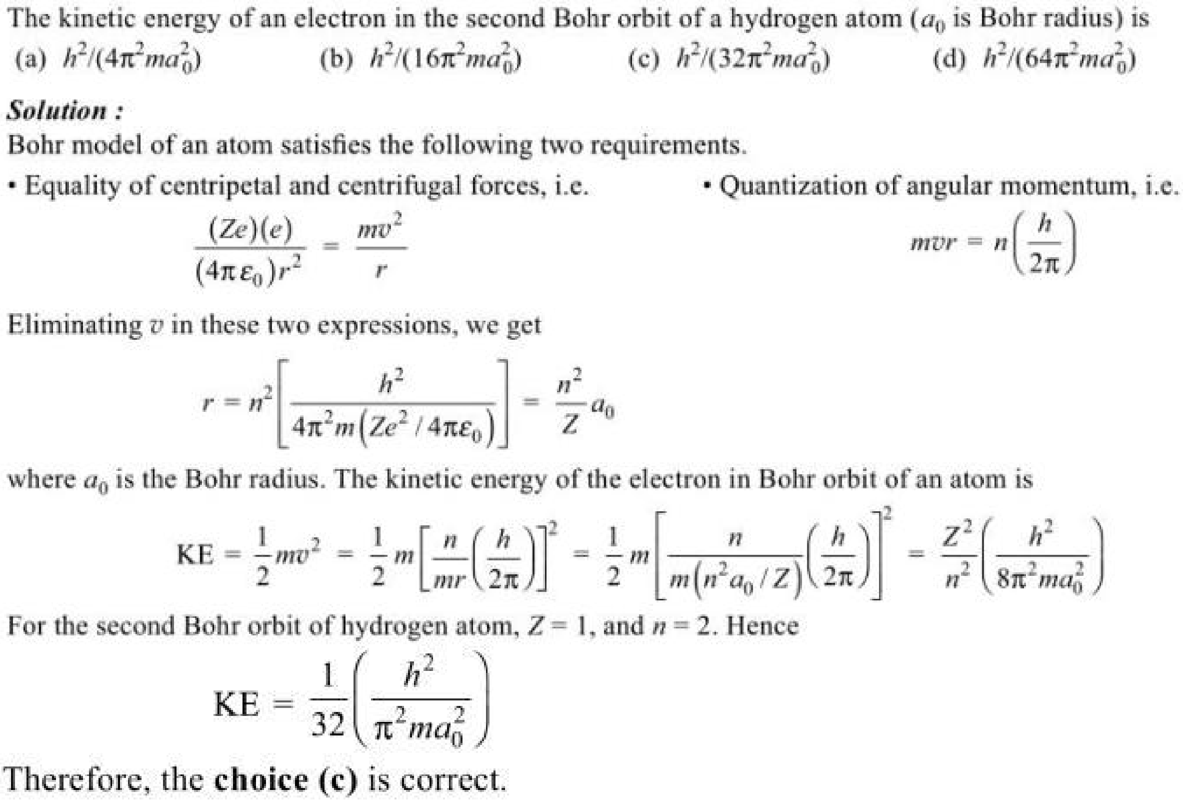
NH_4Cl : $x + 4(+1) + (-1) = 0 \Rightarrow x = -3$ N_2 : $2(x) = 0 \Rightarrow x = 0$

Thus, the decreasing oxidation numbers of nitrogen is HNO_3, NO, N_2 and NH_4Cl.

Therefore, the **choice (b)** is correct.

Gyan Question

The Kinetic energy of an electron in the second Bohr orbit



The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom (a_0 is Bohr radius) is

(a) $h^2/(4\pi^2 m a_0^2)$ (b) $h^2/(16\pi^2 m a_0^2)$ (c) $h^2/(32\pi^2 m a_0^2)$ (d) $h^2/(64\pi^2 m a_0^2)$

Solution :

Bohr model of an atom satisfies the following two requirements.

- Equality of centripetal and centrifugal forces, i.e.

$$\frac{(Ze)(e)}{(4\pi\varepsilon_0)r^2} = \frac{mv^2}{r}$$

- Quantization of angular momentum, i.e.

$$mvr = n\left(\frac{h}{2\pi}\right)$$

Eliminating v in these two expressions, we get

$$r = n^2\left[\frac{h^2}{4\pi^2 m\left(Ze^2/4\pi\varepsilon_0\right)}\right] = \frac{n^2}{Z}a_0$$

where a_0 is the Bohr radius. The kinetic energy of the electron in Bohr orbit of an atom is

$$\mathrm{KE} = \frac{1}{2}mv^2 = \frac{1}{2}m\left[\frac{n}{mr}\left(\frac{h}{2\pi}\right)\right]^2 = \frac{1}{2}m\left[\frac{n}{m\left(n^2a_0/Z\right)}\left(\frac{h}{2\pi}\right)\right]^2 = \frac{Z^2}{n^2}\left(\frac{h^2}{8\pi^2 m a_0^2}\right)$$

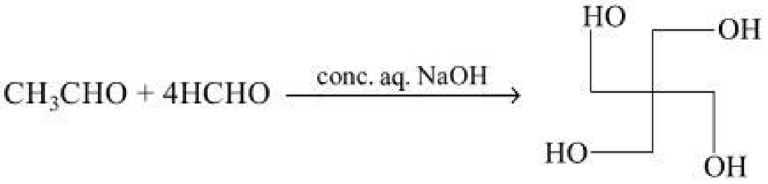
For the second Bohr orbit of hydrogen atom, $Z = 1$, and $n = 2$. Hence

$$\mathrm{KE} = \frac{1}{32}\left(\frac{h^2}{\pi^2 m a_0^2}\right)$$

Therefore, the **choice (c)** is correct.

Question on Aldol reaction

The number of aldol reaction(s) that occurs in the given transformation



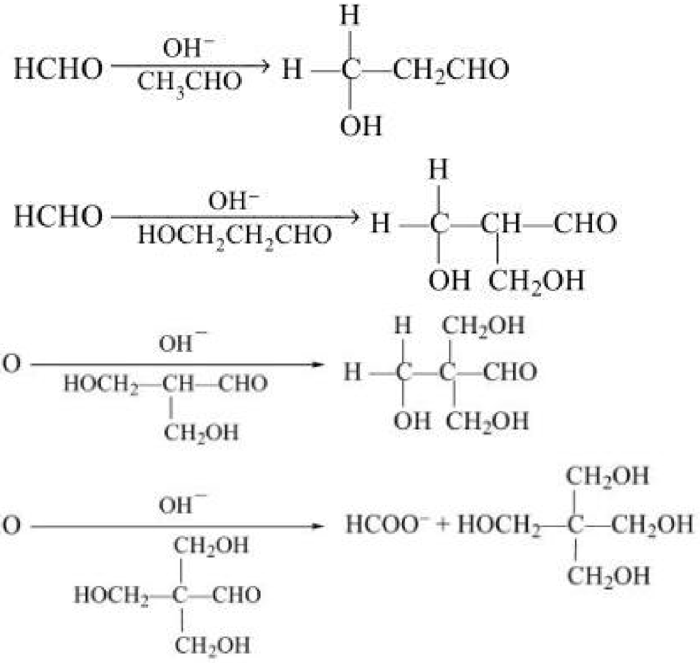
is

(a) 1 (b) 2 (c) 3 (d) 4

Solution :

The given reaction may be formulated as follows.

- *First aldol condensation*
- *Second aldol condensation*
- *Third aldol condensation*
- *Cannizzaro reaction*



$$HCHO \xrightarrow[CH_3CHO]{OH^-} H-\overset{H}{\underset{OH}{C}}-CH_2CHO$$

$$HCHO \xrightarrow[HOCH_2CH_2CHO]{OH^-} H-\overset{H}{\underset{OH}{C}}-\underset{CH_2OH}{CH}-CHO$$

$$HCHO \xrightarrow[HOCH_2-\underset{CH_2OH}{CH}-CHO]{OH^-} H-\overset{H}{\underset{OH}{C}}-\overset{CH_2OH}{\underset{CH_2OH}{C}}-CHO$$

$$HCHO \xrightarrow[HOCH_2-\overset{CH_2OH}{\underset{CH_2OH}{C}}-CHO]{OH^-} HCOO^- + HOCH_2-\overset{CH_2OH}{\underset{CH_2OH}{C}}-CH_2OH$$

There are three aldol condensations and one Cannizzaro reaction.
Therefore, the **choice (c)** is correct

An organic compound undergoes first order decomposition

An organic compound undergoes first-order decomposition. The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are $t_{1/8}$ and $t_{1/10}$, respectively. What is the value of $(t_{1/8}/t_{1/10})*10$? (log 2 = 0.3.)

Solution :

For first-order decomposition of A, the rate law is $\ln([A]/[A]_0) = -kt$

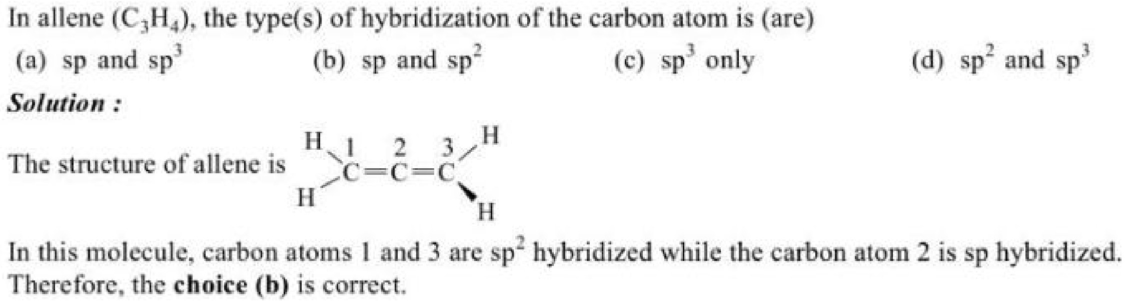
Hence $\ln(1/8) = -k\,t_{1/8}$ and $\ln(1/10) = -k\,t_{1/10}$

Thus $\dfrac{\ln(1/8)}{\ln(1/10)} = \dfrac{t_{1/8}}{t_{1/10}}$ or $\dfrac{\log 8}{\log 10} = \dfrac{t_{1/8}}{t_{1/10}}$

Hence $(t_{1/8}/t_{1/10}) = \log 8 = \log 2^3 = 3\log 2 = 3 \times 0.3 = 0.9$ or $10(t_{1/8}/t_{1/10}) = 10 \times 0.9 = 9$

Therefore, the answer is **9**.

Allene has sp hybridization



In allene (C_3H_4), the type(s) of hybridization of the carbon atom is (are)

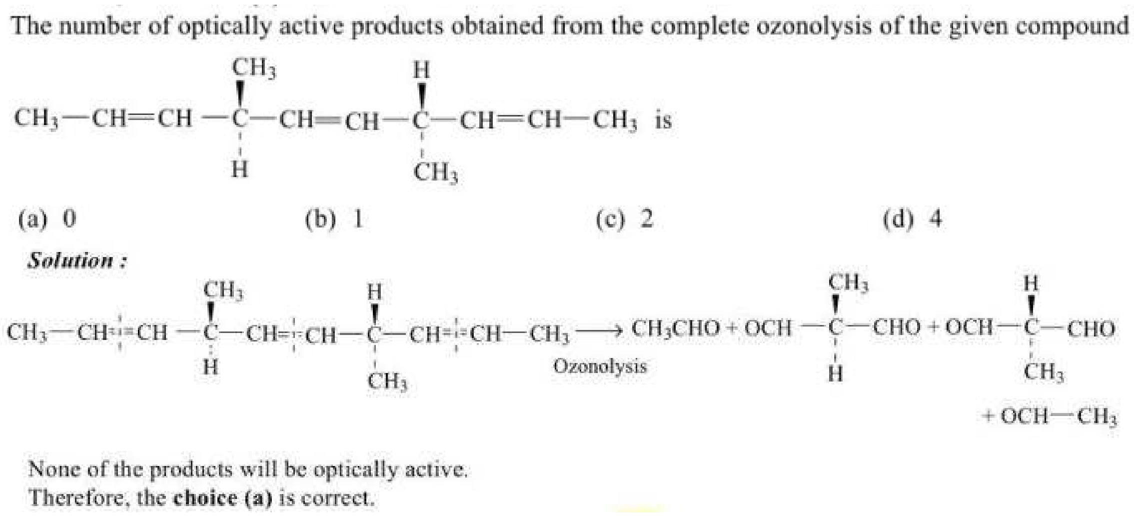
(a) sp and sp^3 (b) sp and sp^2 (c) sp^3 only (d) sp^2 and sp^3

Solution :

The structure of allene is $\mathrm{H_2}\overset{1}{\mathrm{C}}=\overset{2}{\mathrm{C}}=\overset{3}{\mathrm{C}}\mathrm{H_2}$

In this molecule, carbon atoms 1 and 3 are sp^2 hybridized while the carbon atom 2 is sp hybridized. Therefore, the **choice (b)** is correct.

Number of chiral carbon and optically active products



The number of optically active products obtained from the complete ozonolysis of the given compound

$$\mathrm{CH_3{-}CH{=}CH{-}\underset{H}{\overset{CH_3}{C}}{-}CH{=}CH{-}\underset{CH_3}{\overset{H}{C}}{-}CH{=}CH{-}CH_3}$$ is

(a) 0 (b) 1 (c) 2 (d) 4

Solution :

$$\mathrm{CH_3{-}CH{=}CH{-}\underset{H}{\overset{CH_3}{C}}{-}CH{=}CH{-}\underset{CH_3}{\overset{H}{C}}{-}CH{=}CH{-}CH_3 \xrightarrow[\text{Ozonolysis}]{} CH_3CHO + OCH{-}\underset{H}{\overset{CH_3}{C}}{-}CHO + OCH{-}\underset{CH_3}{\overset{H}{C}}{-}CHO + OCH{-}CH_3}$$

None of the products will be optically active.
Therefore, the **choice (a)** is correct.

Carboxylic functional group is present in aspirin

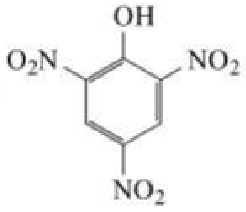
The carboxylic functional group (—COOH) is present in

(a) picric acid (b) barbituric acid (c) ascorbic acid (d) aspirin

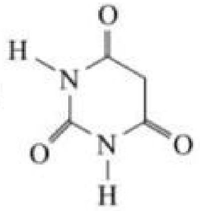
Solution :

The structures of the given compounds are as follows.

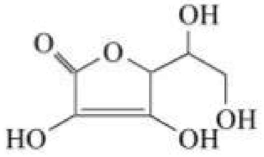
Picric acid



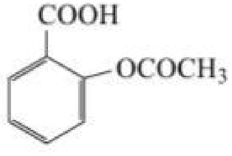
Barbituric acid



Ascorbic acid



Aspirin



Therefore, the **choice (d)** is correct.

Identify the compound

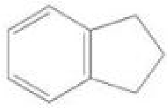
In the following reaction sequence, the compound J is an intermediate

$$I \xrightarrow[CH_3COONa]{(CH_3CO)_2O} J \xrightarrow[\text{(ii) } SOCl_2 \text{, (iii) anhyd. } AlCl_3]{\text{(i) } H_2\text{, Pd/C}} K$$

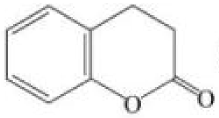
$J(C_9H_8O_2)$ gives effervescence on treatment with $NaHCO_3$ and positive Baeyer's test.

Q-The compound K is

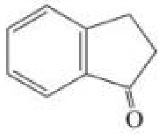
(a)



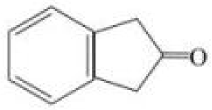
(b)



(c)

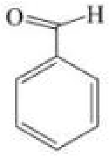


(d)

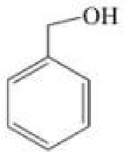


Q-The compound I is

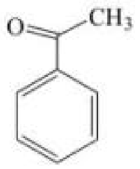
(a)



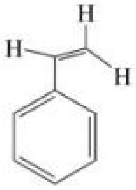
(b)



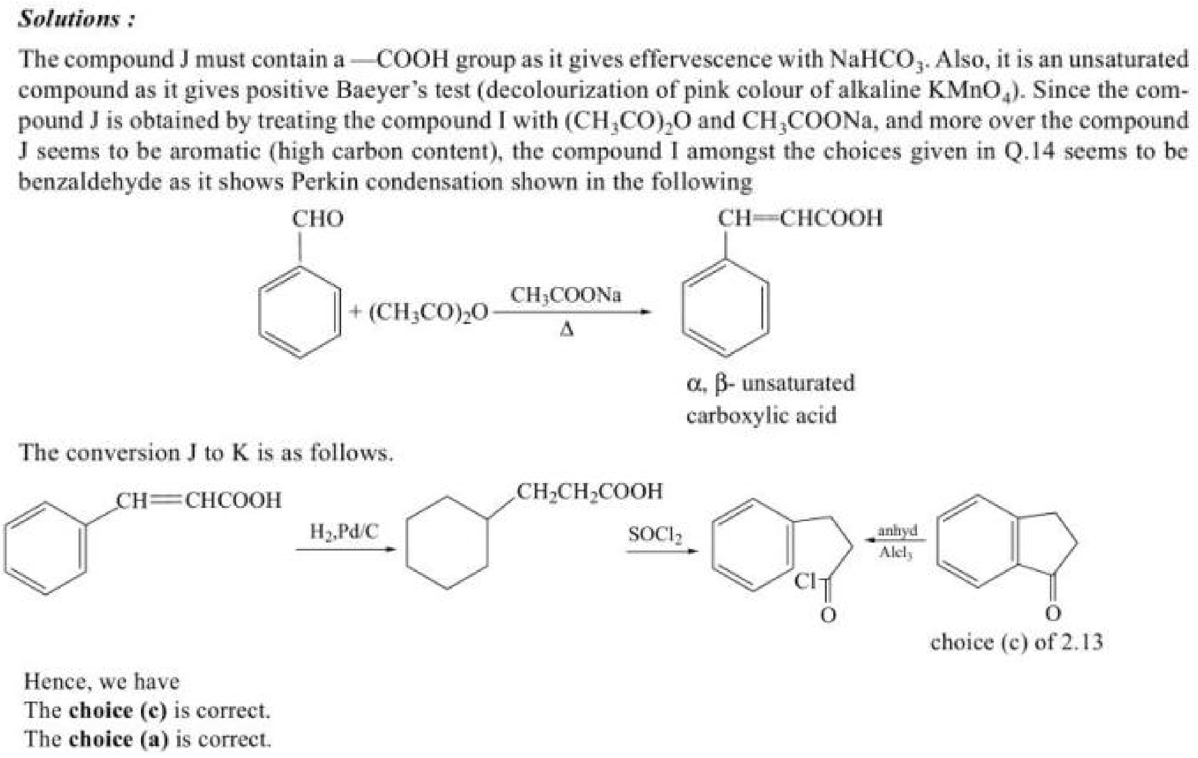
(c)



(d)



Perkin Condensation



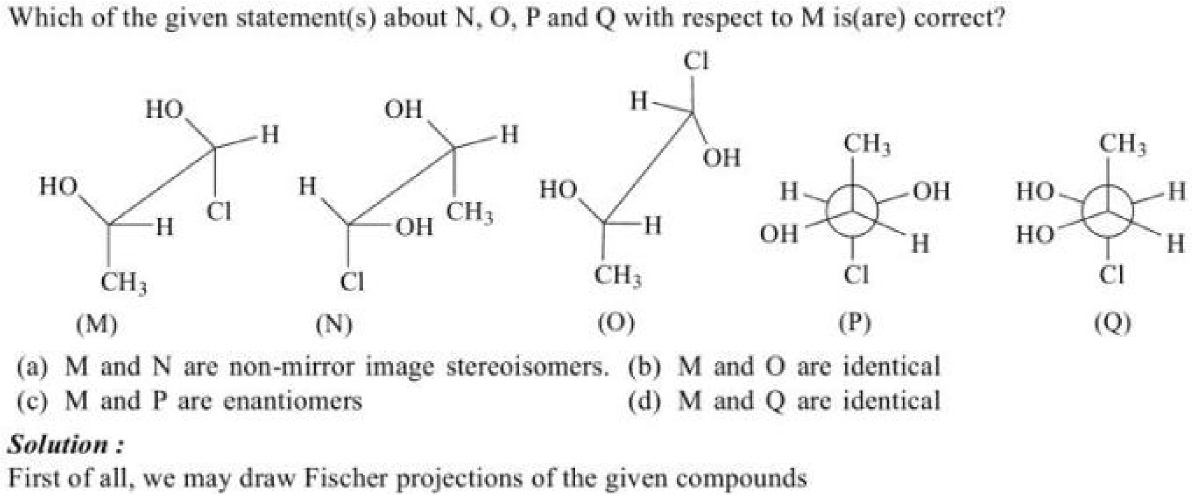
Solutions :

The compound J must contain a —COOH group as it gives effervescence with $NaHCO_3$. Also, it is an unsaturated compound as it gives positive Baeyer's test (decolourization of pink colour of alkaline $KMnO_4$). Since the compound J is obtained by treating the compound I with $(CH_3CO)_2O$ and CH_3COONa, and more over the compound J seems to be aromatic (high carbon content), the compound I amongst the choices given in Q.14 seems to be benzaldehyde as it shows Perkin condensation shown in the following

The conversion J to K is as follows.

Hence, we have
The **choice (c)** is correct.
The **choice (a)** is correct.

Question on isomers

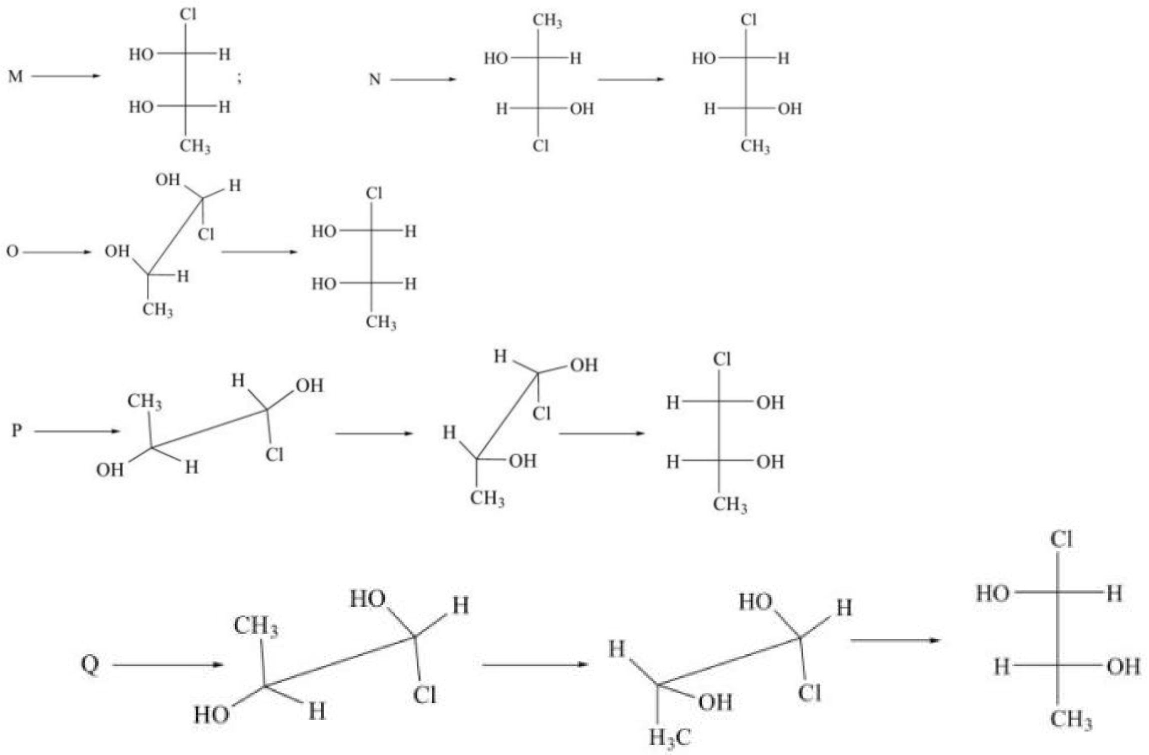


Which of the given statement(s) about N, O, P and Q with respect to M is(are) correct?

(a) M and N are non-mirror image stereoisomers.
(b) M and O are identical
(c) M and P are enantiomers
(d) M and Q are identical

Solution :

First of all, we may draw Fischer projections of the given compounds



From the Fischer projections, it follows that

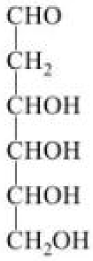
M and N are non-mirror images. M and O are identical.

M and P are enantiomers. M and Q are not identical.

Therefore the **chioces (a) ,(b) and (c)** are correct.

Aldohexose exists in D configuration

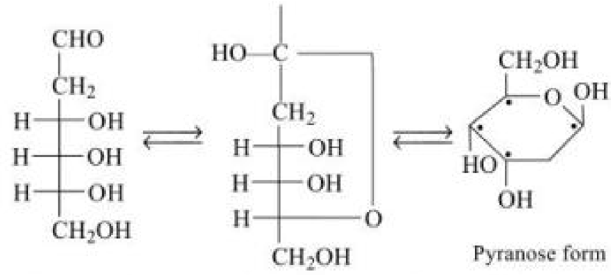
When the following aldohexose exists in D–configuration, the total number of stereoisomers in its pyranose form is



$$\begin{array}{l} CHO \\ | \\ CH_2 \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Solution:

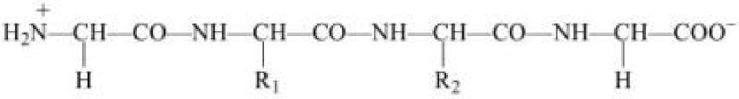
In D-configuration, the hydroxyl group at the assymmetric carbon placed at the bottom of Fischer projection lies to the right of the straight skeleton. Thus, we will have



There are four chiral carbon atoms in the pyranose form of the given aldohexose. Thus, there will be 16 ($= 2^4$) stereoisomers, out of which 8 are of D-configurations (CH_2OH group above the ring) and 8 are of L-configurations (CH_2OH group below the ring).
Therefore, the correct answer is **8**.

Peptides

The substituents R_1 and R_2 for nine peptides are listed in the table given below. How many these peptides are positively charged at pH = 7.0 ?



$$H_2\overset{+}{N}-\underset{H}{CH}-CO-NH-\underset{R_1}{CH}-CO-NH-\underset{R_2}{CH}-CO-NH-\underset{H}{CH}-COO^-$$

Peptide	R_1	R_2
I	H	H
II	H	CH_3
III	CH_2COOH	H
IV	CH_2CONH_2	$(CH_2)_4NH_2$
V	CH_2CONH_2	CH_2CONH_2
VI	$(CH_2)_4NH_2$	$(CH_2)_4NH_2$
VII	CH_2COOH	CH_2CONH_2
VIII	CH_2OH	$(CH_2)_4NH_2$
IX	$(CH_2)_4NH_2$	CH_3

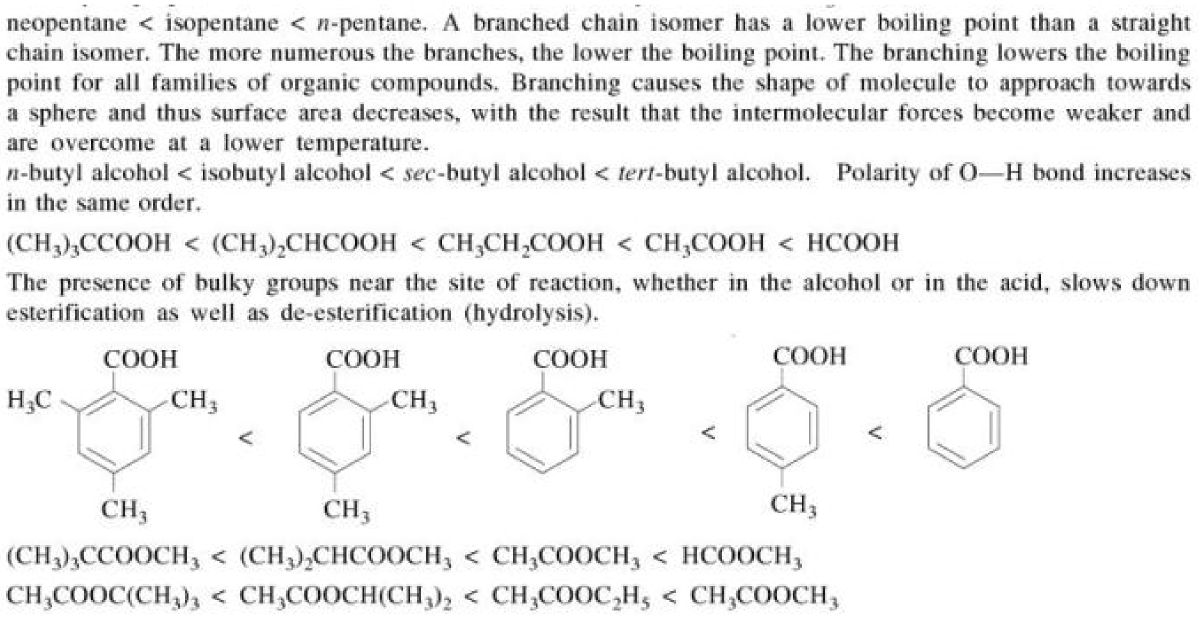
Solution

In general, the pH of the solution at which amino acids exist as zwitterion follows the order :

Acidic side chain < neutral chain < basic side chain
(pH = 3) (pH = 5.5 –6.0) (pH= 9–10)

This pH is known as isoelectric point.
At pH = 7, the acidic side chain (for which isoelectric point < 7) exists as a negatively–charged species (e.g. $-COO^-$) and the basic side chain (for which isoelectric point > 7) exists as a positively charged species (e.g. $-NH_3^+$). Since peptides IV, VI, VIII and IX contain $-NH_2$ group in R_1 or/and R_2 group(s), these are expected to exist as positively–charged species.
Therefore, the correct answer is **4**.

Try to figure out what sequence is depicted



neopentane < isopentane < *n*-pentane. A branched chain isomer has a lower boiling point than a straight chain isomer. The more numerous the branches, the lower the boiling point. The branching lowers the boiling point for all families of organic compounds. Branching causes the shape of molecule to approach towards a sphere and thus surface area decreases, with the result that the intermolecular forces become weaker and are overcome at a lower temperature.

n-butyl alcohol < isobutyl alcohol < *sec*-butyl alcohol < *tert*-butyl alcohol. Polarity of O—H bond increases in the same order.

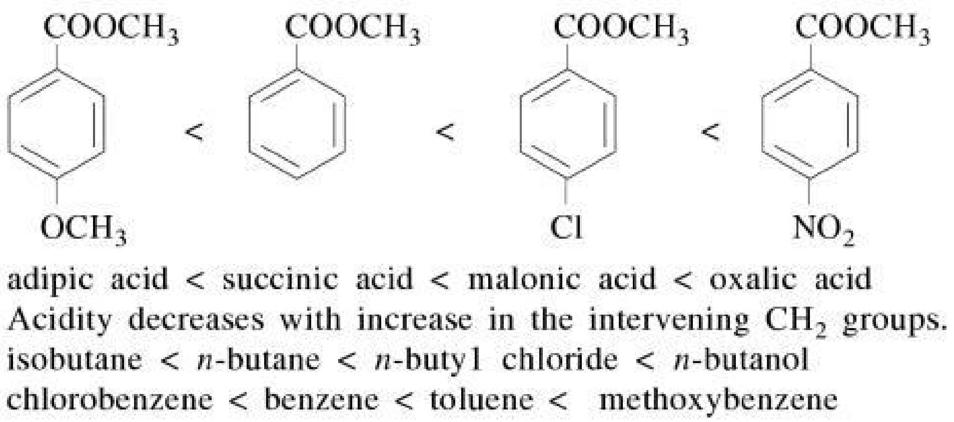
$(CH_3)_3CCOOH < (CH_3)_2CHCOOH < CH_3CH_2COOH < CH_3COOH < HCOOH$

The presence of bulky groups near the site of reaction, whether in the alcohol or in the acid, slows down esterification as well as de-esterification (hydrolysis).

$(CH_3)_3CCOOCH_3 < (CH_3)_2CHCOOCH_3 < CH_3COOCH_3 < HCOOCH_3$

$CH_3COOC(CH_3)_3 < CH_3COOCH(CH_3)_2 < CH_3COOC_2H_5 < CH_3COOCH_3$

Try to figure out the sequences

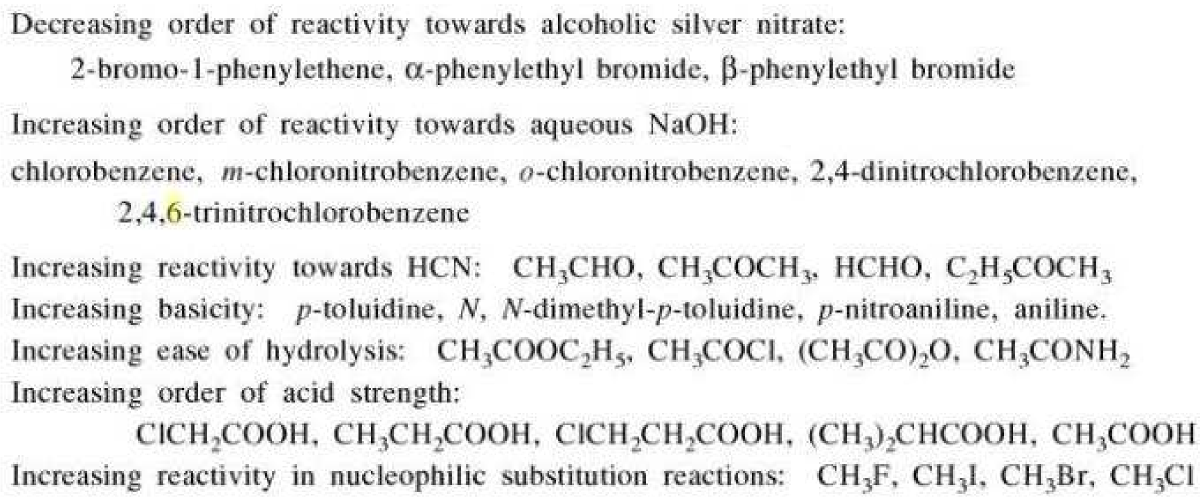


adipic acid < succinic acid < malonic acid < oxalic acid

Acidity decreases with increase in the intervening CH_2 groups.

isobutane < *n*-butane < *n*-butyl chloride < *n*-butanol

chlorobenzene < benzene < toluene < methoxybenzene



Decreasing order of reactivity towards alcoholic silver nitrate:

2-bromo-1-phenylethene, α-phenylethyl bromide, β-phenylethyl bromide

Increasing order of reactivity towards aqueous NaOH:

chlorobenzene, *m*-chloronitrobenzene, *o*-chloronitrobenzene, 2,4-dinitrochlorobenzene, 2,4,6-trinitrochlorobenzene

Increasing reactivity towards HCN: CH_3CHO, CH_3COCH_3, HCHO, $C_2H_5COCH_3$

Increasing basicity: *p*-toluidine, *N*, *N*-dimethyl-*p*-toluidine, *p*-nitroaniline, aniline.

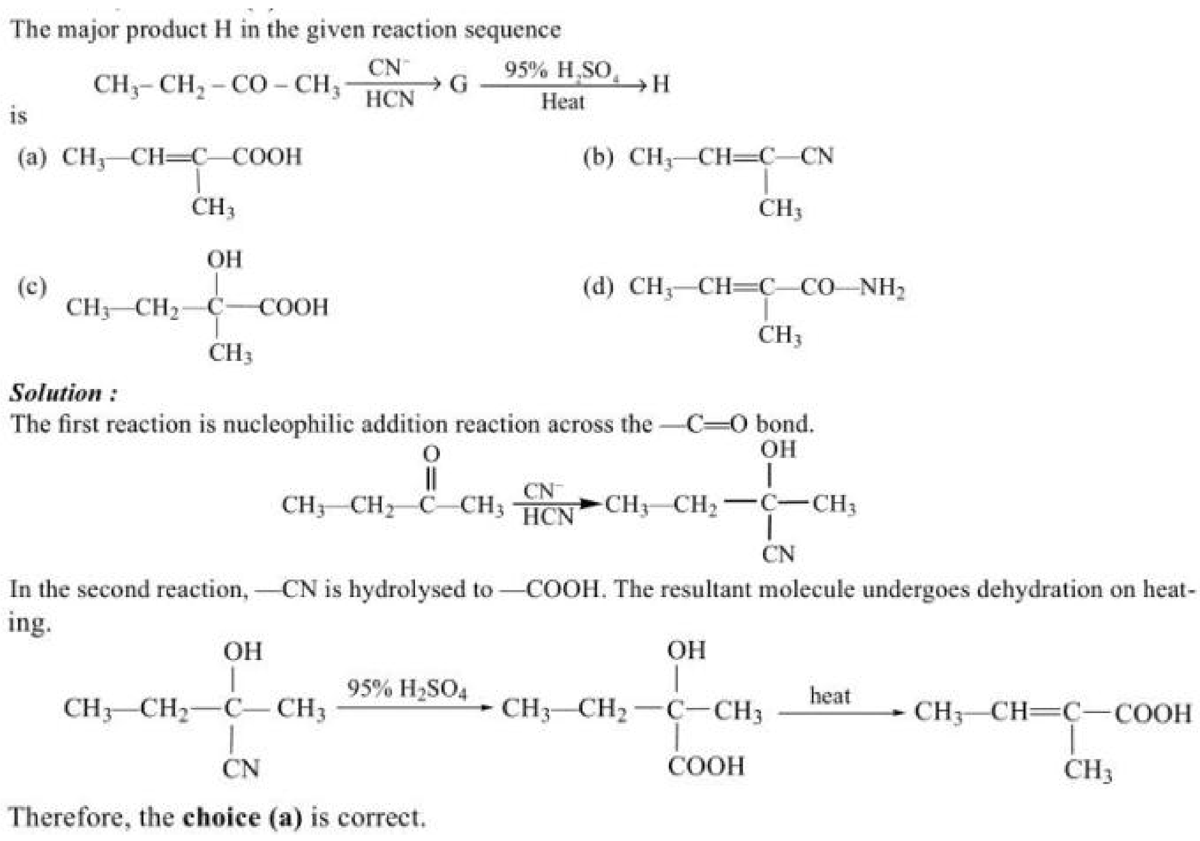
Increasing ease of hydrolysis: $CH_3COOC_2H_5$, CH_3COCl, $(CH_3CO)_2O$, CH_3CONH_2

Increasing order of acid strength:

$ClCH_2COOH$, CH_3CH_2COOH, $ClCH_2CH_2COOH$, $(CH_3)_2CHCOOH$, CH_3COOH

Increasing reactivity in nucleophilic substitution reactions: CH_3F, CH_3I, CH_3Br, CH_3Cl

major product H in the given reaction sequence



The major product H in the given reaction sequence

$$CH_3-CH_2-CO-CH_3 \xrightarrow[HCN]{CN^-} G \xrightarrow[Heat]{95\%\ H_2SO_4} H$$

is

(a) $CH_3-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-COOH$

(b) $CH_3-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CN$

(c) $CH_3-CH_2-\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-COOH$

(d) $CH_3-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CO-NH_2$

Solution :

The first reaction is nucleophilic addition reaction across the —C=O bond.

$$CH_3-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3 \xrightarrow[HCN]{CN^-} CH_3-CH_2-\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle CN}{\underset{|}{C}}}}-CH_3$$

In the second reaction, —CN is hydrolysed to —COOH. The resultant molecule undergoes dehydration on heating.

$$CH_3-CH_2-\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle CN}{\underset{|}{C}}}}-CH_3 \xrightarrow{95\%\ H_2SO_4} CH_3-CH_2-\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle COOH}{\underset{|}{C}}}}-CH_3 \xrightarrow{heat} CH_3-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-COOH$$

Therefore, the **choice (a)** is correct.

Decreasing order of acidity of substituted benzoic acids:
p-chlorobenzoic acid, 2, 4-dichlorobenzoic acid, 2,4,6-trichlorobenzoic acid.
Decreasing order of acidity of carboxylic acids:
α-chlorophenylacetic acid, *p*-chlorophenylacetic acid, phenylacetic acid, α-phenylpropionic acid
Decreasing order of acidity of carboxylic acids:
p-nitrobenzoic acid, *p*-nitrophenylacetic acid, β-(*p*-nitrophenyl) propionic acid
Increasing order of basicity : ammonia, aniline, cyclohexylamine
Decreasing order of basicity: ethylamine, 2-aminoethanol, 3-amino-1-propanol
Decreasing order of basicity : aniline, *p*-methoxyaniline, *p*-nitroaniline
Increasing order of acidity: benzene sulphonic acid, benzoic acid, benzyl alcohol, phenol
Decreasing order of acidity: *m*-bromophenol, *m*-cresol, *m*-nitrophenol, phenol
Decreasing order of acidity of substituted phenol:
p-chlorophenol, 2, 4-dichlorophenol, 2, 4, 6-trichlorophenol
Decreasing order of reactivity towards KCN: benzyl chloride, chlorobenzene, ethyl chloride
Increasing order of nitration: benzene, chlorobenzene, nitrobenzene, toluene
Increasing order of reactivity towards alcoholic silver nitrate:
1-bromo-1-butene, 3-bromo-1-butene, 4-bromo-1-butene

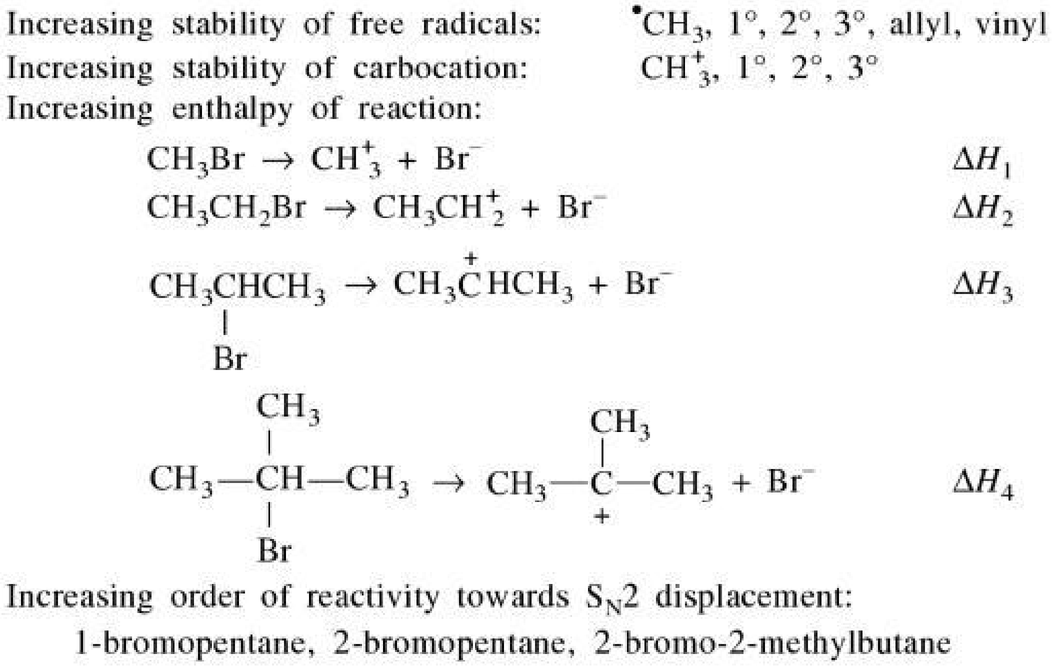
Explain these by solving in right order -

Increasing reactivity towards S_N1 solvolysis:
benzyl chloride, *p*-chlorobenzyl chloride, *p*-methoxybenzyl chloride, *p*-methylbenzyl chloride, *p*-nitrobenzyl chloride
Increasing order of reactivity towards elimination by alcoholic KOH:
1-phenyl-2-bromopropane, 1-phenyl-3-bromopropane
Decreasing order of reactivity towards aqueous HBr: Isomeric pentyl alcohols
Increasing order of reactivity towards aqueous HBr:
1-phenyl-1-propanol, 3-phenyl-1-propanol, 1-phenyl-2-propanol
Decreasing order of reactivity towards aqueous HBr:
benzyl alcohol, *p*-cyanobenzyl alcohol, *p*-hydroxybenzyl alcohol
Increasing order of reactivity towards aqueous HBr:
benzyl alcohol, diphenylmethanol, methanol and triphenylmethanol
Decreasing order of reactivity towards bromination:
anisole, benzene, toluene, chlorobenzene, nitrobenzene, phenol
Increasing order of reactivity towards bromination:
hydroquinone, *p*-methoxyphenol, *p*-methylphenol, *p*-chlorophenol, *p*-nitrophenol, *sym*-trihydroxybenzene
Decreasing order of acidity of carboxylic acids:
butanoic acid, 2-bromobutanoic acid, 3-bromobutanoic acid, 4-bromobutanoic acid

-

Decreasing reactivity towards S_N1 substitution: 1-chloropropene 3-chloropropene, *n*-propylchloride
Decreasing acidity: H_2O, $HC\equiv CH$, NH_3, RH, ROH
Decreasing basicity: R^-, $HC\equiv C^-$, NH_2^-, OH^-, OR^-
Decreasing order of reactivity towards the addition of HCl:
styrene, *p*-chlorostyrene, *p*-methylstyrene, *p*-nitrostyrene
Decreasing order of reactivity towards dehydration:
α-phenyl ethyl alcohol, α-(*p*-nitrophenyl) ethyl alcohol, α-(*p*-aminophenyl) ethyl alcohol

Various Increasing Properties



Increasing stability of free radicals: $^{\bullet}CH_3$, 1°, 2°, 3°, allyl, vinyl

Increasing stability of carbocation: CH_3^+, 1°, 2°, 3°

Increasing enthalpy of reaction:

$$CH_3Br \rightarrow CH_3^+ + Br^- \qquad \Delta H_1$$

$$CH_3CH_2Br \rightarrow CH_3CH_2^+ + Br^- \qquad \Delta H_2$$

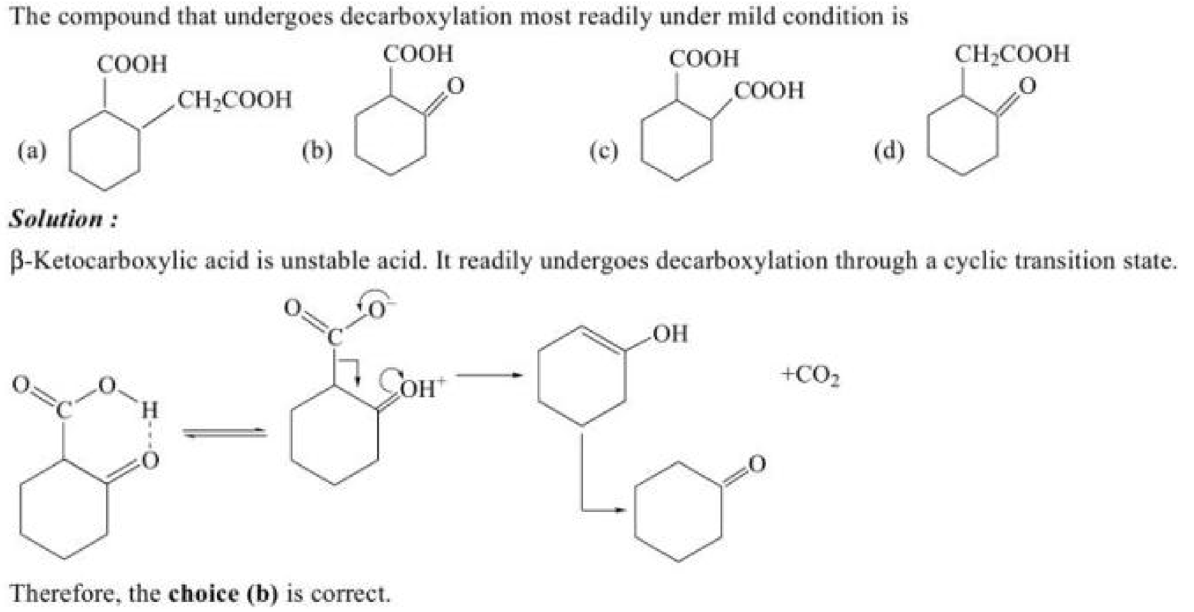
$$CH_3\underset{\underset{Br}{|}}{C}HCH_3 \rightarrow CH_3\overset{+}{C}HCH_3 + Br^- \qquad \Delta H_3$$

$$CH_3-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{CH}}-CH_3 \rightarrow CH_3-\underset{+}{\overset{\overset{CH_3}{|}}{C}}-CH_3 + Br^- \qquad \Delta H_4$$

Increasing order of reactivity towards S_N2 displacement:

1-bromopentane, 2-bromopentane, 2-bromo-2-methylbutane

compound undergoes decarboxylation most readily

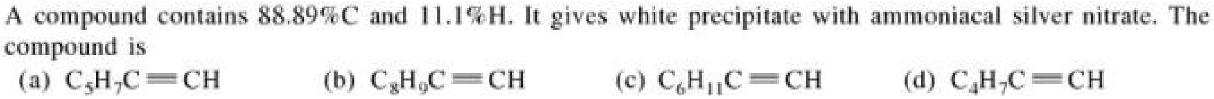


The compound that undergoes decarboxylation most readily under mild condition is

Solution :

β-Ketocarboxylic acid is unstable acid. It readily undergoes decarboxylation through a cyclic transition state.

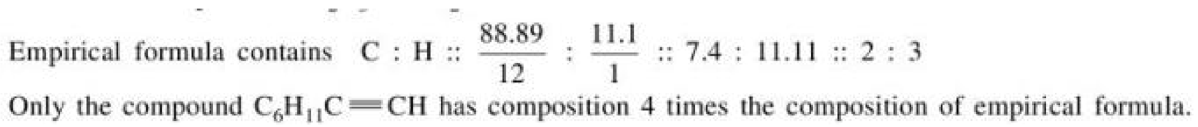
Therefore, the **choice (b)** is correct.



A compound contains 88.89%C and 11.1%H. It gives white precipitate with ammoniacal silver nitrate. The compound is

(a) $C_5H_7C \equiv CH$ (b) $C_8H_9C \equiv CH$ (c) $C_6H_{11}C \equiv CH$ (d) $C_4H_7C \equiv CH$

Ans :



Empirical formula contains C : H :: $\frac{88.89}{12}$: $\frac{11.1}{1}$ :: 7.4 : 11.11 :: 2 : 3

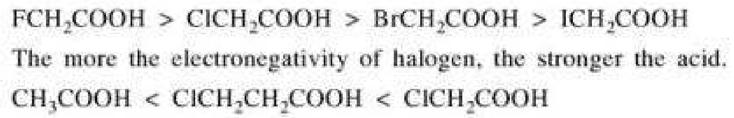
Only the compound $C_6H_{11}C{\equiv}CH$ has composition 4 times the composition of empirical formula.

More the number of electron withdrawing group stronger is the acid

$Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > CH_3COOH$

The more the number of electron-withdrawing group, the stronger the acid.

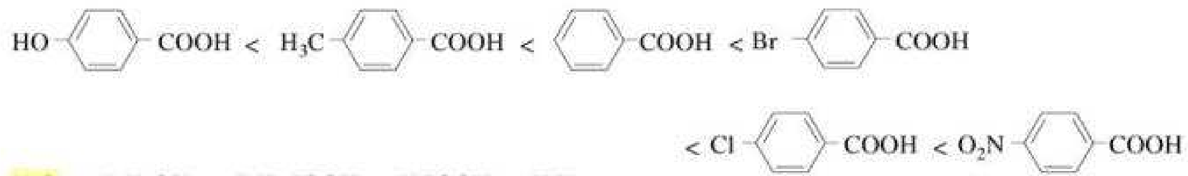
Try to figure out what sequence is depicted

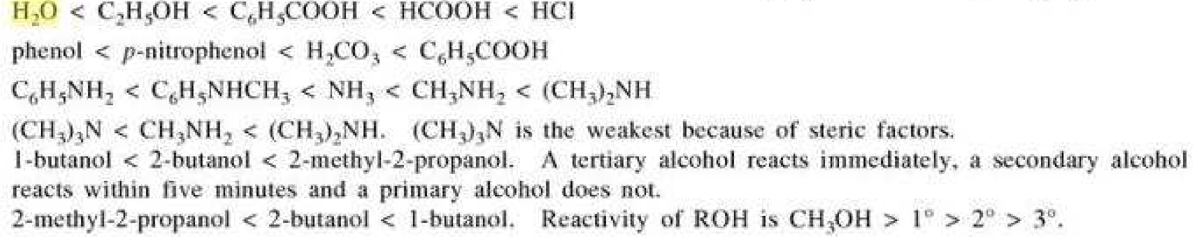


$FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH$

The more the electronegativity of halogen, the stronger the acid.

$CH_3COOH < ClCH_2CH_2COOH < ClCH_2COOH$





$H_2O < C_2H_5OH < C_6H_5COOH < HCOOH < HCl$

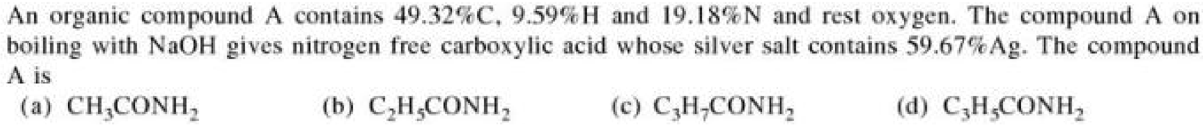
phenol < *p*-nitrophenol < $H_2CO_3 < C_6H_5COOH$

$C_6H_5NH_2 < C_6H_5NHCH_3 < NH_3 < CH_3NH_2 < (CH_3)_2NH$

$(CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$. $(CH_3)_3N$ is the weakest because of steric factors.

1-butanol < 2-butanol < 2-methyl-2-propanol. A tertiary alcohol reacts immediately, a secondary alcohol reacts within five minutes and a primary alcohol does not.

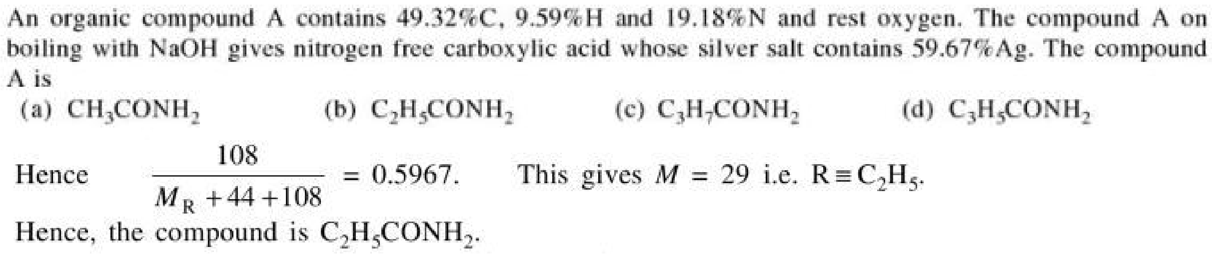
2-methyl-2-propanol < 2-butanol < 1-butanol. Reactivity of ROH is $CH_3OH > 1° > 2° > 3°$.



An organic compound A contains 49.32%C, 9.59%H and 19.18%N and rest oxygen. The compound A on boiling with NaOH gives nitrogen free carboxylic acid whose silver salt contains 59.67%Ag. The compound A is

(a) CH_3CONH_2 (b) $C_2H_5CONH_2$ (c) $C_3H_7CONH_2$ (d) $C_3H_5CONH_2$

Ans :



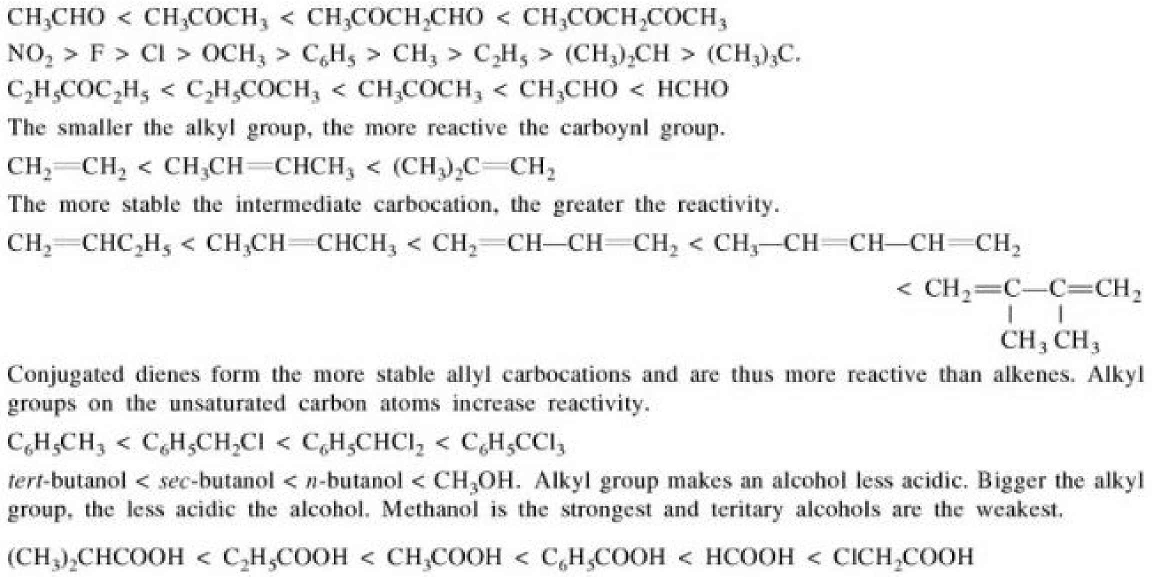
An organic compound A contains 49.32%C, 9.59%H and 19.18%N and rest oxygen. The compound A on boiling with NaOH gives nitrogen free carboxylic acid whose silver salt contains 59.67%Ag. The compound A is

(a) CH_3CONH_2 (b) $C_2H_5CONH_2$ (c) $C_3H_7CONH_2$ (d) $C_3H_5CONH_2$

Hence $\frac{108}{M_R + 44 + 108} = 0.5967$. This gives $M = 29$ i.e. $R \equiv C_2H_5$.

Hence, the compound is $C_2H_5CONH_2$.

Try to figure out what sequence is depicted



$CH_3CHO < CH_3COCH_3 < CH_3COCH_2CHO < CH_3COCH_2COCH_3$

$NO_2 > F > Cl > OCH_3 > C_6H_5 > CH_3 > C_2H_5 > (CH_3)_2CH > (CH_3)_3C$.

$C_2H_5COC_2H_5 < C_2H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$

The smaller the alkyl group, the more reactive the carboynl group.

$CH_2=CH_2 < CH_3CH=CHCH_3 < (CH_3)_2C=CH_2$

The more stable the intermediate carbocation, the greater the reactivity.

$CH_2=CHC_2H_5 < CH_3CH=CHCH_3 < CH_2=CH-CH=CH_2 < CH_3-CH=CH-CH=CH_2$

$$< CH_2=\underset{CH_3}{\underset{|}{C}}-\underset{CH_3}{\underset{|}{C}}=CH_2$$

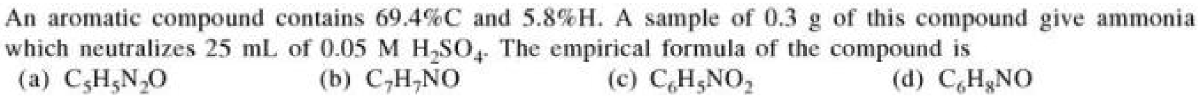
Conjugated dienes form the more stable allyl carbocations and are thus more reactive than alkenes. Alkyl groups on the unsaturated carbon atoms increase reactivity.

$C_6H_5CH_3 < C_6H_5CH_2Cl < C_6H_5CHCl_2 < C_6H_5CCl_3$

tert-butanol < *sec*-butanol < *n*-butanol < CH_3OH. Alkyl group makes an alcohol less acidic. Bigger the alkyl group, the less acidic the alcohol. Methanol is the strongest and teritary alcohols are the weakest.

$(CH_3)_2CHCOOH < C_2H_5COOH < CH_3COOH < C_6H_5COOH < HCOOH < ClCH_2COOH$

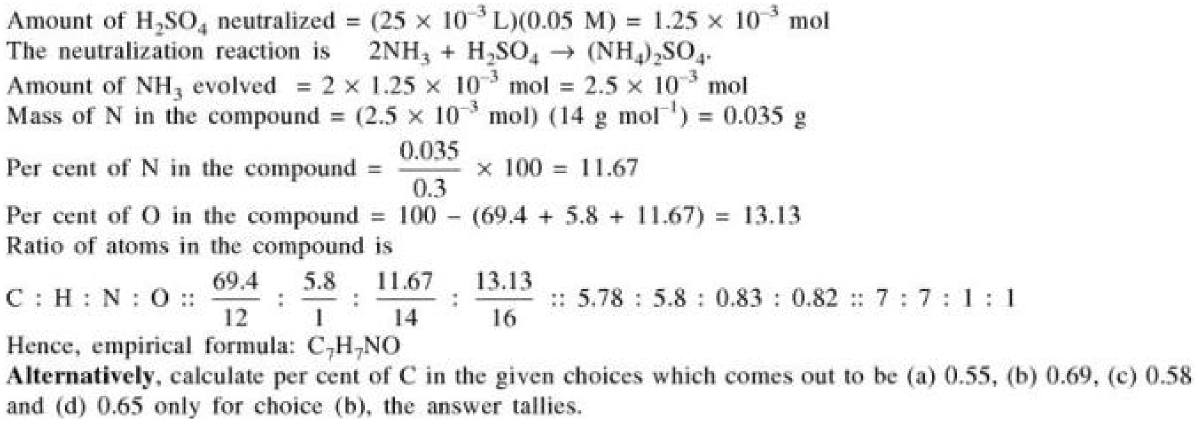
An aromatic compound contains 69.4% C and 5.8% H



An aromatic compound contains 69.4%C and 5.8%H. A sample of 0.3 g of this compound give ammonia which neutralizes 25 mL of 0.05 M H_2SO_4. The empirical formula of the compound is

(a) $C_5H_5N_2O$ (b) C_7H_7NO (c) $C_6H_5NO_2$ (d) C_6H_8NO

Ans :



Amount of H_2SO_4 neutralized = $(25 \times 10^{-3}\ L)(0.05\ M) = 1.25 \times 10^{-3}$ mol

The neutralization reaction is $2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$.

Amount of NH_3 evolved $= 2 \times 1.25 \times 10^{-3}$ mol $= 2.5 \times 10^{-3}$ mol

Mass of N in the compound = $(2.5 \times 10^{-3}\ mol)\ (14\ g\ mol^{-1}) = 0.035$ g

Per cent of N in the compound = $\frac{0.035}{0.3} \times 100 = 11.67$

Per cent of O in the compound = $100 - (69.4 + 5.8 + 11.67) = 13.13$

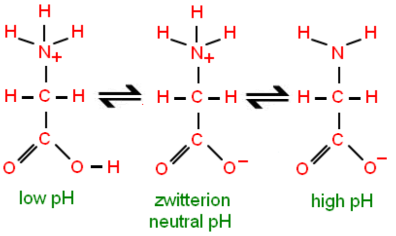
Ratio of atoms in the compound is

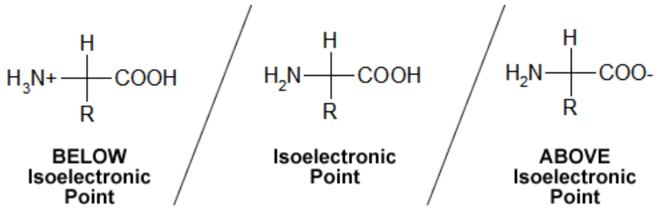
$$C : H : N : O :: \frac{69.4}{12} : \frac{5.8}{1} : \frac{11.67}{14} : \frac{13.13}{16} :: 5.78 : 5.8 : 0.83 : 0.82 :: 7 : 7 : 1 : 1$$

Hence, empirical formula: C_7H_7NO

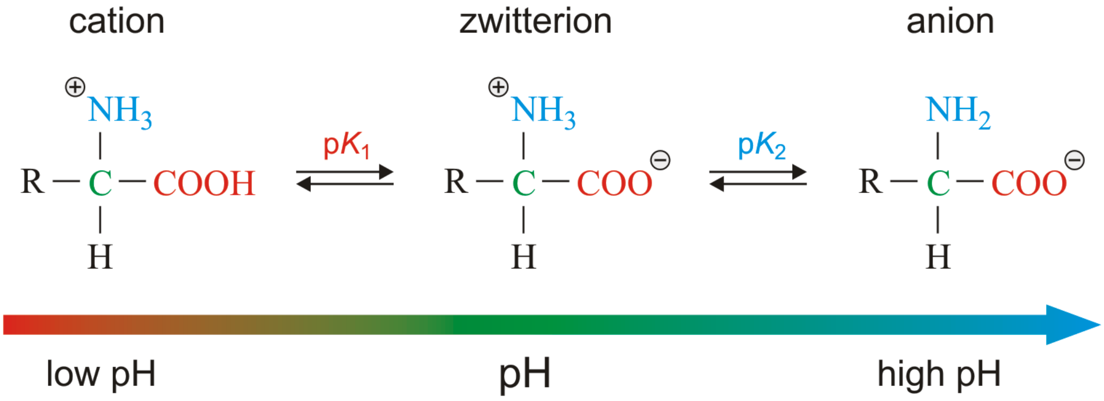
Alternatively, calculate per cent of C in the given choices which comes out to be (a) 0.55, (b) 0.69, (c) 0.58 and (d) 0.65 only for choice (b), the answer tallies.

Zwitter Ions - The Hydrogen atom (rather ion) moves to different positions depending on the PH (So can have a positive charge at some position, or a negative charge at some other position, depending on the pH)



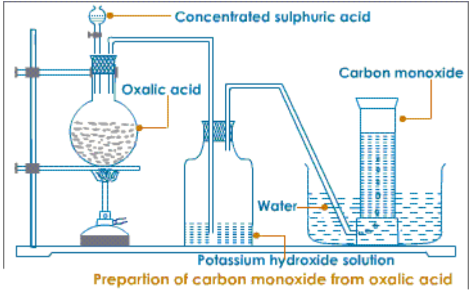


Electrophoresis - is a method to confirm if a positive charge is present or a negative charge is present in the ion.



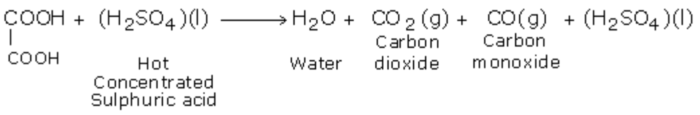
Iso -Electric point - the pH at which the ion (molecule) does not migrate to any electrodes.

What happens if oxalic acid is heated with conc sulphuric acid ?



Prepartion of carbon monoxide from oxalic acid

We get Carbonmonoxide



$$\begin{matrix}COOH\\ |\\ COOH\end{matrix} + \underset{\text{Hot Concentrated Sulphuric acid}}{(H_2SO_4)(l)} \longrightarrow \underset{\text{Water}}{H_2O} + \underset{\text{Carbon dioxide}}{CO_2(g)} + \underset{\text{Carbon monoxide}}{CO(g)} + (H_2SO_4)(l)$$

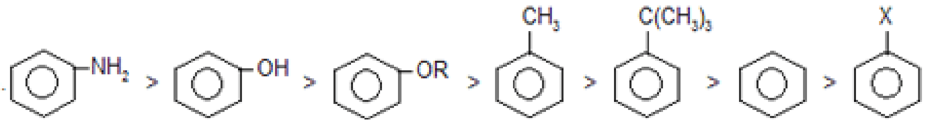
IMPORTANT ORDER AND FACTS OF ORGANIC CHEMISTRY

1. RCOCl > RCOOCOR > RCOOR > $RCONH_2$ Nucleophilic substitution reaction.

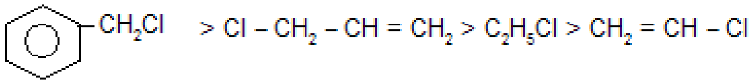
2. HI > HBr > HCl > RCOOH > C_6H_5OH > H_2O > CH ≡CH > NH_3 (Acidic nature).

3. $CCl_3CHO > HCHO > CH_3CHO > CH_3COCH_3$ Nucleophilic addition reaction.

4. $CH_2 = CH_2 > CH \equiv CH > C_6H_6$ Electrophilic addition reaction.

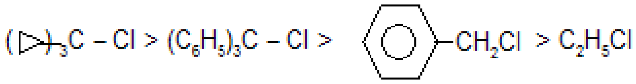
5.


Electrophilic Substitution Reaction

6.


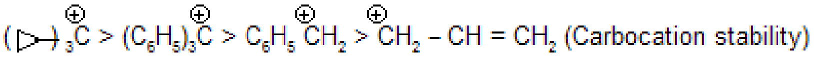
$> Cl - CH_2 - CH = CH_2 > C_2H_5Cl > CH_2 = CH - Cl$

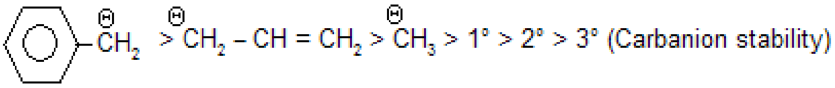
Nucleophilic Substitution Reaction

7.


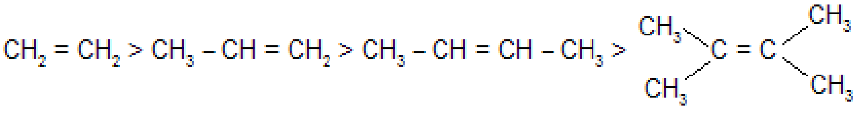
$(\triangleright)_3C - Cl > (C_6H_5)_3C - Cl >$ $-CH_2Cl > C_2H_5Cl$

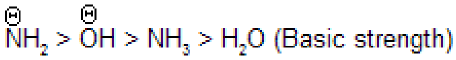
Nucleophilic Substitution Reaction

8.

$(\triangleright)_3\overset{\oplus}{C} > (C_6H_5)_3\overset{\oplus}{C} > C_6H_5\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_2 - CH = CH_2$ (Carbocation stability)

9.

$-\overset{\ominus}{C}H_2 > \overset{\ominus}{C}H_2 - CH = CH_2 > \overset{\ominus}{C}H_3 > 1^\circ > 2^\circ > 3^\circ$ (Carbanion stability)

10. $(CH_3)_2C = C(CH_3)_2 > CH_3 - CH = C -(CH_3)_2 > CH_3 - CH = CH - CH_3 > CH_3 - CH = CH_2$ (Stability)

11.

$CH_2 = CH_2 > CH_3 - CH = CH_2 > CH_3 - CH = CH - CH_3 > (CH_3)_2C = C(CH_3)_2$ (Heat of Hydration)

12.

$\overset{\ominus}{N}H_2 > \overset{\ominus}{O}H > NH_3 > H_2O$ (Basic strength)

13. $NI_3 > NBr_3 > NCl_3 > NF_3$ (Basic strength)

14. $Br_2 > Cl_2 > I_2$ (Selectivity for halogenation)

15. Halogenation of alkenes by cyclic halonium state, so anti attack takes place.

16. Hydroboration followed by oxidation is always anti markownikoff's addition due to steric effect.

17. Oximercuration - demercuration is markownikoff's addition of water because some carbocation character in cyclic mercurium state.

18. $CHCl_3$ in the presence of strong bases forms biradical : CCl_2 which undergo addition with double or triple bonds.

19. When conjugated diene reacts with alkene or alkyne it is known as diel's elder synthesis.

20. Ozonolysis of cyclo alkene forms one mole dialdehyde while ozonolysis of cyclo alkadiene forms two moles of dialdehyde.

21. Ozonolysis with $(CH_3)_2S$ is known as reductive ozonolysis.

22. Hydration of alkyne occur's in $HgSO_4$ and dil H_2SO_4.

23. 1-alkynes forms ppt with $Ag(NH_3)_2^{\oplus}$ and $Cu(NH_3)_4^{+}$.

24. Cis-2-butene reacts with Br2 to forms dl(±) pair of enantiomers of 2,3-dibromobutane while in case of trans-2-butene forms meso-2,3-dibromo butane due to anti addition always.

25. Haloform test given by species with CH_3CO-group but not in case of A.A.E. and tert. Butyl alcohol.

26. Chloral reacts with chloro benzene in con. H_2SO_4 to form insectiside DDT.

27. NBS is used for free radical allylation.

28. Rate for S_N^1 reaction is 3° > 2° > 1° in protic polar solvent.

29. Rate for S_N^2 reaction is 1° > 2° > 3° in polar aprotic solvent like DMSO, DMF, HMPT.

30. Chemical reactions like Hoffmann carbylamine and Reimer Tiemann's reaction active species is biradical CCl_2.

31. If cyclo 1,3-penta diene reacts with $CHCl_3$ and potassium tert. butoxide to form chlorobenzene.

32. Alkyl halides reacts with AgCN to form isocyanides due to ambident nature of nucleophile, other ambident nucleophiles are $\overset{\ominus}{N}O_2$and SO_3^{-2}.

33. In dehydration of alcohols active species is carbocation so rearrangement occurs like hydride shift or alkyl shift.

34. Dehydration of cyclobutyl methyl alcohol ring expansion takes place, formation of cyclo pentene occurs.

35. In esterification where acid reacts with alcohol to form ester, - OH given by acid while - H by alcohol

$$CH_3CO\overset{18}{O}H + C_2H_5\overset{16}{O}H \xrightarrow{\overset{\oplus}{H}} CH_3COOC_2H_5 + H_2\overset{18}{O}$$

36.Ether's reacts with HI to form alcohol and halide where fission of lower ether by S_N^2 mechanism while higher ethers like ter. butyl methyl ether or alkyl methyl ether by S_N^1 mechanism.

37. Quantitative estimation of ethers is done by ziesal's method.

38. If unsym. cyclic ether undergo fission it depends upon medium weather it is acid or basic like in acidic medium some character of carbocation so nucleophile goes to carbon where more alkyl groups are there while reverse in basic medium due to steric factor.

39. Aldehydes are reducing agent while ketones are not.

40. Aldehydes and ketones are separated by tollen's reagent.

41. Carbonyl and noncarbonyl are seprated by sodium bi sulphite and bradye's reagent.

42. As the size of alkyl group increases steric hindrance comes into play, reactivity towards nucleophilic addition decreases.

43. Aldehydes with ∝hydrogen atom in the presence of dil base undergo enolization and form ∝

carbonian to give aldol product.

44. If there is two-CHO group with $\propto$hydrogen atom to form cyclic intra aldol product.

45. Aldehydes without -hydrogen atom in the presence of con. alkali to form each molecule of acid and alcohol by hydride active species.

46. Glyoxal reacts with con. KOH to form glycolate ion by Intra Cannizaro's.

47. Pinacol pinacolone type reactions involve protonation, deprotonation and alkyl shift.

48. Aldol, Perkin, reformatsky and knovengel's reactions are classified as carbanian active reaction.

49. In Beckmann's rearrangement migration of group which is anti to-OH group takes place.

50. Beckmann's rearrangent is a reaction of oximes in the presence of H_2SO_4 or PCl_5 to produce N-alkyl amide derivatives.

51. Migratory attitude of alkyl group in Pinacol-pinacolone, beckmann's and bayer villegar oxidation is - C_6H_5 > $(CH_3)_3C$ - > $(CH_3)_2CH$ - > C_2H_5 - > CH_3-

52. Cyclo hexanoneoxime on beckmann's reaction gives caprolectum which on reaction with $\overset{\oplus}{H}$ to give polymer nylon-6

53. 2-methyl propanal even contains $\propto$-hydrogen atom but does not give aldol reaction.

54. Diphenyl glyoxal reacts with con. KOH to form salt of benzillic acid.

55. Propanone in the presence of dry HCl gas by enolic intermediate to form diacetone alcohol undergo heating form mesityl oxide. If this again reacts with propanone to form phoron.

56. Benzaldehyde reacts with alc. KCN to form Benzoin which on oxidation form benzil.

57. By wittig reaction carbonyl compounds are converted into E-Z form of alkene.

58. Benzaldehyde do not respond to benedict's and fehling's solution due to less redusing power of aromatic aldehyde.

59. HCOOH respond to oxidising agent due to presence of - CHO group.

60. $HI > H_2SO_4 > HNO_3 > RCOOH > H_2CO_3 > C_6H_5OH > H_2O > CH \equiv CH > NH_3 > CH_3 - C \equiv CH > CH_2 = CH_2 > H_2$ this is decreasing acidic nature.

61. Acids with $\propto$-hydrogen atom when reacts with halogen in the presence of P to form $\propto$-haloacid (HVZ).

62. Carboxyllic acid on reaction with PCl_5, CH_2N_2 and H_2O to form higher acid or next homologue.

63. For reactivity of acid derivatives use funda weaker the base better the leaving group.

64. Acid amide on reaction with PCl_5 to form alkane nitrile.

65. Anhydride on reaction with carbonyl compound in the presence of base (carbanian) forms $\propto$, β-unsaturated carboxyllic acid (perkin reaction)

66. Amide on reaction with Br_2 and alkali to form primary amine of lower homologue. Intermediate species is nitrene which undergo intra rearrangement to form RNH_2.

67. Ester's with α-hydrogen atom in the presence of strong base to form carbanian undergo nucleophilic substitution reaction forms β-keto ester for example ethyl acetate in the presence of pot. ter. Butoxide form aceto acetic ester (AAE). reaction is known as clesen's ester condensation of four types

(a) Simple clesen's ester condensation.
(b) CROSS clesen's ester condensation.
(c) Intra CEC (Dieckmann's condensation).
(d) mixed clesen ester condensation.

68. For a compound to be aromatic it must be cyclic, planar and obey (4n + 2) π electron rule.

69. Cyclooctatetraene is non aromatic compound while pyrrole, pyredene, furan, cyclopentadieneylanion all are aromatic.

70. In aromatic electrophilic substitution reaction there is no hydrogen isotopic effect except sulphonation and iodination.

71. m- directing groups like nitrobenzene and benzaldehyde cannot undergo fridal craft reaction.

72. Phenol is less acidic than general carboxylic acid, cannot react with $NaHCO_3$.

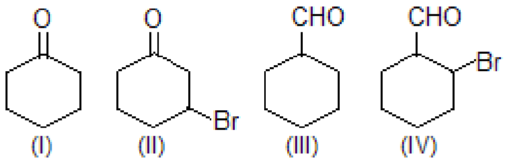
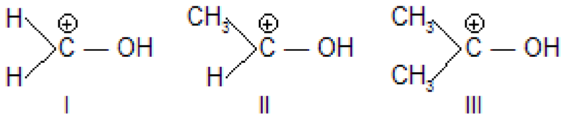
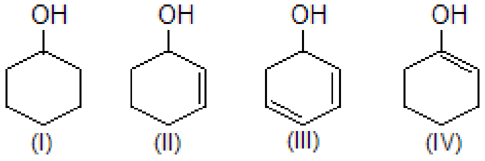
73. Anilene is more reactive than phenol towards electrophilic substitution reaction because less energy difference between nitrogen and carbon.

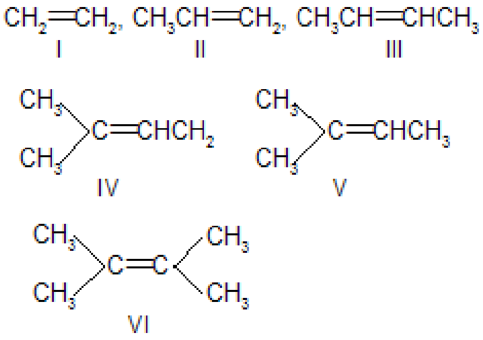
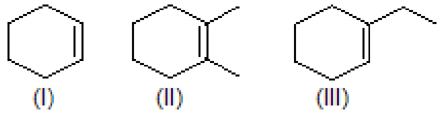
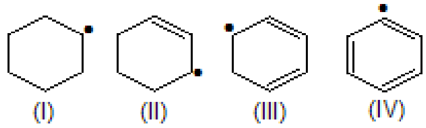
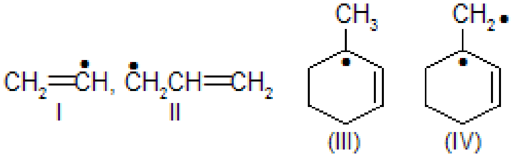
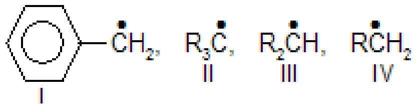
74. Benzene diazonium chloride reacts with phenol or anilene to form azo compounds.

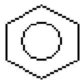
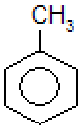
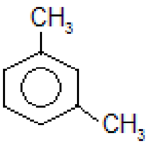
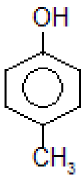
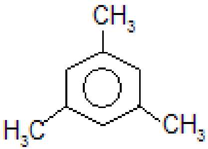
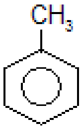
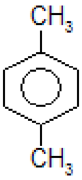
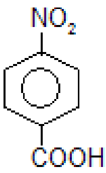
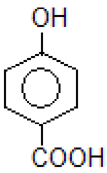
75. $C_6H_5NH_2 > C_6H_5OH > C_6H_5OR > C_6H_5Br > C_6H_5NO_2$ (Reactivity towards electrophilic substitution reaction

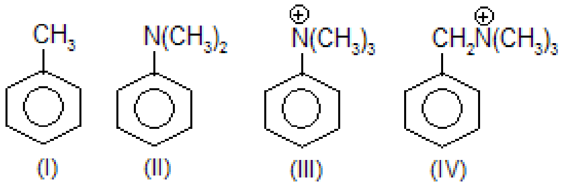
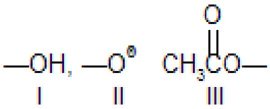
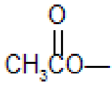
General Series - Chemistry Fact Sheet - 3

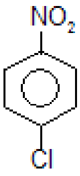
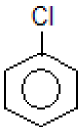
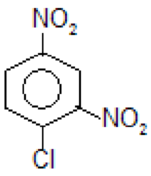
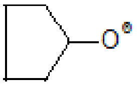
General series	Order	Why ?	
1.	**B.P. of** $\underset{I}{CH_3CH_2OH}$, $\underset{II}{CH_3OCH_3}$, $\underset{III}{CH_3CH_3}$	I > II > III	There is intermolecular H-bonding I. III has weak force of attraction and is most volatile.
2.	**B.P. of *o*, *m*, *p*-nitro phenol**	o < m < p	Intramolecular H-bonding in o-isomer makes it more volatile.

3.	**Reactivity of … with Tollen's reagent** $HCHO$, CH_3CHO, CH_3COCH_3 C_6H_5CHO I II III IV	I > II > IV > III	—CHO group is easily oxidised compared to keto group due to redusing hydrogen.
4.	**Reactivity of … with Fehling's solution** I II III IV (above)	I > II > IV > III	—do—
5.	**Extent of hydration of** 	I < II < III < IV	Aldehydes are more hydrated than ketones. Halide makes C of carbonyl group more electropositive.
6.	**Electrophilic nature of …….. for nucleophilic attack** 	I > II > III	CH_3 group decreases +ve charge on C hence nucleophilic attack.
7.	**Reactivity of isomeric 1°, 2°, 3° butyl halide towards elimination (E1 or E2)**	3° < 2° < 1°	due to stability of intermediate carbocation
8.	**Dehydration of** 	IV < I < II < III	Alcohol leading to increase in conjugation due to dehydration is more easily dehydration is more easily dehydrated. IV is vinylic, hence least.
9.	**Stability of**		

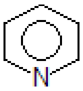
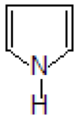
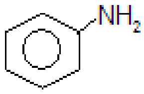
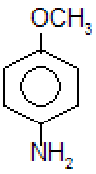
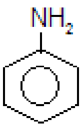
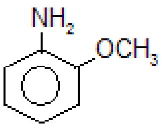
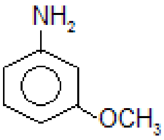
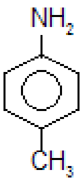
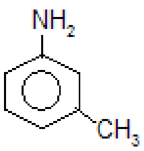
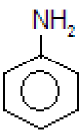
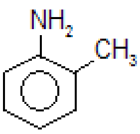
		I < II < III < IV < V < VI	Substituted alkenes are more stable.More the alkyl groups are attached to the doubly bonded carbon atom more is the stability.
10.	**Stability of** 	I < III < II	II is more substituted than III (More hyperconjugation more stability)
11.	**Stability of** 	III > II > I > IV	IV is vinylic while in conjugative, II allylic.
12.	**Stability of** 	I < IV < II < III	III is 3° allylic and II is 1° allylic
13.	**Dehydration of** 1°, 2°, 3° isomeric butyl alcohol	3° < 2° < 1°	More the stability of intermediate, greater the reactivity of chemical reaction.
14.	**Boiling points of** *n*-butyl amine, *n*-butyl alcohol, *n*-pentane I II III	II > I > III	I, II have H-bonding but electronegativity of O > N hence H-bonding in II > I
15.	**Formation of** 	I > II > III > IV (easiest I)	greater the stability, easier the formation of perticular species.
16.	**Reactivity of C—H bond (abstraction of H)**		

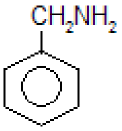
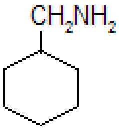
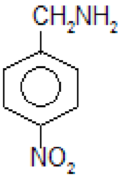
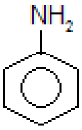
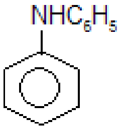
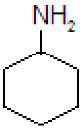
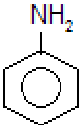
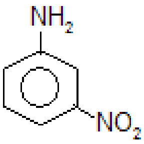
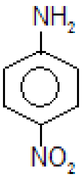
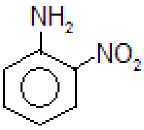
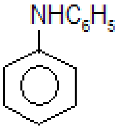
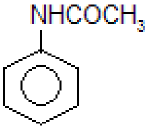
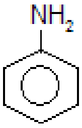
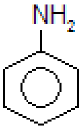
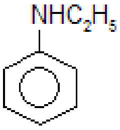
	$CH_2{=}CH—\mathbf{H}$, vinylic (I) $CH_3—\mathbf{H}$, methyl (II) 1° $CH_3CH_2—\mathbf{H}$ (III) $(CH_3)_2CH—\mathbf{H}$ 2° (IV) $(CH_3)_3C—\mathbf{H}$, 3° (V) $CH_2{=}CHCH_2—\mathbf{H}$ (allylic) (VI)	I < II < III < IV < V < VI	Vinyl < methyl 1° < 2° < 3° < allylic
17.	**Leaving nature (tendency) of … in S_N reaction.** H^-, R^-, MeO^-, OH^-, CN^-, CH_3COO^-, I II III IV V VI $ROSO_2^-$, $ArSO_3^-$ VII VIII	I < II < III ~ IV < V < VI < VII < VIII	If acid is strong, its conjugate base is weak and greater the leaving tendency.
18.	**Rate of esterification of the following acids with MeOH** $MeCH_2COOH$, $Me_2CHCOOH$, $MeCCOOH$, I II III Et_3CCOOH $(i-Pr)_2CHCOOH$ IV V	I > II > III > IV > V	As the size of the substituents on the $\alpha—C$ increases, the tetrahedrally bonded interme. diate becomes more crowded and these slower the rate.
19.	**Relative reactivity of … with electrophile in S_E reaction**  (I)  (II)  (III)  (IV)  (V)	I > II > IV > III > V	$—CH_3$ is *o*-, *p*-directing and responsible for activation.
20.	**Relative reactivity of these compunds with electrophile inS_E reaction**  (I)  (II)  (III)  (IV)	II > I > III > IV	$—CH_3$ is *o*-, *p*-directing due to activation while $—COOH$ is m-directing and deactivating group.
21.	**Relative reactivity of … with electrophile in S_E reaction.**	II > I > IV > II	As the number of sp^3 hybridised C

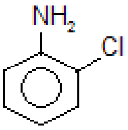
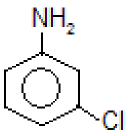
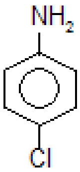
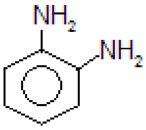
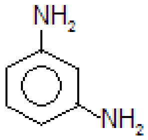
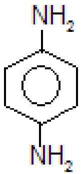
			atoms separating the ring from the positively charged substituent increases, deactivating effect decreases due to less electronegativity.
22.	**Activating effects of the following o, p-directors.**  $—OH, —O^{\ominus}, CH_3\overset{O}{\overset{\|\|}{C}}O—$ I II III	II > I > III	$—O^{\ominus}$ is best able to donate electrons there by giving a very stable uncharged intermediate. In  $CH_3\overset{O}{\overset{\|\|}{C}}O—$ cross conjugation diminished its ability to donate electrons to an arenium ion.
23.	**Relative reactivity of … towards S_N1 reaction** benzyl chloride (I), *p* - methoxy benzyl chloride (II) and *p* - nitro benzyl chloride (III)	II > I > III	Intermediates are benzylic cations. So CH_3O(electron repelling) gives greater stability through delocalisation while NO_2 (electron attracting) decreases stability.
24.	**Relative reactivity of … towards S_N1 and S_N2 reaction** $PhCH_2Cl$ (I) $PhCHClMe$ (II) $PhCClMe_2$ (III) (Ph stands for phenyl, C_6H_5)	**S_N1 :** III > II > I **S_N2 :** II < II < I	**S_N1 :** 1° < 2° < 3° alkyl halide **S_N2 :** 3° < 2° < 1° alkyl halide
25.	**Relative reactivity of … with E^+ (electrophile) in S_E reaction.**	II > I > III	$—NO_2$ deactivates benzene ring for S_E

	 (I)  (II)  (III)		
26.	**Order of S_N2 reactivity of alkoxide nucleophiles** Me_3CO^-, MeO^-, $MeCH_2O^-$, Me_2CHO^- I II III IV  V	I < IV < V < III < II	S_N2 reactivity is suseptible to steric hindrance by the nucleophile as well as by the size of alkyl group.

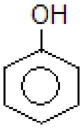
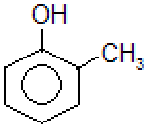
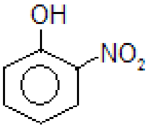
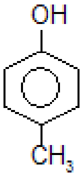
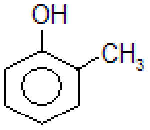
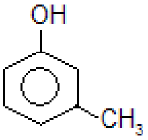
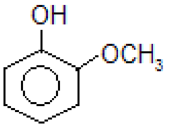
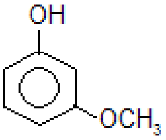
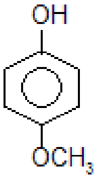
Basic power - Chemistry Fact Sheet - 2

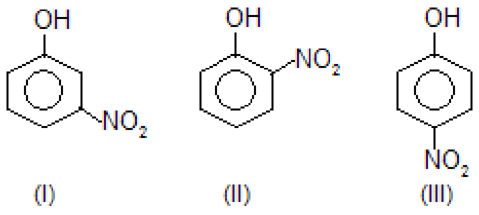
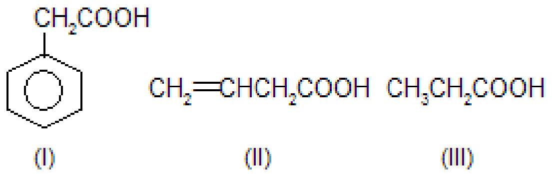
	Basic power	Order	Why ?
1.	 (I)  (II)  (III)	I > III > II	lone pair on N is not used in resonance of π - electrons in I. In II lone pair of the ring is itself used in delocalisation while that of outside ring in III.
2.	 (I)  (II)  (III)  (IV)	I > II > III > IV	$-OCH_3$ is strong electron donating group. This is due to **ortho** effect, all the aniline are less basic than *p*-substituted aniline due to **steric hindrance.**
3.	 (I)  (II)  (III)  (IV)	I > II > III > IV	I (hyper conugation and induction) II (induction) IV (ortho effect), ortho effect normally decreases basic nature.

4.	 (I)  (II)  (III)	II > I > III	In II there is sp^3 hybridised C, In I, sp^2. NO_2 is electron withdrawing.
5.	 (I)  (II)  (III)	III > I > II	lone pair on N is used in delocalisation of π-electrons in aromatic amines while cyclohexyl is electron repelling (III); in II, lone pair on N is used by two benzene ring.
6.	 (I)  (II)  (III)  (IV)	I > II > III > IV	NO_2 is electron-withdrawing, thus nitro-anilines are less basic than aniline. IV is less basic than III because $-NO_2$ is closer and exerts a stronger inductive effect.
7.	 (I)  (II)  (III)	III > I > II	phenyl and $-COCH_3$ are electronwithdrawing and $-C_6H_5$ < $COCH_3$
8.	 (I)  (II)  (III)	I < II < III	Electron donating nature of $C_2H_5 > CH_3$ So more basic strength.

9.	 (I)  (II)  (III)	I < II < III	ortho effect in I.
10.	 (I)  (II)  (III)	I < II < III	ortho effect in (I)

Acidic Powers & Their Orders - Chemistry Fact Sheet

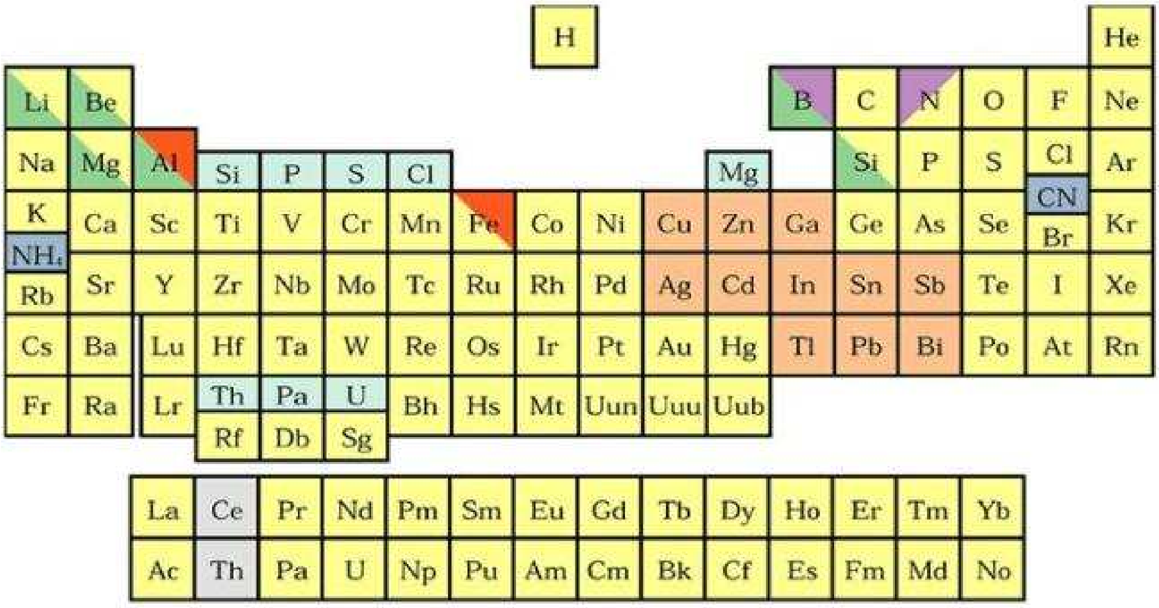
Acidic power	Order	Why ?	
1.	1- , 2- , 3- chlorobutanoic acid I II III	III < II < I	Farther the (-I) group (Cl), lesser the acidic strength
2.	1-, 2-, 3- methyl pentanoic acid I II III	I < II < III	Farther the (+I) group, greater the acidic power
3.	 (I)  (II)  (III)	II < I < III	$-CH_3$ is electron donating and $-NO_2$ is electron attracting
4.	 (I)  (II)  (III)	II < I < III	$-CH_3$ is electron repelling; decreases acidic strength of phenol
5.	 (I)  (II)  (III)	III < I < II	$-OCH_3$ group contains +M effect and decreases acidic poer.

6.		I < II < III	— NO_2 is electron attracting; III is more resonance stabilised than I and also than II. In I, only inductive effect is operative.
7.		I > II > III	sp^2 hybridised carbon of I, II are more electronegative hence acid strength is increased. Benzylic ($C_6H_5CH_2$) is more stabilised than allylic ($CH_2{=}{=}CHCH_2$).
8.	oxalic acid, succinic acid, malonic acid, adipic acid I II III adipic acid (all dibasic) IV	I > II > III > IV	Effect of one —COOH on the other decreases as its distance between them increases, $(COOH)_2$ is maximum acidic.
9.	*o* - *m* - *p* - nitrobenzoic acid I II III	II < III < I	—NO_2 is electron attracting (-I effect)
10.	*o* - *m* - *p* - hydroxy benzoic acid I II III	III < II < I	—OH shows electron withdrawing nature at *o* - and *m* - and electron repelling at *p* -, *o* - isomer due to intramolecular bonding in salicylate ion is stronger than *m* - isomer

11.	*o*- *m*- *p*- methoxy benzoic acid I II III	III < II < I	—do—
12.	*o*- *m*- *p*- amino benzoic acid I II III	I < III < II	—NH_2 is electron donating.

-

Topic wise grouping of information kind of Dictionary of Inorganic Chemistry



Given two Equations

(1) B_2O_3 + 6NaOH -> (X) + $3H_2O$

(2) B_2O_3 + 2NaOH -> (Y) + H_2O

What are (X) and (Y) ?

Ans : X is Sodium Borate and Y is Sodium meta borate

B_2O_3 + 6NaOH -> $2Na_3BO_3$ (Sodium Borate) + $3H_2O$

B_2O_3 + 2NaOH -> $2NaBO_2$ (Sodium metaborate) + H_2O

-

Silica is soluble in which of the following acids ?

(1) HF   (2) HCl   (3) HBr   (4) HI

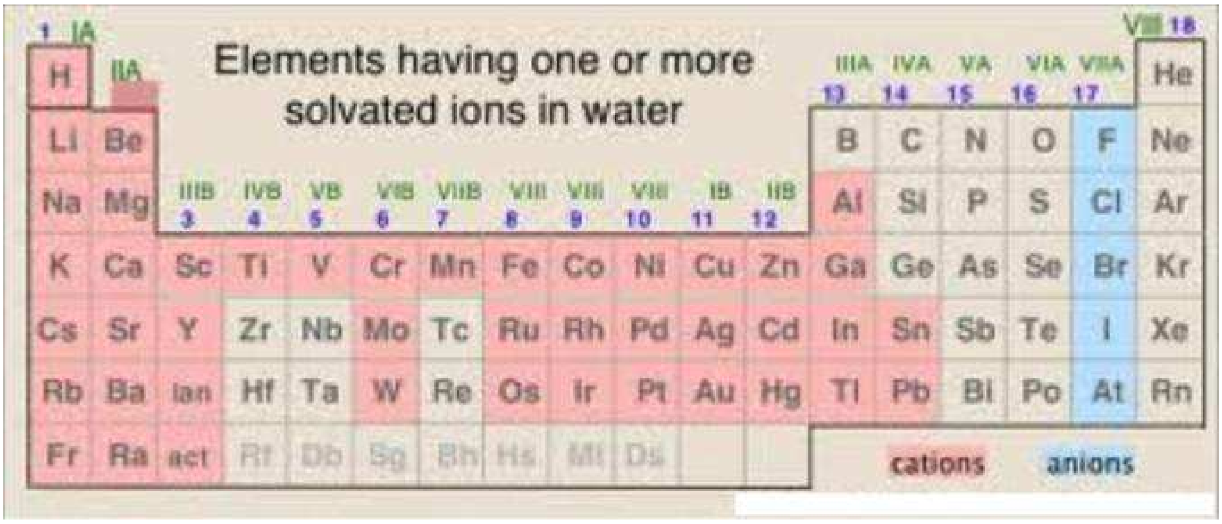
Solution : $SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$ and again $SiF_4 + 2HF \rightarrow H_2SiF_6$ (Hydroflurosilicic acid)

-

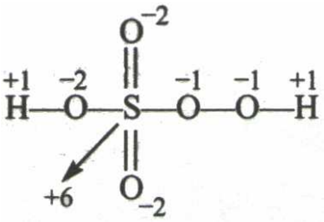
$K_3Co(NO_2)_6$ is Fischer's Salt

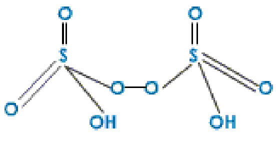
The brown ring test for NO_3^- is due to formation of the complex $[Fe(H_2O)_5NO]^{2+}$

Merck's perhydrol is 30.4% H_2O_2

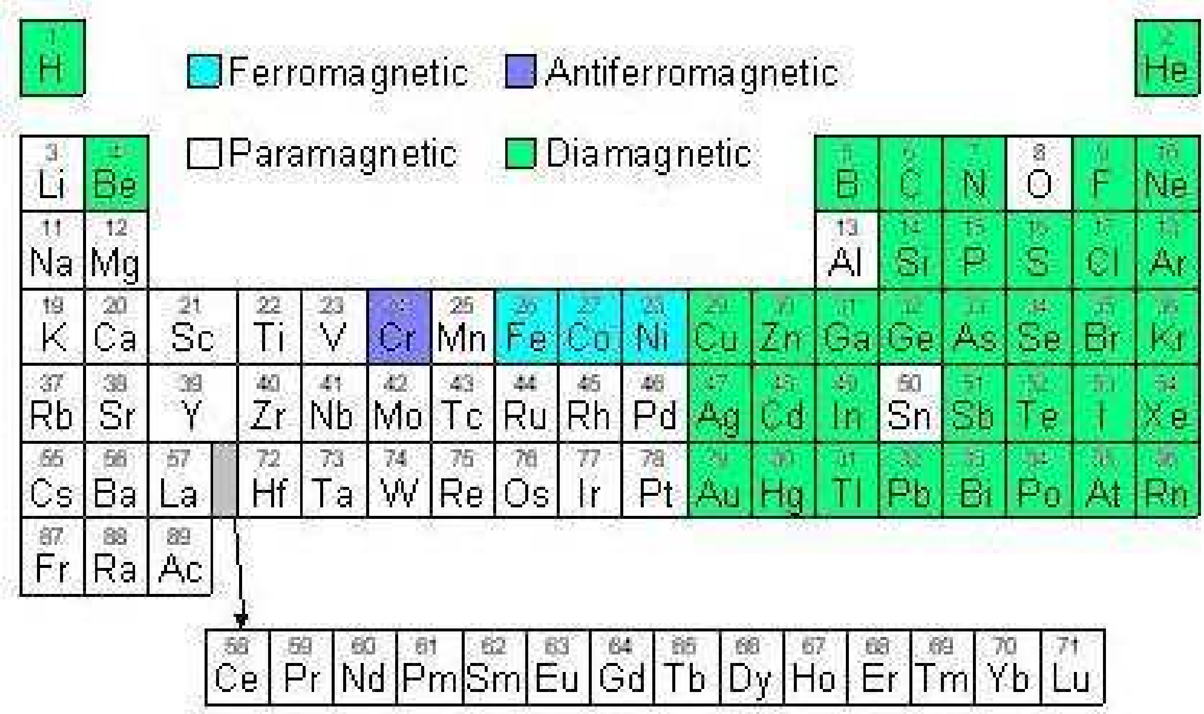


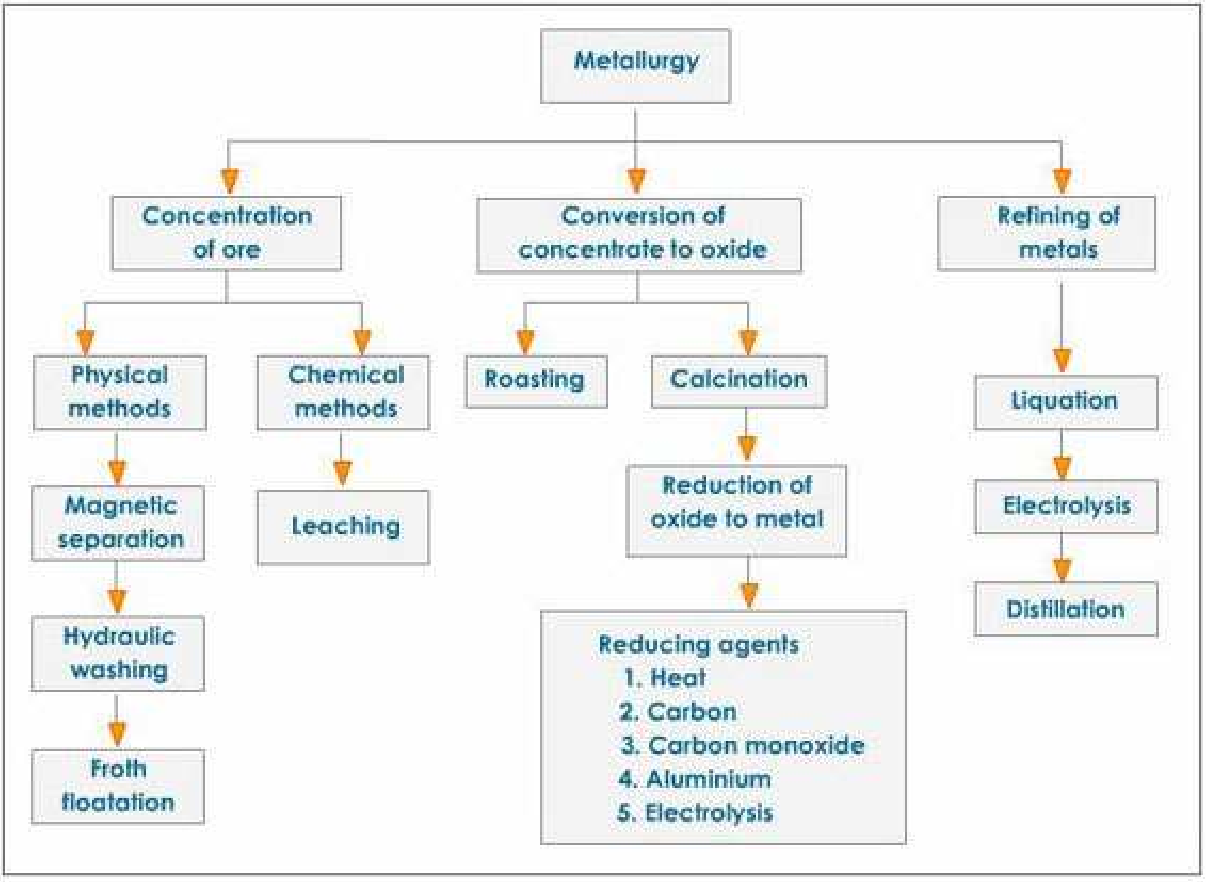
H_2SO_5 , $H_2S_2O_8$ have peroxide linkages

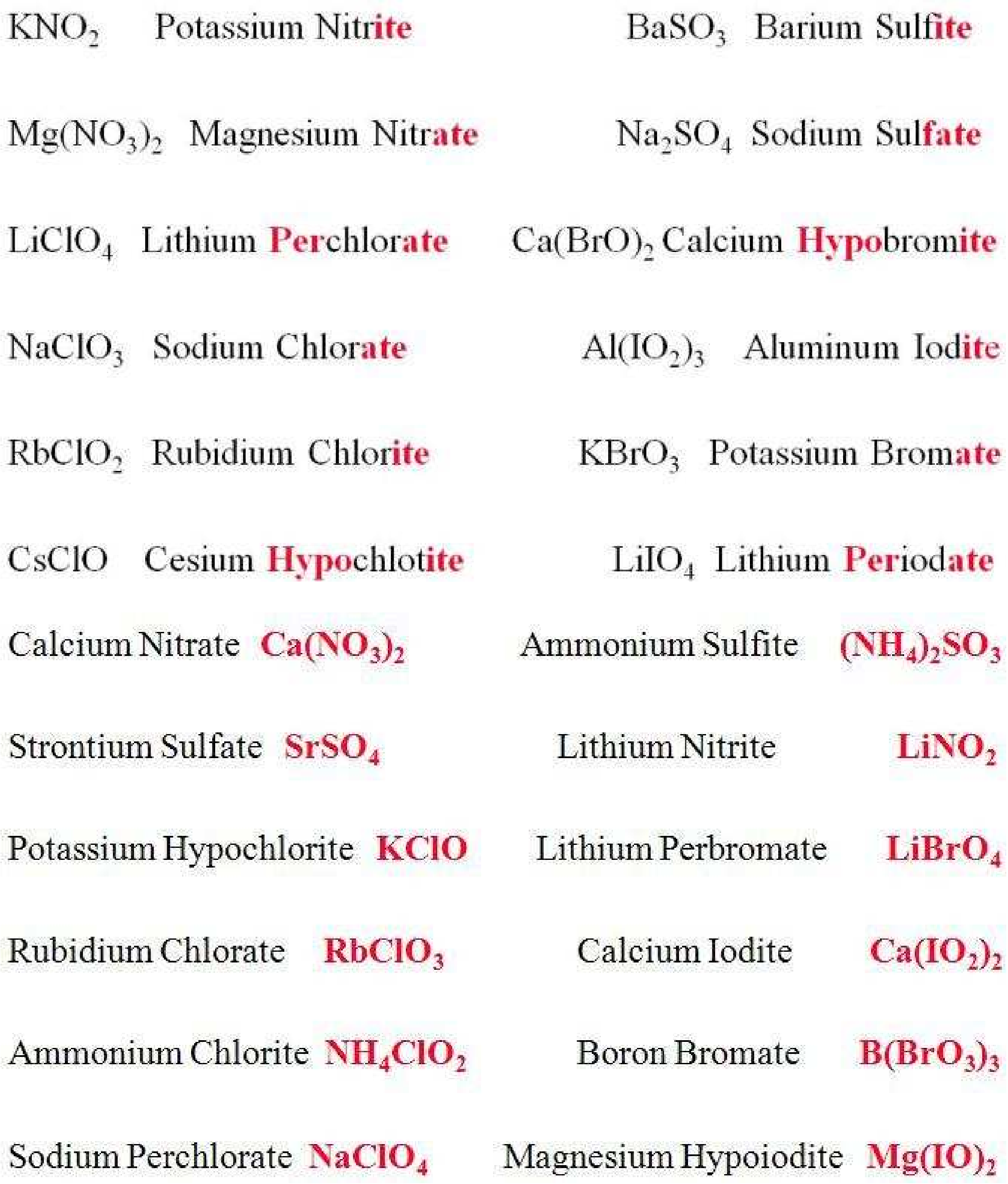




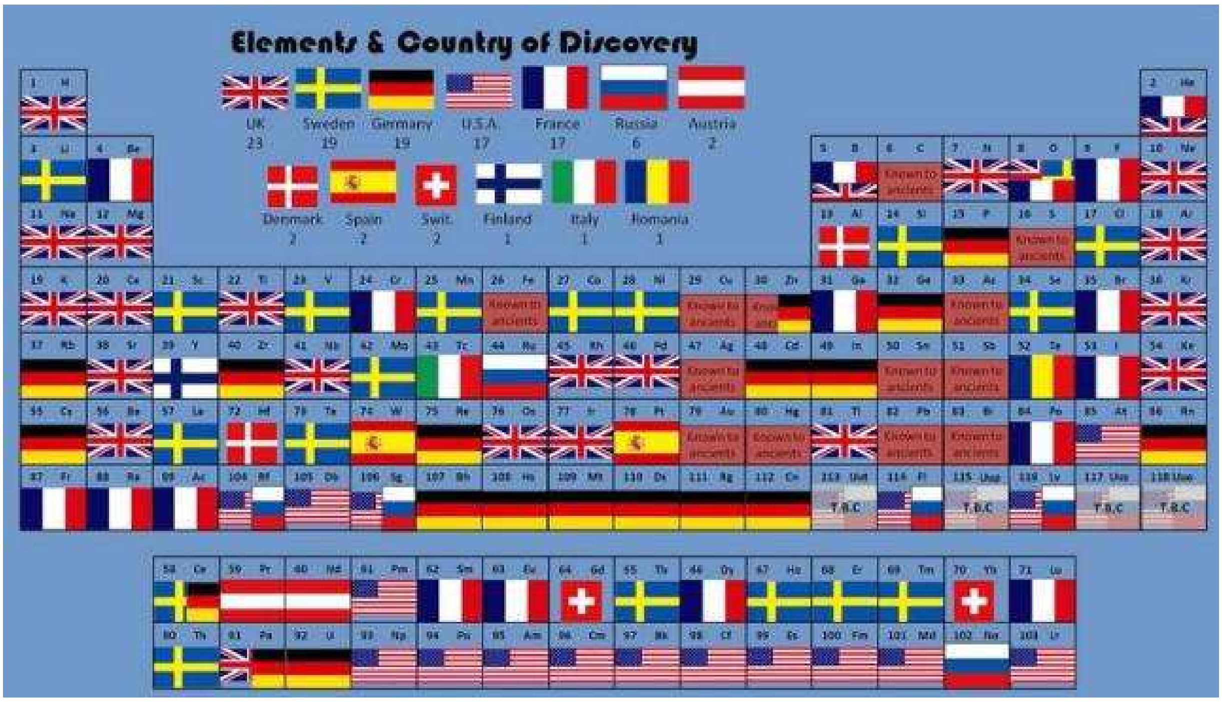
$H_2S_2O_8(+6)$
Peroxydisulphuric acid
(or Marshall's acid)


Ferromagnetic
Antiferromagnetic
Paramagnetic
Diamagnetic


Metallurgy
Concentration of ore
Conversion of concentrate to oxide
Refining of metals
Physical methods
Chemical methods
Roasting
Calcination
Liquation
Magnetic separation
Leaching
Reduction of oxide to metal
Electrolysis
Hydraulic washing
Distillation
Reducing agents
1. Heat
2. Carbon
3. Carbon monoxide
4. Aluminium
5. Electrolysis
Froth floatation



KNO_2	Potassium Nitr**ite**	$BaSO_3$	Barium Sulf**ite**
$Mg(NO_3)_2$	Magnesium Nitr**ate**	Na_2SO_4	Sodium Sulf**ate**
$LiClO_4$	Lithium **Per**chlor**ate**	$Ca(BrO)_2$	Calcium **Hypo**brom**ite**
$NaClO_3$	Sodium Chlor**ate**	$Al(IO_2)_3$	Aluminum Iod**ite**
$RbClO_2$	Rubidium Chlor**ite**	$KBrO_3$	Potassium Brom**ate**
$CsClO$	Cesium **Hypo**chlot**ite**	$LiIO_4$	Lithium **Per**iod**ate**
Calcium Nitrate	$Ca(NO_3)_2$	Ammonium Sulfite	$(NH_4)_2SO_3$
Strontium Sulfate	$SrSO_4$	Lithium Nitrite	$LiNO_2$
Potassium Hypochlorite	$KClO$	Lithium Perbromate	$LiBrO_4$
Rubidium Chlorate	$RbClO_3$	Calcium Iodite	$Ca(IO_2)_2$
Ammonium Chlorite	NH_4ClO_2	Boron Bromate	$B(BrO_3)_3$
Sodium Perchlorate	$NaClO_4$	Magnesium Hypoiodite	$Mg(IO)_2$



Bromine reacting with NaOH in cold and hot give different mix of products. Specify

Br_2 + 2NaOH (cold) -> NaBr + NaOBr + H_2O

$3Br_2$ + 6 NaOH (Hot) -> 5NaBr + $NaBrO_3$ + $3H_2O$

Malachite decomposes to give A + CO_2 + H_2O and compound A on reduction with Carbon gives CO + B

Identify A and B

Solution : $CuCO_3.Cu(OH)_2$ -> 2CuO (A) + CO_2 + H_2O

CuO + C -> Cu (B) + CO

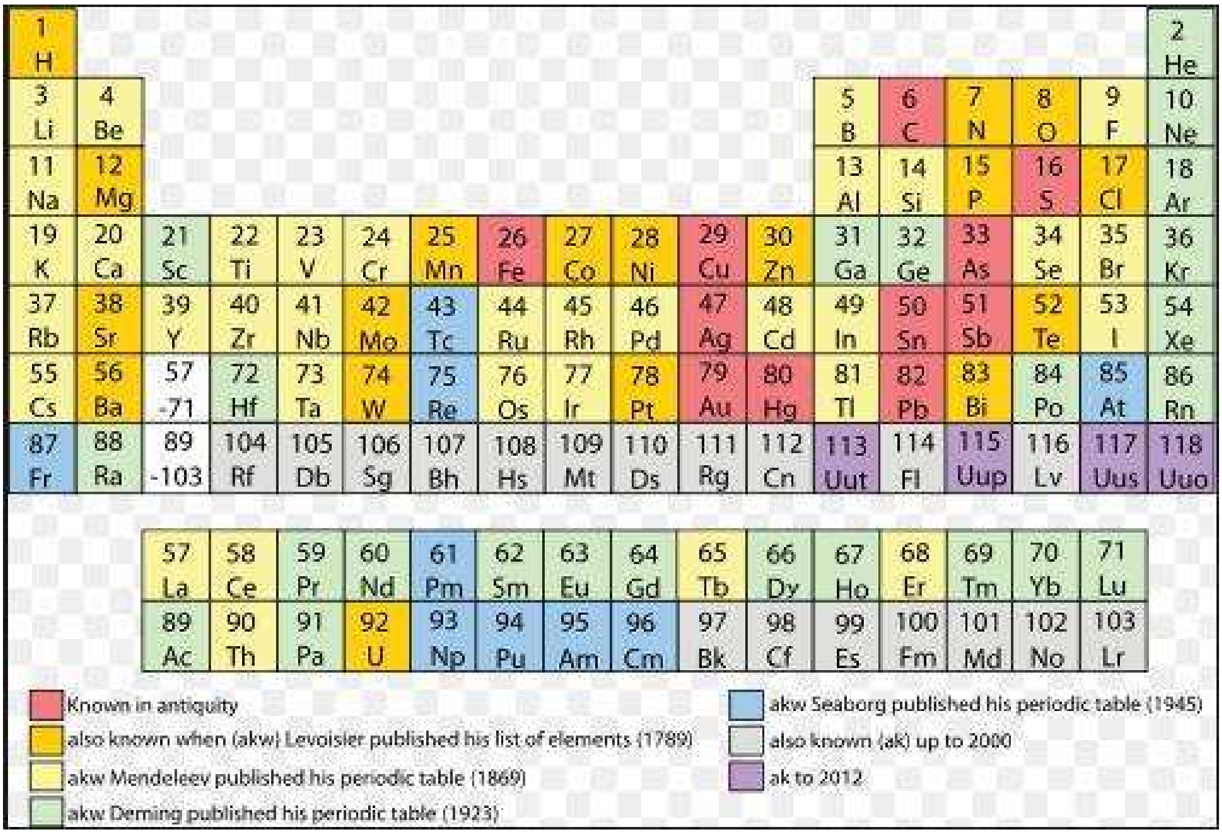
-

Some examples of Complex Anions

K_2PtCl_6 < == > $2K^+ + [PtCl_6]^{2-}$

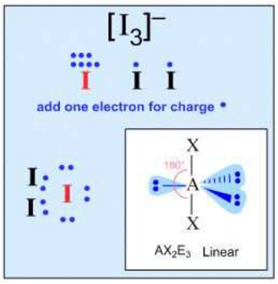
Na_3AlF_6 < == > $3Na^+ + AlF_6^{-3}$

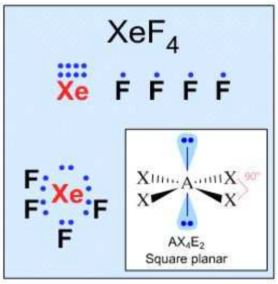
K_2SiF_6 < == > $2K^+ + SiF6^{-2}$



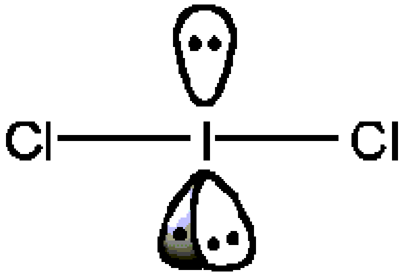
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 -71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 -103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
		57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
		89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

🟥 Known in antiquity
🟧 also known when (akw) Levoisier published his list of elements (1789)
🟨 akw Mendeleev published his periodic table (1869)
🟩 akw Deming published his periodic table (1923)
🟦 akw Seaborg published his periodic table (1945)
⬜ also known (ak) up to 2000
🟪 ak to 2012

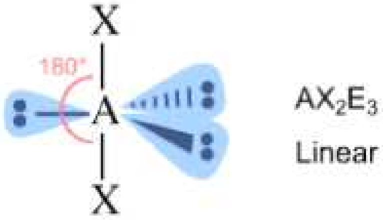




and ICl_2^-



Sp^{3}d hybridization



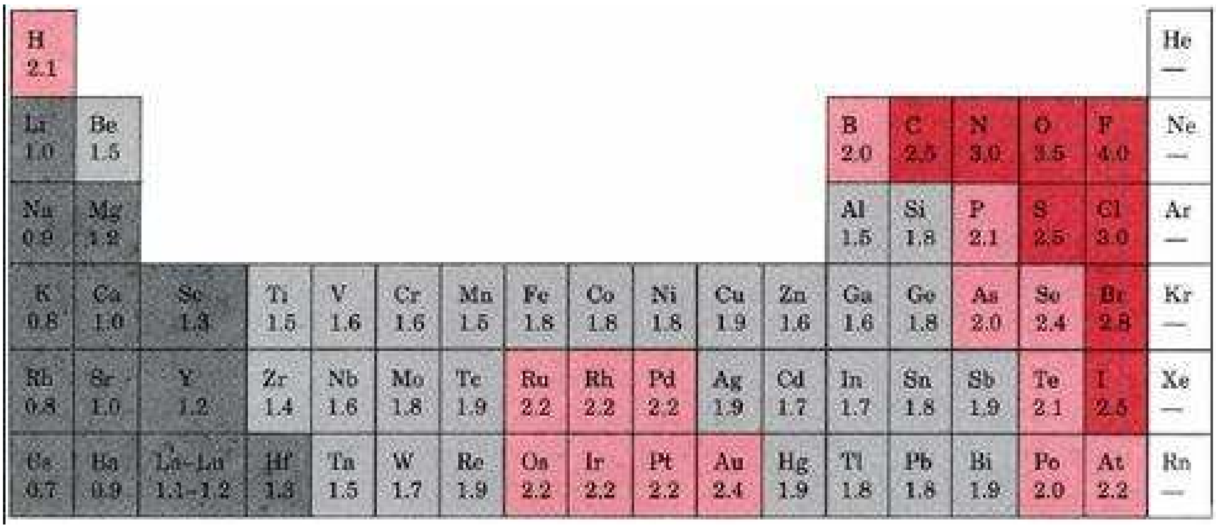
for I_3^- and ICl_2^-

The ionization potential of Pb is higher than Sn due to poor shielding by 14f electrons present in Pb

Selenous acid H_2SeO_3 (Oxidation Number of Se is +4)

Telluric acid H_6TeO_6 (Oxidation Number of Te is +6)

Electronegativity Values (in Pauling Scale)



H 2.1																	He —
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne —
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar —
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr —
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe —
Cs 0.7	Ba 0.9	La-Lu 1.1-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn —

Microcosmic Salt is $Na(NH_4)HPO_4$ Sodium ammonium hydrogen phosphate

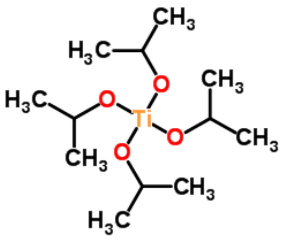
Which of the following electrolyte will be most effective in coagulation of gold sol ?

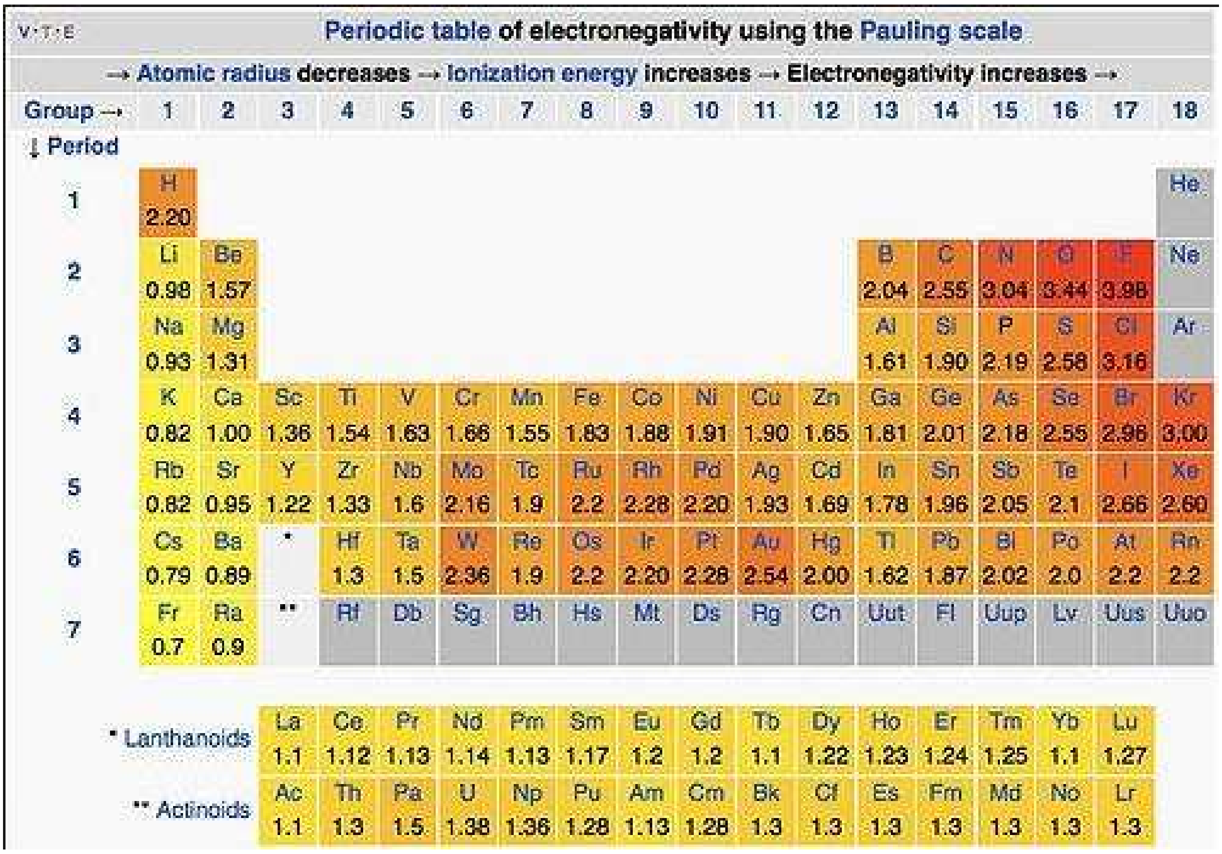
(1) $NaNO_3$ (2) $K_4Fe(CN)_6$ (3) Na_3PO_4 (4) $MgCl_2$

Gold sol is a negatively charged coagulation which is carried out by positively charged ion furnished by electrolyte

Coagulating power depends on the valency of cation of electrolyte. (Schulze Hardy Law) Mg^{2+} ion has highest valency so $MgCl_2$ is most effective.

Organometallic compounds are Metal atoms directly linked with Carbon. So $Ti(OC_3H_7)_4$ is not an organometallic compound.





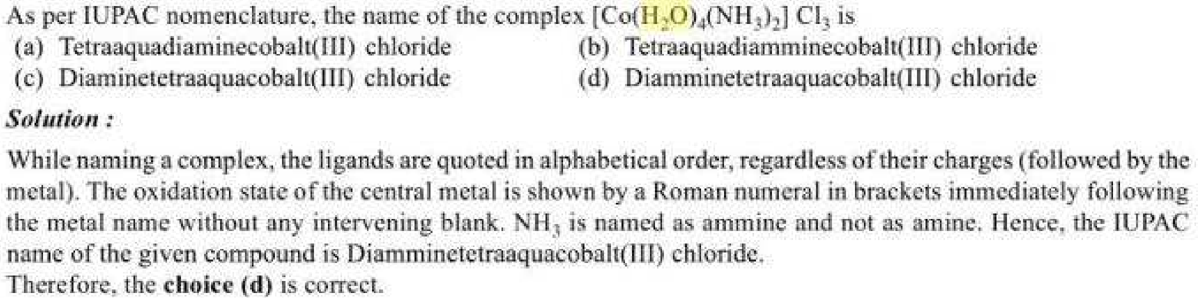
V·T·E

Periodic table of electronegativity using the Pauling scale

→ Atomic radius decreases → Ionization energy increases → Electronegativity increases →

Group → ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.60
6	Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 1.87	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
7	Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo
* Lanthanoids			La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27	
** Actinoids			Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.3	

IUPAC name of Diamminetetraaquacobalt III chloride

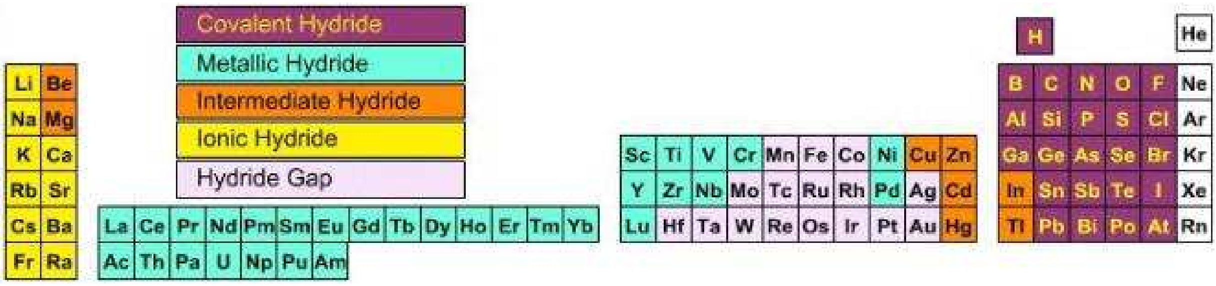


As per IUPAC nomenclature, the name of the complex $[Co(H_2O)_4(NH_3)_2]Cl_3$ is

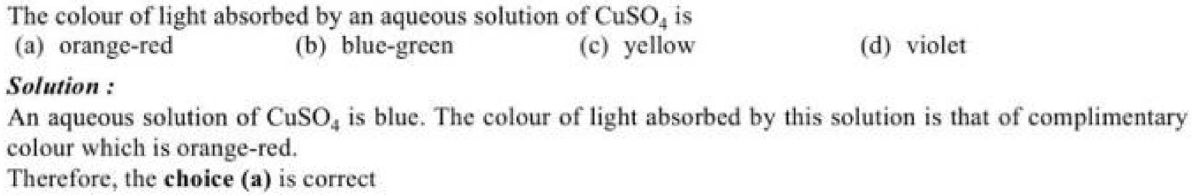
(a) Tetraaquadiaminecobalt(III) chloride
(b) Tetraaquadiamminecobalt(III) chloride
(c) Diaminetetraaquacobalt(III) chloride
(d) Diamminetetraaquacobalt(III) chloride

Solution :

While naming a complex, the ligands are quoted in alphabetical order, regardless of their charges (followed by the metal). The oxidation state of the central metal is shown by a Roman numeral in brackets immediately following the metal name without any intervening blank. NH_3 is named as ammine and not as amine. Hence, the IUPAC name of the given compound is Diamminetetraaquacobalt(III) chloride.
Therefore, the **choice (d)** is correct.



Color of light absorbed by aqueous solution of CuSO4



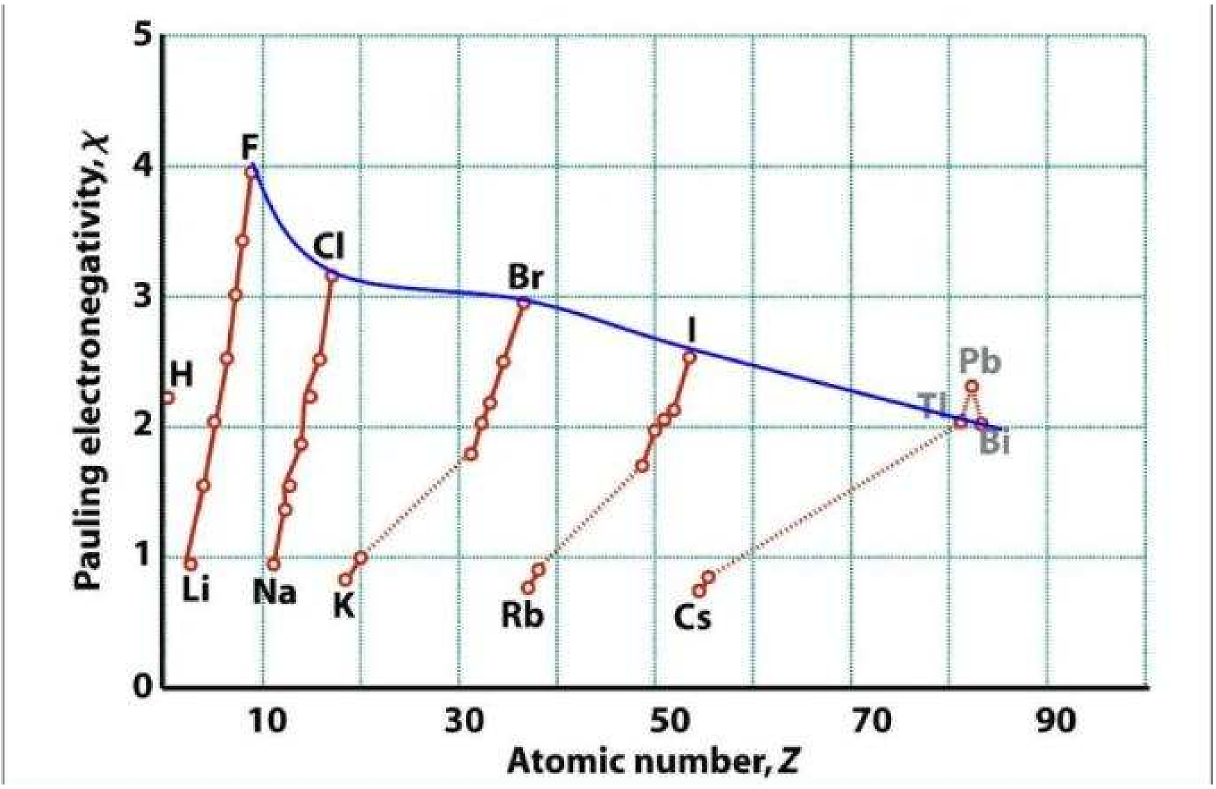
The colour of light absorbed by an aqueous solution of $CuSO_4$ is

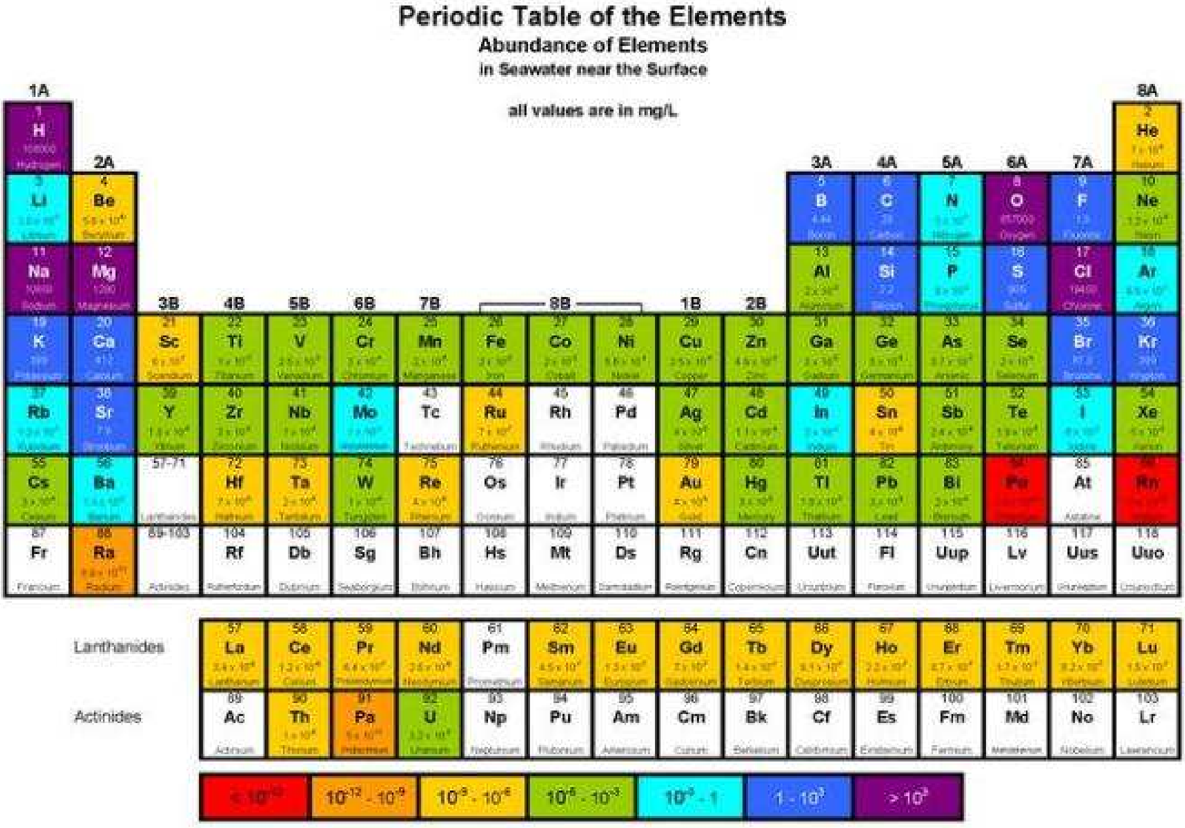
(a) orange-red (b) blue-green (c) yellow (d) violet

Solution :

An aqueous solution of $CuSO_4$ is blue. The colour of light absorbed by this solution is that of complimentary colour which is orange-red.

Therefore, the **choice (a)** is correct





Periodic Table of the Elements
Abundance of Elements
in Seawater near the Surface

all values are in mg/L

🟥	🟧	🟨	🟩	▨	🟦	🟪
< 10^{-12}	10^{-12} - 10^{-9}	10^{-9} - 10^{-6}	10^{-6} - 10^{-3}	10^{-3} - 1	1 - 10^{3}	> 10^{3}

$BaCl_2 \cdot 5H_2O$ Ba^{+2} is the cation Barium, Cl^- is the Chloride anion. There are five water molecules therefore the name is: **Barium Chloride Pentahydrate**

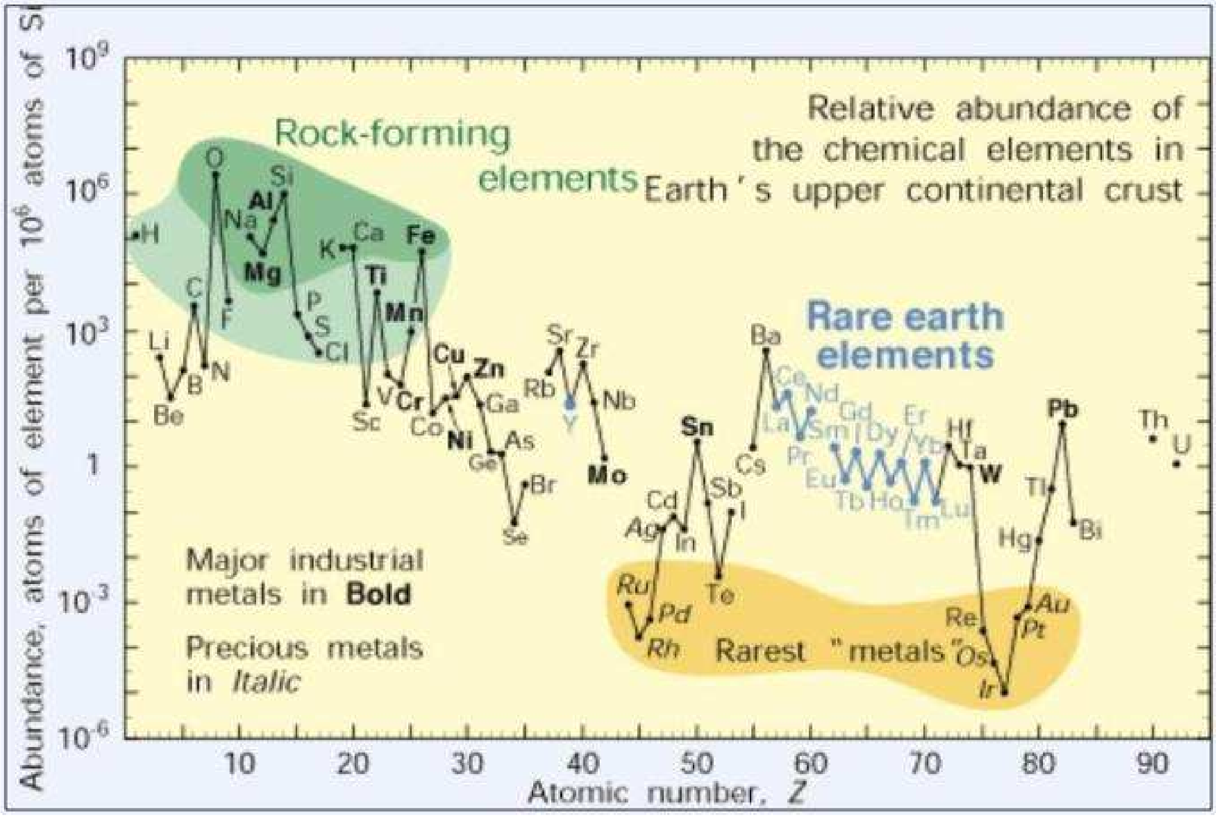
Magnesium Perchlorate Magnesium is the Mg^{+2} cation, and perchlorate is the ClO_4^- anion, therefore we need two perchlorate anions for each Mg cation therefore the formula is: **$Mg(ClO_4)_2$**

$(NH_4)_2SO_3$ NH_4^+ is the ammonium ion, and SO_3^{-2} is the sulfite anion, therefore the name is:

Ammonium Sulfite

Calcium Nitrate Calcium is the Ca^{+2} cation, and nitrate is the NO_3^- anion, therefore the formula is:

$Ca(NO_3)_2$



Group 1 Elements—Alkali Metals

Group 1 contains lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs) and francium (Fr). All alkali metals contain one electron in their outermost orbitals. Due to contribution of one electron per atom towards the metallic bonding, all the elements are soft and low melting. Because of low ionization energies, the metals are strong reducing agents. The alkali metals dissolve in liquid ammonia and form a deep blue solution when dilute. The blue colour is due to the solvated electrons. The conducting ability of their ions in aqueous solution follows the order: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$.

The alkali metals are very reactive and tarnish in air to form oxide. They burn in air, Li forms Li_2O, Na forms Na_2O_2 and higher alkali metals form superoxide (MO_2). The oxides of alkali metals are basic in nature. The peroxides are diamagnetic and are oxidizing agents. The superoxides are paramagnetic and are stronger oxidising agents than peroxides.

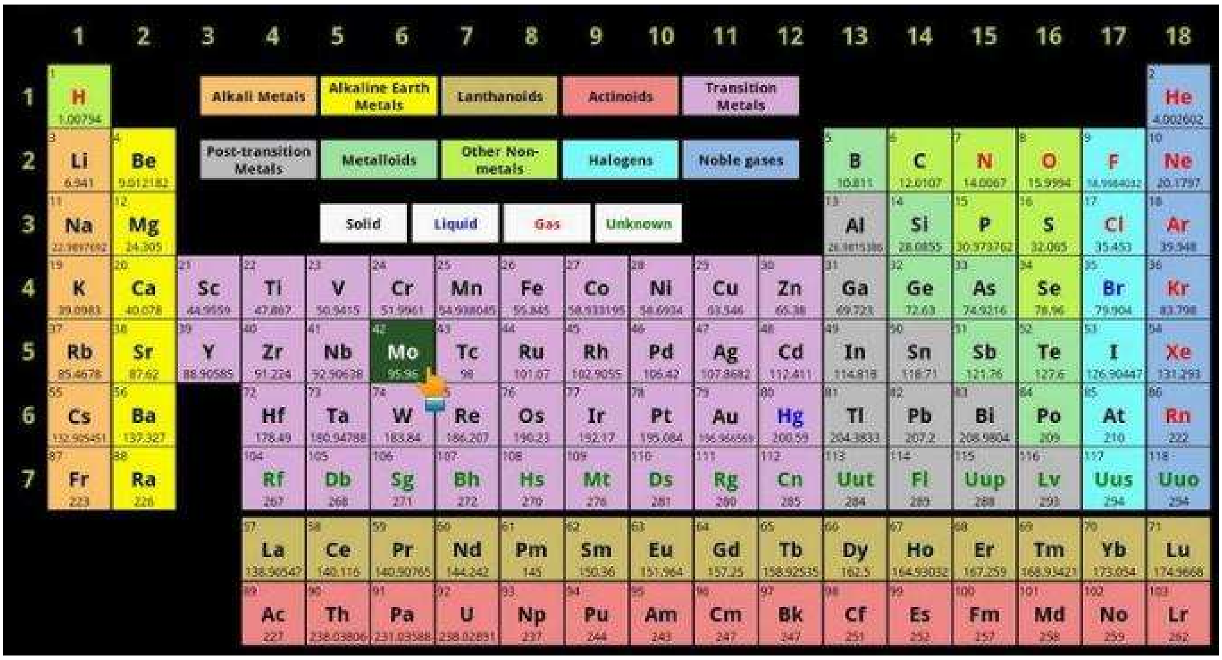
The melting points of alkali metal halides decrease in the order MF > MCl > MBr > MI. Lithium halides have melting points less than those of sodium halides due to the more covalent character possessed by lithium salts.

The solubilities of carbonates and bicarbonates increase on descending the group.

Lother Meyer Plot of Atomic Volume vs Atomic mass

In Lother Meyer plot of atomic volume versus atomic mass, the peaks are occupied by
(a) alkali metals (b) alkaline earth metals (c) halogens (d) noble gases

Ans : (a)



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.00794			Alkali Metals		Alkaline Earth Metals		Lanthanoids		Actinoids		Transition Metals						2 He 4.002602
2	3 Li 6.941	4 Be 9.012182		Post-transition Metals		Metalloids		Other Non-metals		Halogens		Noble gases	5 B 10.811	6 C 12.0107	7 N 14.0067	8 O 15.9994	9 F 18.9984032	10 Ne 20.1797
3	11 Na 22.9897692	12 Mg 24.305			Solid		Liquid	Gas	Unknown				13 Al 26.9815386	14 Si 28.0855	15 P 30.973762	16 S 32.065	17 Cl 35.453	18 Ar 39.948
4	19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938045	26 Fe 55.845	27 Co 58.933195	28 Ni 58.6934	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.63	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.798
5	37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.96	43 Tc 98	44 Ru 101.07	45 Rh 102.9055	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.411	49 In 114.818	50 Sn 118.71	51 Sb 121.76	52 Te 127.6	53 I 126.90447	54 Xe 131.293
6	55 Cs 132.905451	56 Ba 137.327		72 Hf 178.49	73 Ta 180.94788	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.17	78 Pt 195.084	79 Au 196.966569	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.9804	84 Po 209	85 At 210	86 Rn 222
7	87 Fr 223	88 Ra 226		104 Rf 267	105 Db 268	106 Sg 271	107 Bh 272	108 Hs 270	109 Mt 276	110 Ds 281	111 Rg 280	112 Cn 285	113 Uut 284	114 Fl 289	115 Uup 288	116 Lv 293	117 Uus 294	118 Uuo 294
				57 La 138.90547	58 Ce 140.116	59 Pr 140.90765	60 Nd 144.242	61 Pm 145	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.92535	66 Dy 162.5	67 Ho 164.93032	68 Er 167.259	69 Tm 168.93421	70 Yb 173.054	71 Lu 174.9668
				89 Ac 227	90 Th 238.03806	91 Pa 231.03588	92 U 238.02891	93 Np 237	94 Pu 244	95 Am 243	96 Cm 247	97 Bk 247	98 Cf 251	99 Es 252	100 Fm 257	101 Md 258	102 No 259	103 Lr 262

KOBr Potassium hypobromite Structure

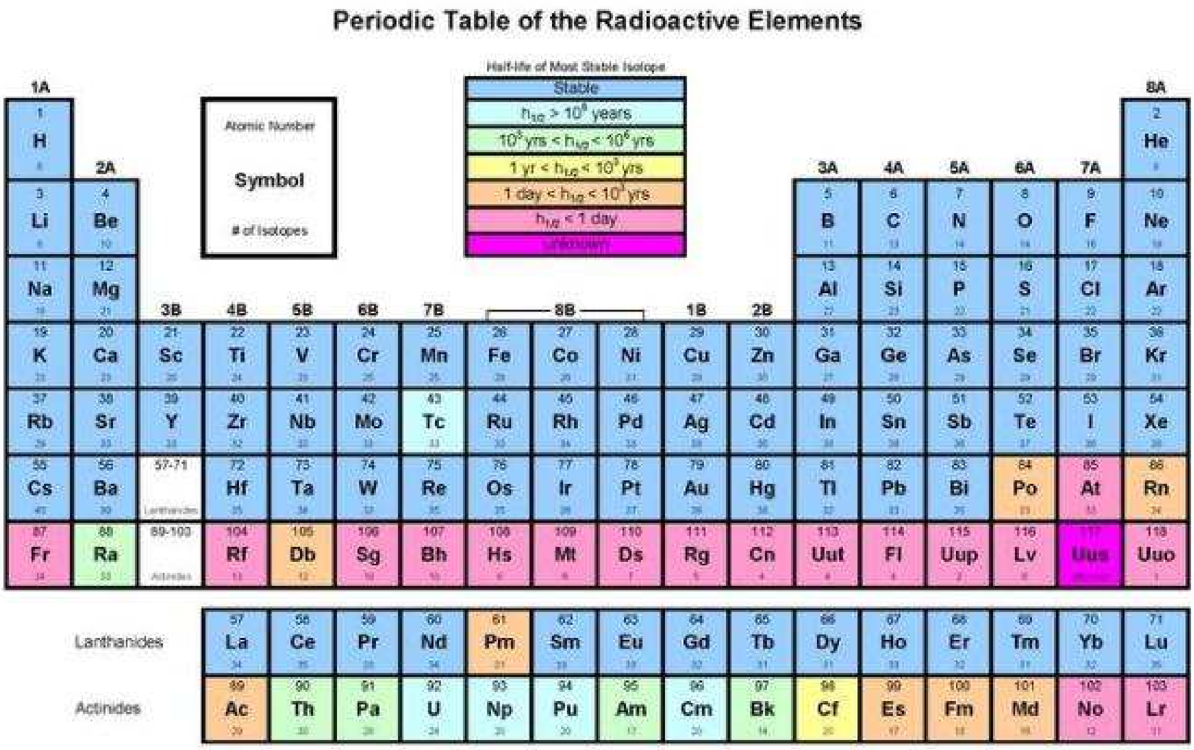
Group 2 Elements—Alkaline Earth Metals

Group 2 contains beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra).

All alkaline earth metals contain two electrons in their outermost orbitals. These are soft. But compared to alkali metals, they are harder and have higher cohesive energy. Their melting points are higher than those of Group 1 elements and vary irregularly because of different structures. The atomic and ionic radii are smaller than those of the elements of Group 1. The alkaline earth metals dissolve in liquid ammonia giving bright blue colour due to the solvated electrons.

Alkaline earth metals are typically divalent and form colourless ionic compounds. When burnt in air, Be, Mg and Ca form monoxide while Sr, Ba and Ra form peroxides. When burnt in oxygen, they all form oxides which are basic in nature. The base strength of hydroxides increases on descending the group. Their solubility also increases on descending the group.

The solubilities of carbonates and sulphates decrease on descending the group. In deciding the solubilities of hydroxides, lattice energy predominates over hydration energy whereas in carbonates and sulphates, hydration energy predominates over lattice energy.



Periodic Table of the Radioactive Elements

1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-71 Lanthanides	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-103 Actinides	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo

Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Temperature dependent Magnetic behaviour

$NiCl_2\{P(C_2H_5)_2(C_6H_5)\}_2$ exhibits temperature dependent magnetic behaviour (paramagnetic/diamagnetic). The coordination geometries of Ni^{2+} in the paramagnetic and diamagnetic states are respectively

(a) tetrahedral and tetrahedral	(b) square planar and square planar
(c) tetrahedral and square planar	(d) square planar and tetrahedral

Solution :

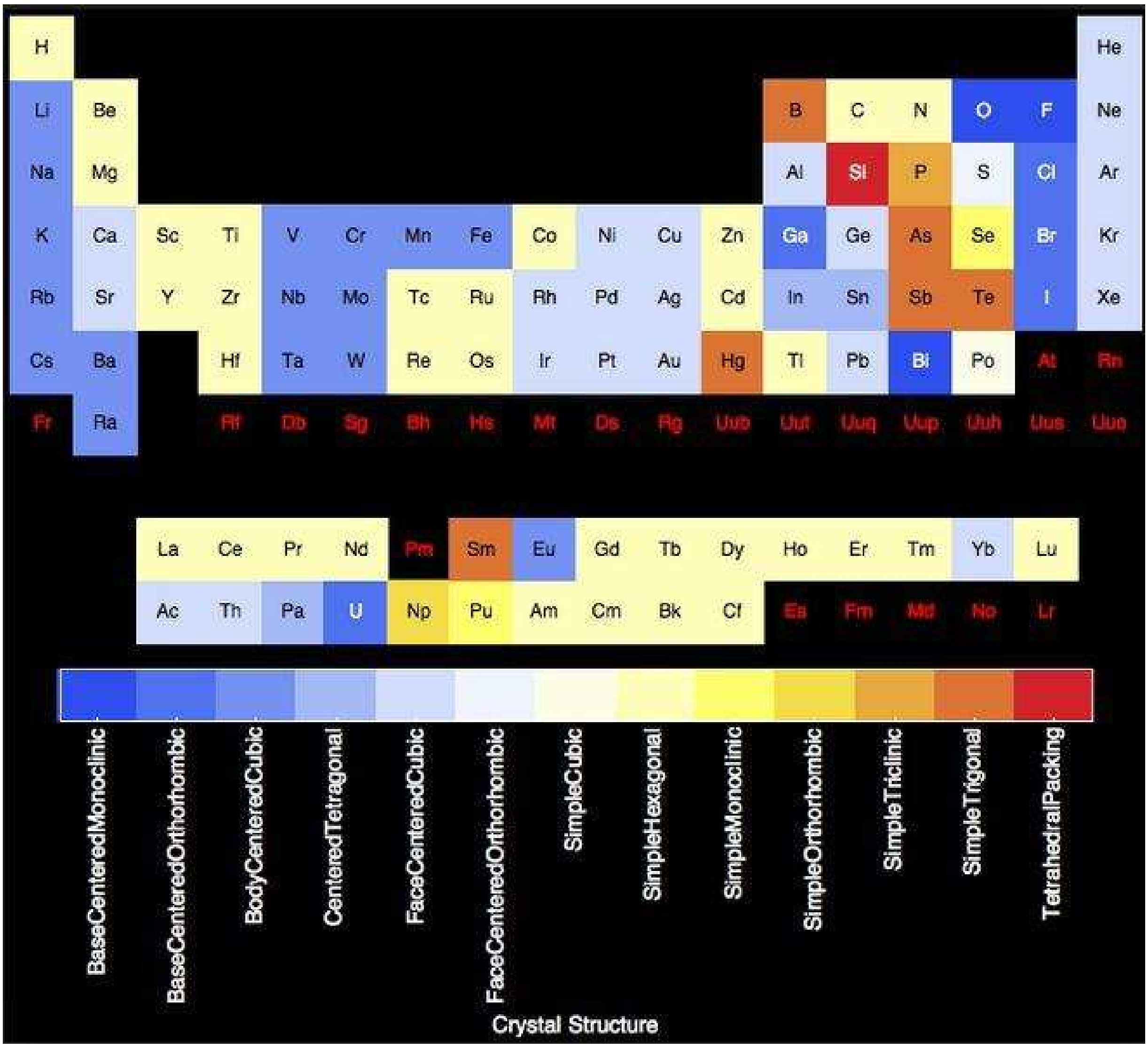
In the paramagnetic state, the complex will have unpaired 3d electrons in Ni^{2+} ion, whereas no such electrons (i.e. all the 3d elctrons will be paired) are present in the diamagnetic state.

The electronic configuration of $_{28}Ni^{2+}$ is $\overset{3d}{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}}\quad\overset{4s}{\boxed{}}\quad\overset{4p}{\boxed{}\boxed{}\boxed{}}$

If the two unpaired electrons remain present in the ion, it will undergo sp^3 hybridization to accommodate ligands and the geometry of the complex ion will be tetrahedral.

If the two unpaired electrons are coupled, the ion will be diamagnetic and it can undergo dsp^2 hybridization to accommodate ligands leading to the square planar geometry to the complex ion.

Therefore, the **choice (c)** is correct.


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Rf Db Sg Bh Hs Mt Ds Rg Uub Uut Uuq Uup Uuh Uus Uuo
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr
BaseCenteredMonoclinic
BaseCenteredOrthorhombic
BodyCenteredCubic
CenteredTetragonal
FaceCenteredCubic
FaceCenteredOrthorhombic
SimpleCubic
SimpleHexagonal
SimpleMonoclinic
SimpleOrthorhombic
SimpleTriclinic
SimpleTrigonal
TetrahedralPacking
Crystal Structure

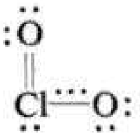
Chlorine dioxide can be made by carefully adding sulfuric acid to potassium chlorate, $KClO_3$. It would be expected that this mixture would react to produce chloric acid, $HClO_3$, and then, because of the dehydrating power of sulfuric acid, to produce the anhydride of chloric acid, Cl_2O_5:

$$KClO_3 + H_2SO_4 \longrightarrow KHSO_4 + HClO_3$$
$$2HClO_3 \longrightarrow H_2O + Cl_2O_5$$

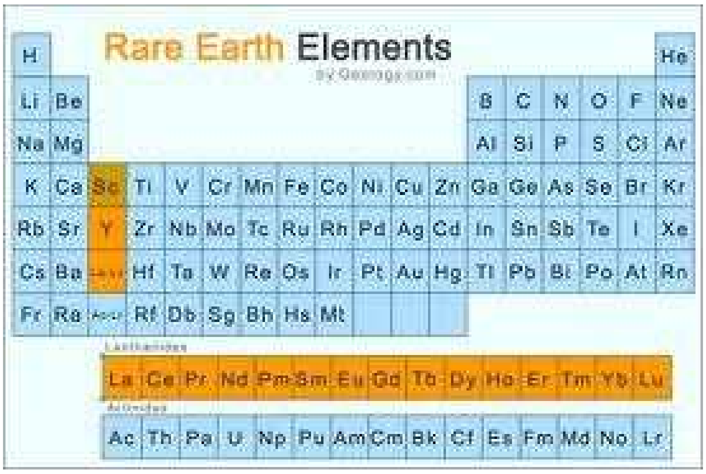
Dichlorine pentoxide, Cl_2O_5, however, is very unstable—its existence has never been verified. If it is formed at all, it decomposes at once to give chlorine dioxide and oxygen:

$$2Cl_2O_5 \longrightarrow 4ClO_2 + O_2$$

The molecule has a triangular structure, with O—Cl—O angle 118° and bond lengths 1.49 Å. We assign it the structure



, with interchange of the two kinds of bonds (resonance).

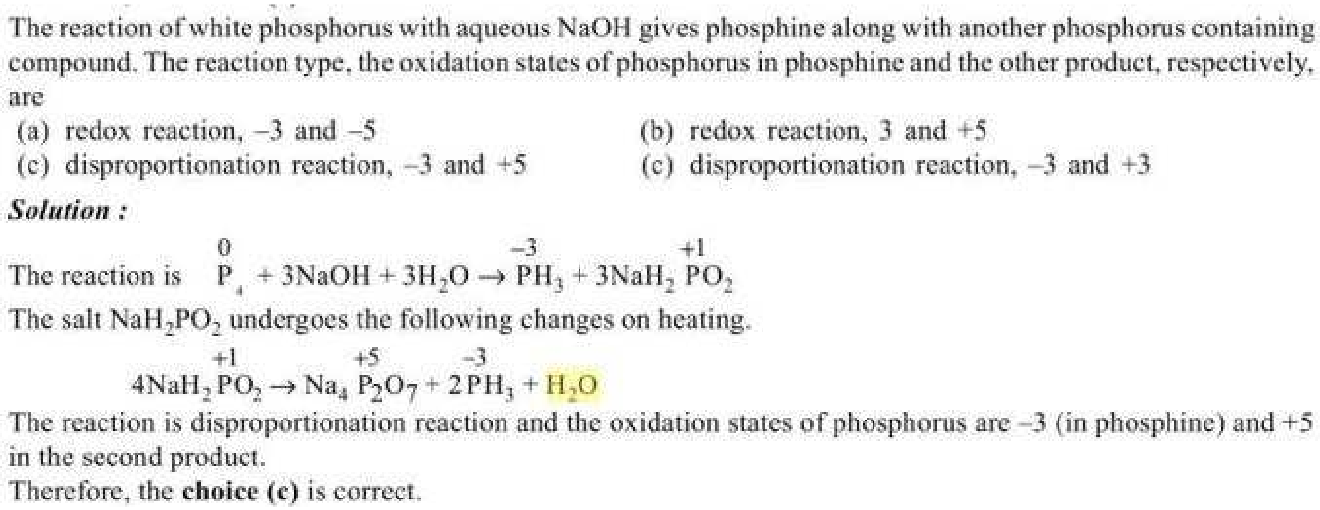


Atomic radii of fluorine and neon in Angstrom units are respectively given by
(a) 0.72, 1.60 (b) 1.60, 1.60 (c) 0.72, 0.72 (d) none of these values

Ans : (a)

Atomic radius of Neon will be larger than Fluorine

Reaction of white phosphorus with aqueous NaOH



The reaction of white phosphorus with aqueous NaOH gives phosphine along with another phosphorus containing compound. The reaction type, the oxidation states of phosphorus in phosphine and the other product, respectively, are

(a) redox reaction, –3 and –5 (b) redox reaction, 3 and +5
(c) disproportionation reaction, –3 and +5 (c) disproportionation reaction, –3 and +3

Solution :

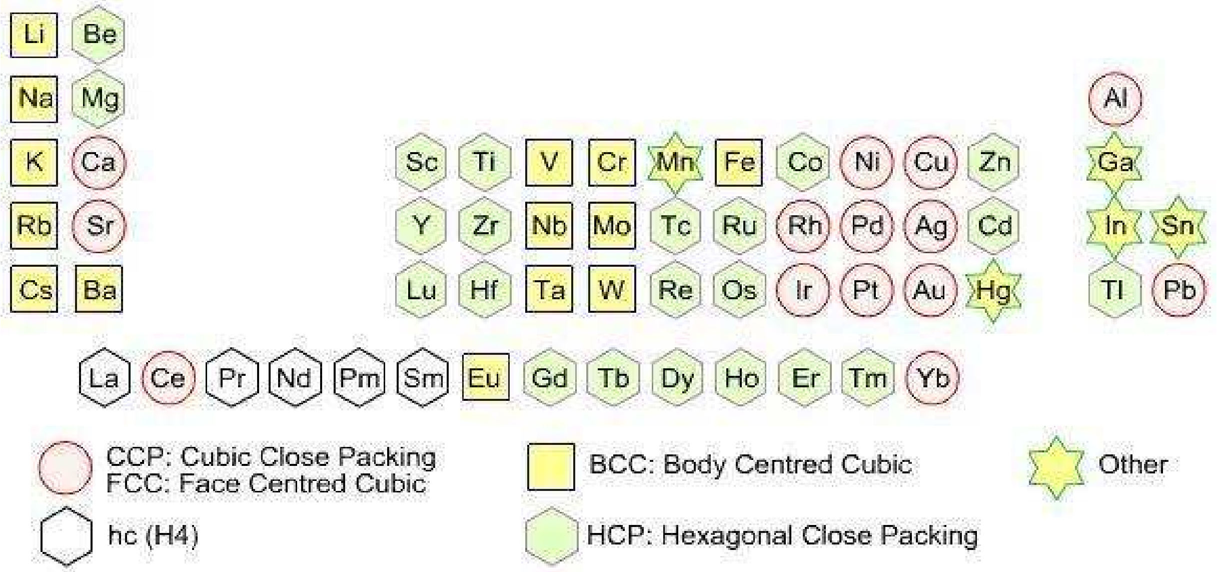
The reaction is $\overset{0}{P_4} + 3NaOH + 3H_2O \rightarrow \overset{-3}{PH_3} + 3NaH_2\overset{+1}{P}O_2$

The salt NaH_2PO_2 undergoes the following changes on heating.

$$4NaH_2\overset{+1}{P}O_2 \rightarrow Na_4\overset{+5}{P_2}O_7 + 2\overset{-3}{P}H_3 + H_2O$$

The reaction is disproportionation reaction and the oxidation states of phosphorus are –3 (in phosphine) and +5 in the second product.

Therefore, the **choice (c)** is correct.

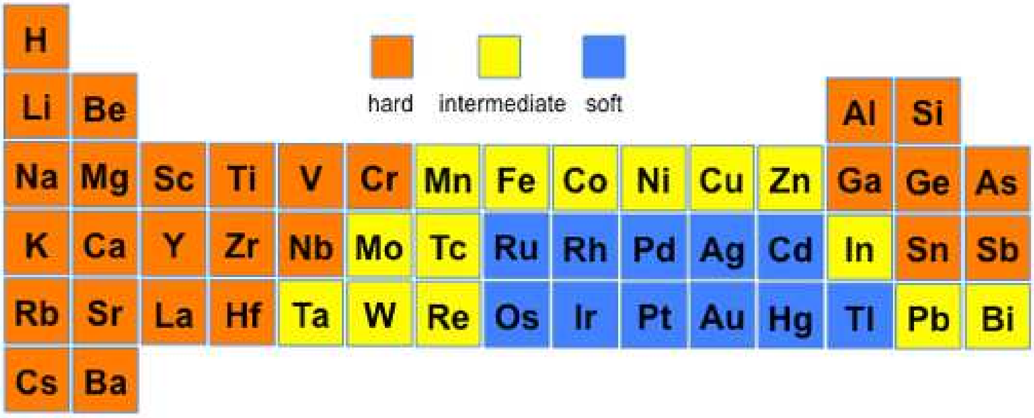


Generally the stabilities of complexes decreases with increasing atomic number for the electropositive metals e.g. group IIA or hard Lewis acids, and increase with increasing atomic number for the noble metals (soft acids), following the general trend of ionization energy.

(a) For electropositive metals (hard acids) the order of stabilities of the Halide complexes F > Cl > Br > I but for highly polarizing soft acid metal ions such as Hg^{+2} , we see the reverse order.

(b) The most electropositive metals (hardest acids) show a greater tendency of forming complexes, with hard ligands such as F^- or Oxygen containing ligands.

Class A



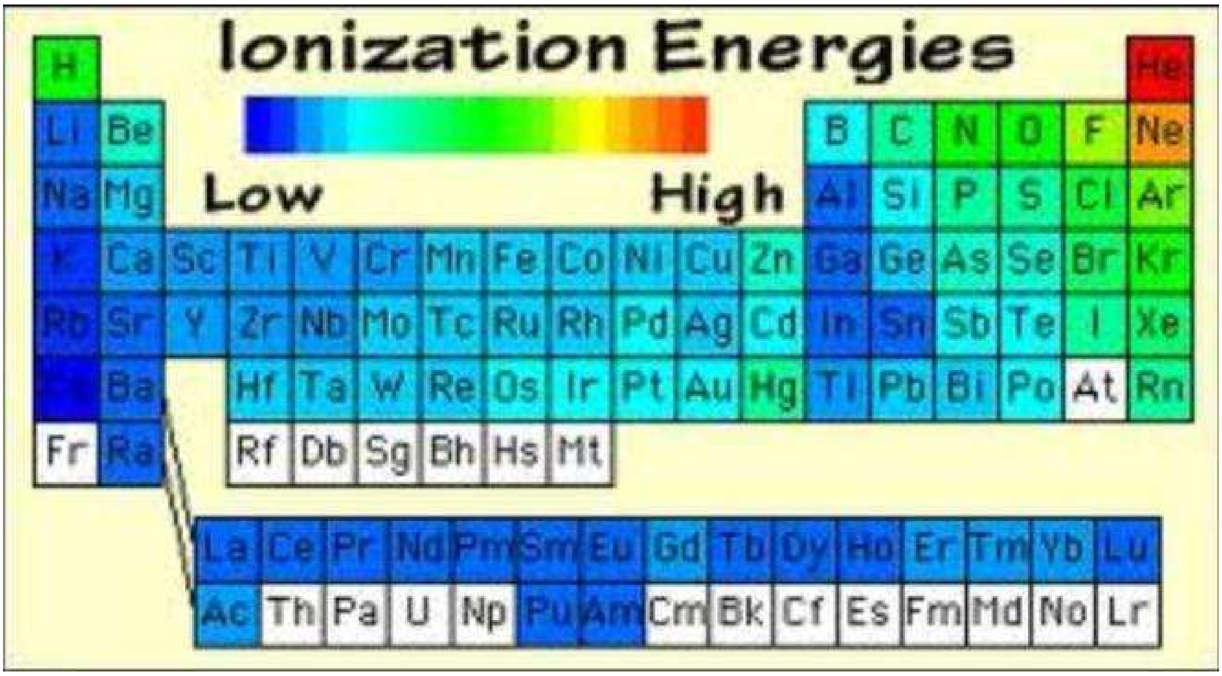
Class A **Class C(Yellow)** **Class B** **Class C (Yellow)**

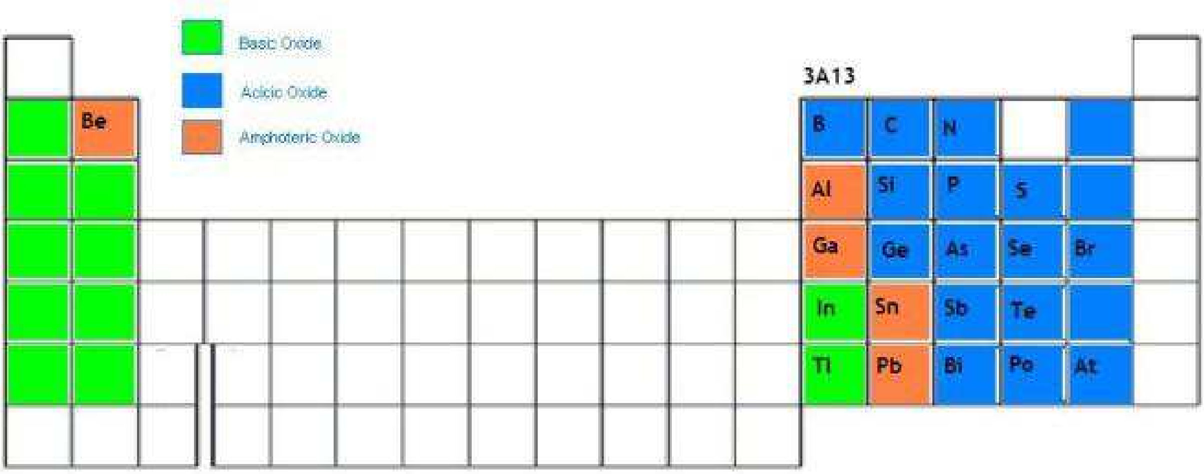
Metals are classified according to their acceptor properties.

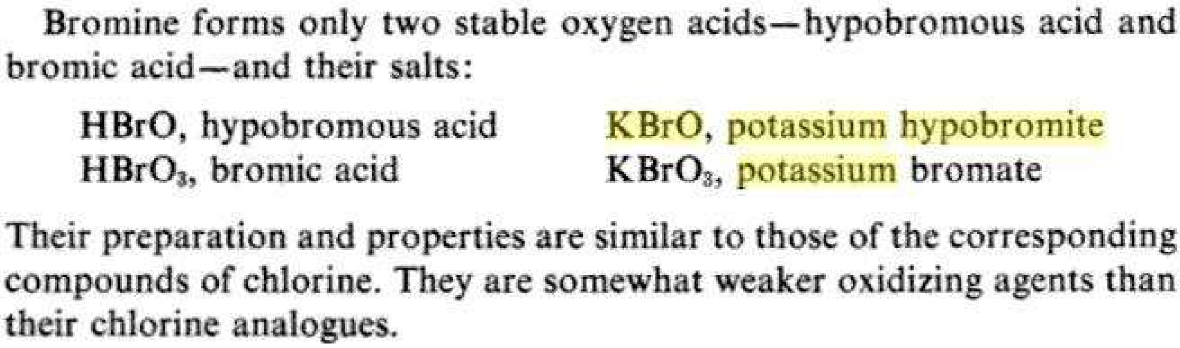
Class A - Hard Acids. Show affinities to ligands whose basicity is proportional to protons.

Class B - Soft acids form stable olefin complexes.

Class C - Borderline metals



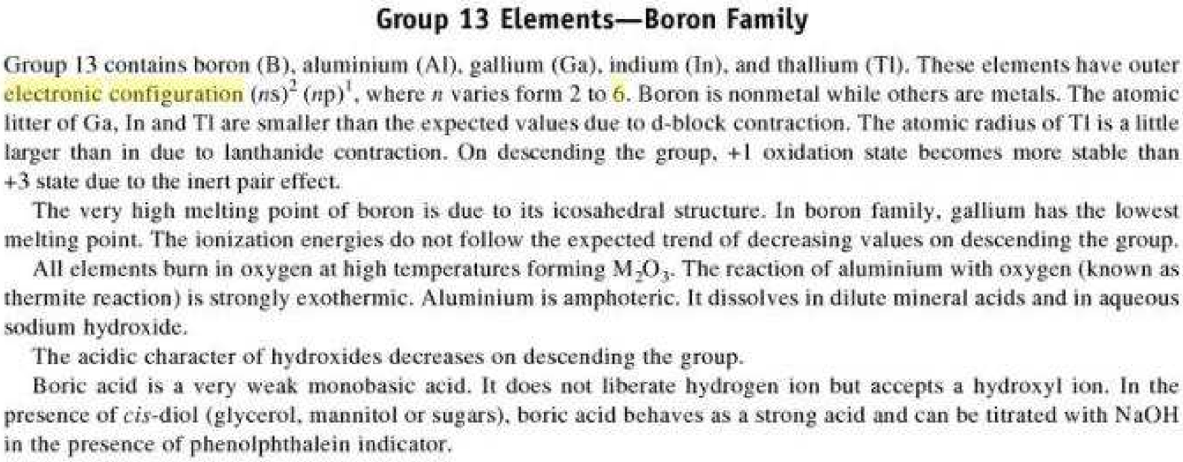



Bromine forms only two stable oxygen acids—hypobromous acid and bromic acid—and their salts:

HBrO, hypobromous acid	KBrO, potassium hypobromite
$HBrO_3$, bromic acid	$KBrO_3$, potassium bromate

Their preparation and properties are similar to those of the corresponding compounds of chlorine. They are somewhat weaker oxidizing agents than their chlorine analogues.

Group 13 Elements Boron Family


Group 13 Elements—Boron Family

Group 13 contains boron (B), aluminium (Al), gallium (Ga), indium (In), and thallium (Tl). These elements have outer electronic configuration $(ns)^2\,(np)^1$, where n varies form 2 to 6. Boron is nonmetal while others are metals. The atomic litter of Ga, In and Tl are smaller than the expected values due to d-block contraction. The atomic radius of Tl is a little larger than in due to lanthanide contraction. On descending the group, +1 oxidation state becomes more stable than +3 state due to the inert pair effect.

The very high melting point of boron is due to its icosahedral structure. In boron family, gallium has the lowest melting point. The ionization energies do not follow the expected trend of decreasing values on descending the group.

All elements burn in oxygen at high temperatures forming M_2O_3. The reaction of aluminium with oxygen (known as thermite reaction) is strongly exothermic. Aluminium is amphoteric. It dissolves in dilute mineral acids and in aqueous sodium hydroxide.

The acidic character of hydroxides decreases on descending the group.

Boric acid is a very weak monobasic acid. It does not liberate hydrogen ion but accepts a hydroxyl ion. In the presence of *cis*-diol (glycerol, mannitol or sugars), boric acid behaves as a strong acid and can be titrated with NaOH in the presence of phenolphthalein indicator.

BF_3 is hydrolysed as follows.

$$4BF_3 + 12H_2O \rightarrow 4H_3BO_3 + 12HF$$
$$12HF + 3H_3BO_3 \rightarrow 3H^+ + 3[BF_4]^- + 9H_2O$$

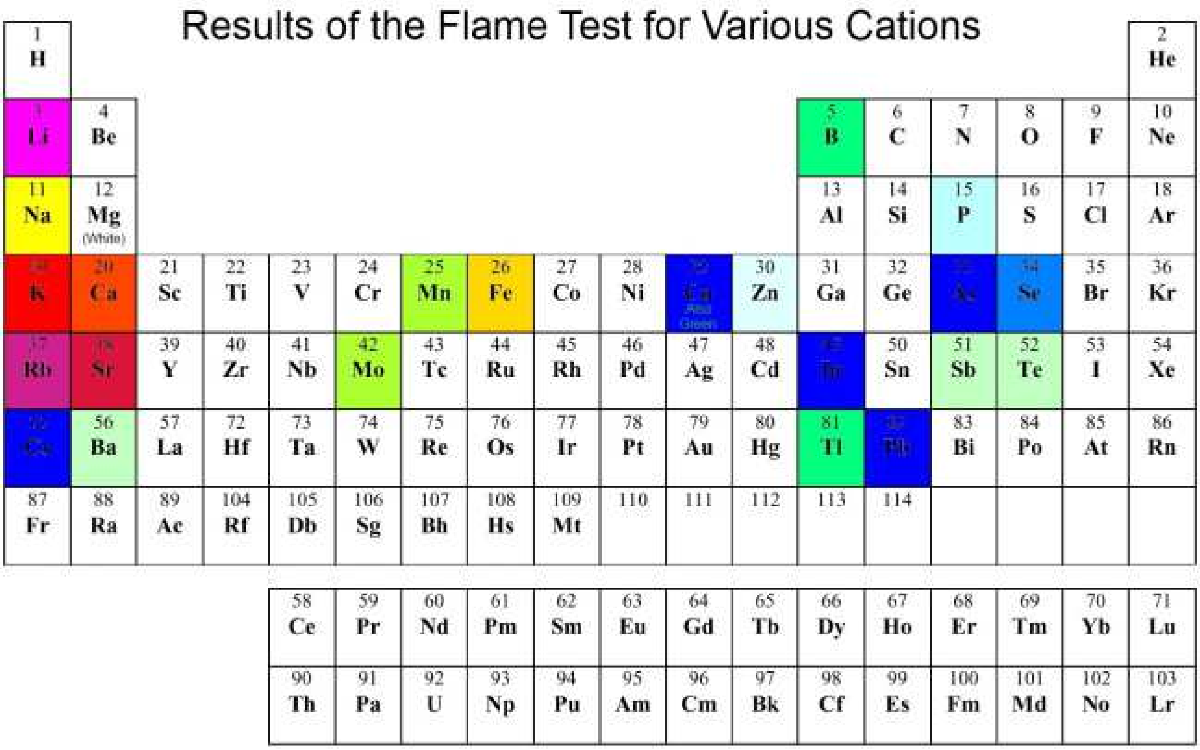
$$4BF_3 + 3H_2O \rightarrow H_3BO_3 + 3H^+ + 3[BF_4]^-$$

Hydrolysis of BCl_3 or BI_3 produces boric acid.

$$BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl$$

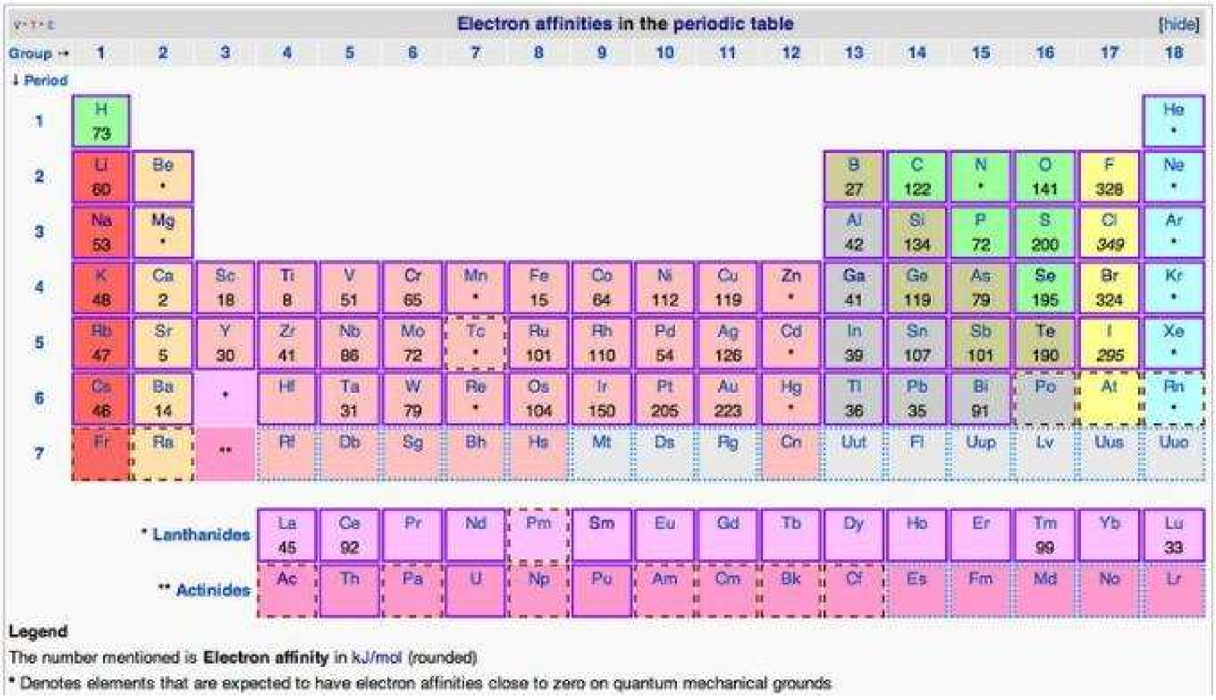
The fluorides of Al, Ga, In and Tl are ionic while the other halides are generally covalent and exist as dimer.

The trihalides of boron are electron-deficient compounds. Due to back bonding, the electron density on boron is increased. The tendency to form pπ-pπ bond is maximum in BF_3 and falls rapidly on passing to BCl_3 to BBr_3. The increasing order of acid strength follows the order $BF_3 < BCl_3 < BBr_3$.



Results of the Flame Test for Various Cations

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg (White)											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu Also Green	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112	113	114				
				58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
				90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr



v · t · e **Electron affinities in the periodic table** [hide]

Group → ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 73																	He •
2	Li 60	Be •											B 27	C 122	N •	O 141	F 328	Ne •
3	Na 53	Mg •											Al 42	Si 134	P 72	S 200	Cl *349*	Ar •
4	K 48	Ca 2	Sc 18	Ti 8	V 51	Cr 65	Mn •	Fe 15	Co 64	Ni 112	Cu 119	Zn •	Ga 41	Ge 119	As 79	Se 195	Br 324	Kr •
5	Rb 47	Sr 5	Y 30	Zr 41	Nb 86	Mo 72	Tc •	Ru 101	Rh 110	Pd 54	Ag 126	Cd •	In 39	Sn 107	Sb 101	Te 190	I *295*	Xe •
6	Cs 46	Ba 14	*	Hf	Ta 31	W 79	Re •	Os 104	Ir 150	Pt 205	Au 223	Hg •	Tl 36	Pb 35	Bi 91	Po	At	Rn •
7	Fr	Ra	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo
* Lanthanides				La 45	Ce 92	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm 99	Yb	Lu 33
** Actinides				Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

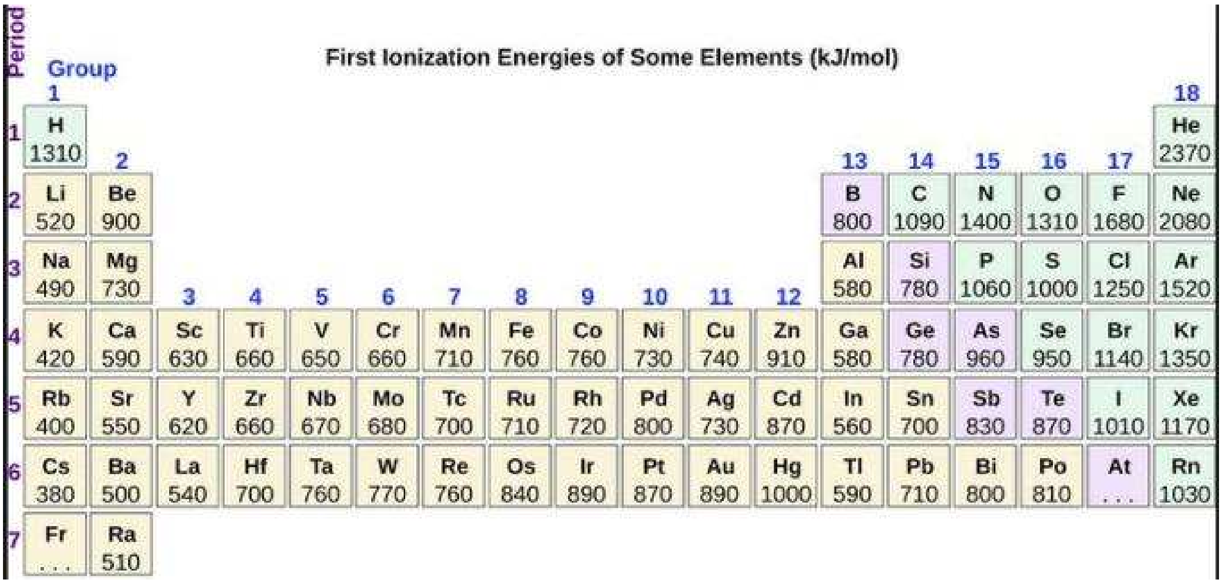
Legend

The number mentioned is **Electron affinity** in kJ/mol (rounded)

* Denotes elements that are expected to have electron affinities close to zero on quantum mechanical grounds

The halogens other than fluorine form stable compounds corresponding to nearly all values of the oxidation number from −1 to +7, as shown in the accompanying chart.

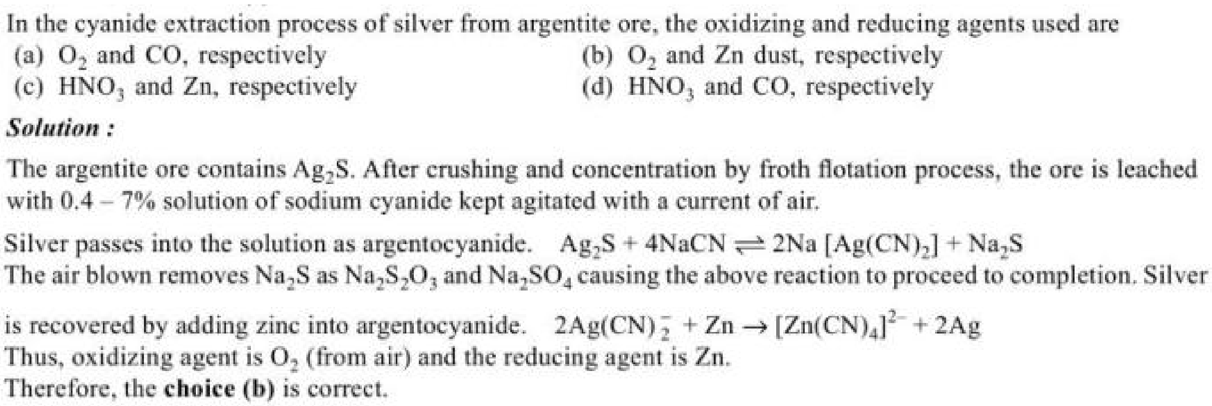
+7		$HClO_4$, Cl_2O_7		H_5IO_6
+6		Cl_2O_6		
+5		$HClO_3$	$HBrO_3$	HIO_3, I_2O_5
+4		ClO_2	BrO_2	IO_2
+3		$HClO_2$		
+2				
+1		$HClO$, Cl_2O	$HBrO$, Br_2O	HIO
0	F_2	Cl_2	Br_2	I_2
−1	HF, F^-	HCl, Cl^-	HBr, Br^-	HI, I^-



First Ionization Energies of Some Elements (kJ/mol)

Period \ Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 1310																	He 2370
2	Li 520	Be 900											B 800	C 1090	N 1400	O 1310	F 1680	Ne 2080
3	Na 490	Mg 730											Al 580	Si 780	P 1060	S 1000	Cl 1250	Ar 1520
4	K 420	Ca 590	Sc 630	Ti 660	V 650	Cr 660	Mn 710	Fe 760	Co 760	Ni 730	Cu 740	Zn 910	Ga 580	Ge 780	As 960	Se 950	Br 1140	Kr 1350
5	Rb 400	Sr 550	Y 620	Zr 660	Nb 670	Mo 680	Tc 700	Ru 710	Rh 720	Pd 800	Ag 730	Cd 870	In 560	Sn 700	Sb 830	Te 870	I 1010	Xe 1170
6	Cs 380	Ba 500	La 540	Hf 700	Ta 760	W 770	Re 760	Os 840	Ir 890	Pt 870	Au 890	Hg 1000	Tl 590	Pb 710	Bi 800	Po 810	At . . .	Rn 1030
7	Fr . . .	Ra 510																

cyanide extraction process of silver from argentite ore



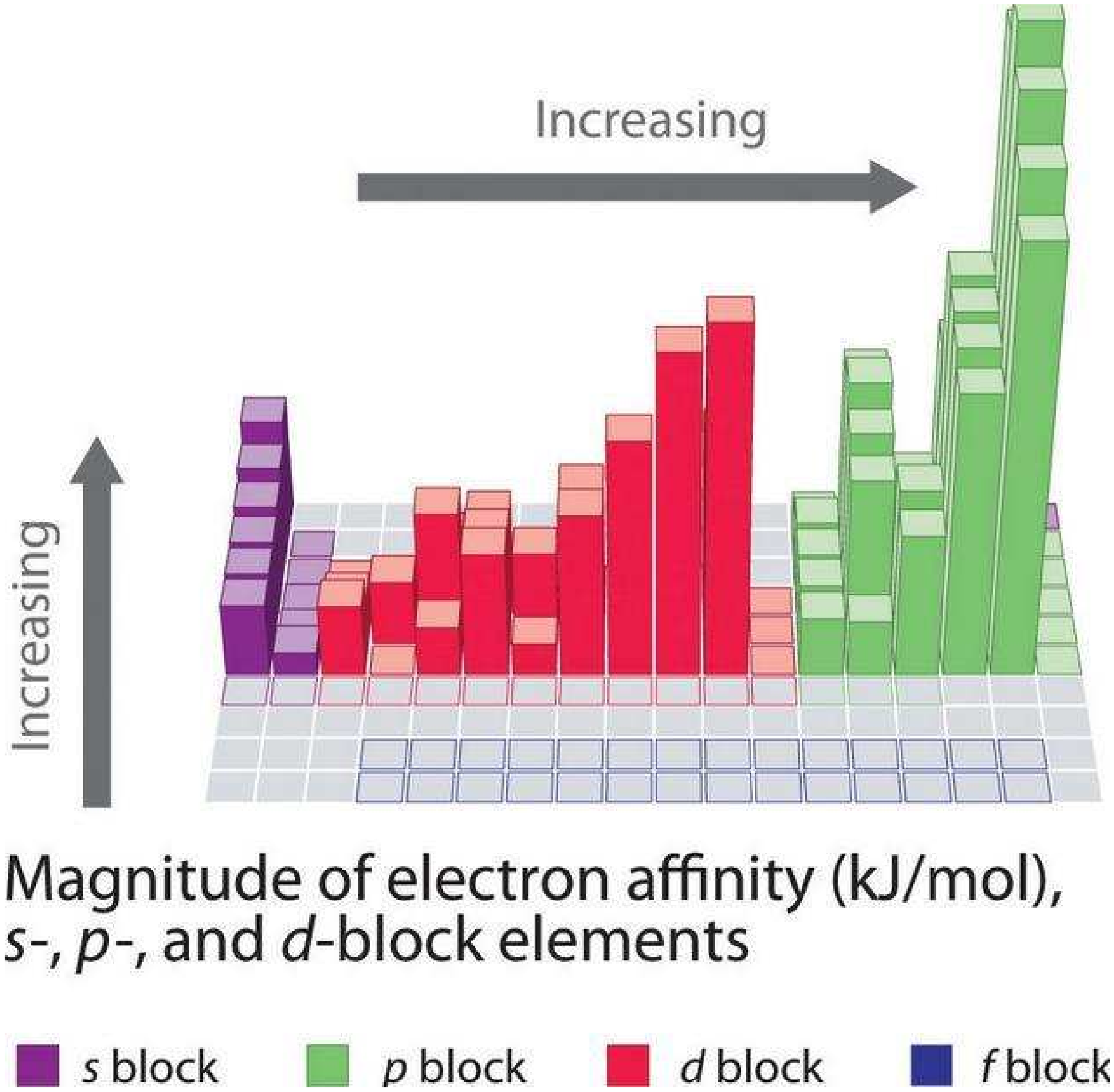
In the cyanide extraction process of silver from argentite ore, the oxidizing and reducing agents used are

(a) O_2 and CO, respectively
(b) O_2 and Zn dust, respectively
(c) HNO_3 and Zn, respectively
(d) HNO_3 and CO, respectively

Solution :

The argentite ore contains Ag_2S. After crushing and concentration by froth flotation process, the ore is leached with 0.4 – 7% solution of sodium cyanide kept agitated with a current of air.

Silver passes into the solution as argentocyanide. $Ag_2S + 4NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S$
The air blown removes Na_2S as $Na_2S_2O_3$ and Na_2SO_4 causing the above reaction to proceed to completion. Silver is recovered by adding zinc into argentocyanide. $2Ag(CN)_2^- + Zn \rightarrow [Zn(CN)_4]^{2-} + 2Ag$
Thus, oxidizing agent is O_2 (from air) and the reducing agent is Zn.
Therefore, the **choice (b)** is correct.



Common Name	**Chemical Name**
acetone	dimethyl ketone; 2-propanone (usually known as acetone)
acid potassium sulfate	potassium bisulfate
acid of sugar	oxalic acid
ackey	nitric acid
alcali volatil	ammonium hydroxide
alcohol, grain	ethyl alcohol
alcohol sulfuris	carbon disulfide

alcohol, wood	methyl alcohol
alum	aluminum potassium sulfate
alumina	aluminum oxide
antichlor	sodium thiosulfate
antimony black	antimony trisulfide
antimony bloom	antimony trioxide
antimony glance	antimony trisulfide
antimony red (vermillion)	antimony oxysulfide
aqua ammonia	aqueous solution of ammonium hydroxide
aqua fortis	nitric acid
aqua regia	nitrohydrochloric acid
aromatic spirit of ammonia	ammonia in alcohol
arsenic glass	arsenic trioxide
azurite	mineral form of basic copper carbonate
asbestos	magnesium silicate
aspirin	acetylsalicylic acid
baking soda	sodium bicarbonate
banana oil (artificial)	isoamyl acetate
barium white	barium sulfate
benzol	benzene
bicarbonate of soda	sodium hydrogen carbonate or sodium bicarbonate
bichloride of mercury	mercuric chloride
bichrome	potassium dichromate
bitter salt	magnesium sulfate
black ash	crude form of sodium carbonate
black copper oxide	cupric oxide
black lead	graphite (carbon)
blanc-fixe	barium sulfate
bleaching powder	chlorinated lime; calcium hypochlorite
blue copperas	copper sulfate (crystals)
blue lead	lead sulfate
blue salts	nickel sulfate
blue stone	copper sulfate (crystals)

blue vitriol	copper sulfate
bluestone	copper sulfate
bone ash	crude calcium phosphate
bone black	crude animal charcoal
boracic acid	boric acid
borax	sodium borate; sodium tetraborate
bremen blue	basic copper carbonate
brimstone	sulfur
burnt alum	anhydrous potassium aluminum sulfate
burnt lime	calcium oxide
burnt ochre	ferric oxide
burnt ore	ferric oxide
brine	aqueous sodium chloride solution
butter of antimony	antimony trichloride
butter of tin	anhydrous stannic chloride
butter of zinc	zinc chloride
calomel	mercury chloride; mercurous chloride
carbolic acid	phenol
carbonic acid gas	carbon dioxide
caustic lime	calcium hydroxide
caustic potash	potassium hydroxide
caustic soda	sodium hydroxide
chalk	calcium carbonate
Chile saltpeter	sodium nitrate
Chile nitre	sodium nitrate
Chinese red	basic lead chromate
Chinese white	zinc oxide
chloride of soda	sodium hypochlorite
chloride of lime	calcium hypochlorite
chrome alum	chromic potassium sulfate
chrome green	chromium oxide
chrome yellow	lead (VI) chromate
chromic acid	chromium trioxide

copperas	ferrous sulfate
corrosive sublimate	mercury (II) chloride
corundum (ruby, sapphire)	chiefly aluminum oxide
cream of tartar	potassium bitartrate
crocus powder	ferric oxide
crystal carbonate	sodium carbonate
dechlor	sodium thiophosphate
diamond	carbon crystal
emery powder	impure aluminum oxide
epsom salts	magnesium sulfate
ethanol	ethyl alcohol
farina	starch
ferro prussiate	potassium ferricyanide
ferrum	iron
flores martis	anhydride iron (III) chloride
fluorspar	natural calcium fluoride
fixed white	barium sulfate
flowers of sulfur	sulfur
'flowers of' any metal	oxide of the metal
formalin	aqueous formaldehyde solution
French chalk	natural magnesium silicate
French vergidris	basic copper acetate
galena	natural lead sulfide
Glauber's salt	sodium sulfate
green verditer	basic copper carbonate
green vitriol	ferrous sulfate crystals
gypsum	natural calcium sulfate
hard oil	boiled linseed oil
heavy spar	barium sulfate
hydrocyanic acid	hydrogen cynanide
hypo (photography)	sodium thiosulfate solution
Indian red	ferric oxide
Isinglass	agar-agar gelatin

jeweler's rouge	ferric oxide
killed spirits	zinc chloride
lampblack	crude form of carbon; charcoal
laughing gas	nitrous oxide
lead peroxide	lead dioxide
lead protoxide	lead oxide
lime	calcium oxide
lime, slaked	calcium hydroxide
limewater	aqueous solution of calcium hydroxide
liquor ammonia	ammonium hydroxide solution
litharge	lead monoxide
lunar caustic	silver nitrate
liver of sulfur	sufurated potash
lye or soda lye	sodium hydroxide
magnesia	magnesium oxide
manganese black	manganese dioxide
marble	mainly calcium carbonate
mercury oxide, black	mercurous oxide
methanol	methyl alcohol
methylated spirits	methyl alcohol
milk of lime	calcium hydroxide
milk of magnesium	magnesium hydroxide
milk of sulfur	precipitated sulfur
"muriate" of a metal	chloride of the metal
muriatic acid	hydrochloric acid
natron	sodium carbonate
nitre	potassium nitrate
nordhausen acid	fuming sulfuric acid
oil of mars	deliquescent anhydrous iron (III) chloride
oil of vitriol	sulfuric acid
oil of wintergreen (artificial)	methyl salicylate
orthophosphoric acid	phosphoric acid
Paris blue	ferric ferrocyanide

Paris green	copper acetoarsenite
Paris white	powdered calcium carbonate
pear oil (artificial)	isoamyl acetate
pearl ash	potassium carbonate
permanent white	barium sulfate
plaster of Paris	calcium sulfate
plumbago	graphite
potash	potassium carbonate
potassa	potassium hydroxide
precipitated chalk	calcium carbonate
Prussic acid	hydrogen cyanide
pyro	tetrasodium pyrophosphate
quicklime	calcium oxide
quicksilver	mercury
red lead	lead tetraoxide
red liquor	aluminum acetate solution
red prussiate of potash	potassium ferrocyanide
red prussiate of soda	sodium ferrocyanide
Rochelle salt	potassium sodium tartrate
rock salt	sodium chloride
rouge, jeweler's	ferric oxide
rubbing alcohol	isopropyl alcohol
sal ammoniac	ammonium chloride
sal soda	sodium carbonate
salt, table	sodium chloride
salt of lemon	potassium binoxalate
salt of tartar	potassium carbonate
saltpeter	potassium nitrate
silica	silicon dioxide
slaked lime	calcium hydroxide
soda ash	sodium carbonate
soda nitre	sodium nitrate
soda lye	sodium hydroxide

soluble glass	sodium silicate
sour water	dilute sulfuric acid
spirit of hartshorn	ammonium hydroxide solution
spirit of salt	hydrochloric acid
spirit of wine	ethyl alcohol
spirits of nitrous ether	ethyl nitrate
sugar, table	sucrose
sugar of lead	lead acetate
sulfuric ether	ethyl ether
talc or talcum	magnesium silicate
tin crystals	stannous chloride
trona	natural sodium carbonate
unslaked lime	calcium oxide
Venetian red	ferric oxide
verdigris	basic copper acetate
Vienna lime	calcium carbonate
vinegar	impure dilute acetic acid
vitamin C	ascorbic acid
vitriol	sulfuric acid
washing soda	sodium carbonate
water glass	sodium silicate
white caustic	sodium hydroxide
white lead	basic lead carbonate
white vitriol	zinc sulfate crystals
yellow prussiate of potash	potassium ferrocyanide
yellow prussiate of soda	sodium ferrocyanide
zinc vitriol	zinc sulfate
zinc white	zinc oxide

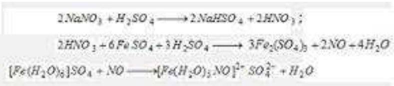
Westron - A refrigerant.  $C_2H_2Cl_4$

Colours of Compounds

Cr2(SO4)3 - green

PbS - Black

[Fe(H2O)5NO]SO4 - brown



$2NaNO_3 + H_2SO_4 \longrightarrow 2NaHSO_4 + 2HNO_3$;

$2HNO_3 + 6FeSO_4 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$

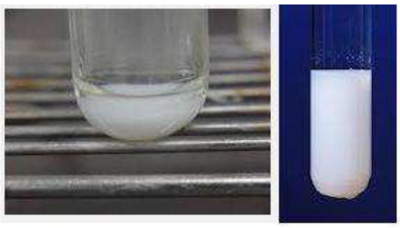
$[Fe(H_2O)_6]SO_4 + NO \longrightarrow [Fe(H_2O)_5NO]^{2+} SO_4^{2-} + H_2O$

(CH3COO)3Fe - blood red

NH4Cl - white fumes

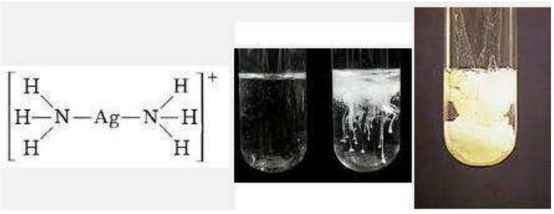
NH4Cl - white fumes

AgCl - curdy white precipitate



AgCl - curdy white precipitate

AgCl + NH4OH -> Ag(NH3)2Cl +H2O



AgCl + NH4OH --> Ag(NH3)2Cl +H2O

CrO3 + HCl -> CrO2Cl2 (deep red fumes) + H2O

CrO2Cl2 (deep red fumes)

$NaOH + CrO_2Cl_2 \rightarrow Na_2CrO_4$ (yellow) $+ NaCl + H_2O$

Sodium Chromate

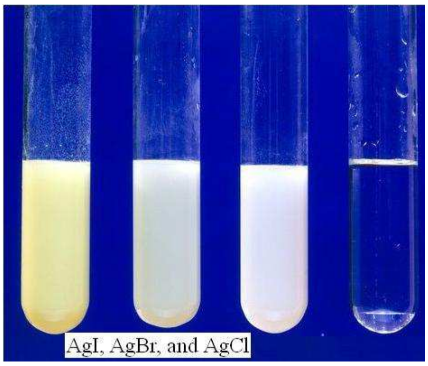
Sodium chromate is used in the industry to manufacture chromium compounds. Sodium chromate (Na2CrO4) is a yellow solid chemical compound. It is used in many industries like petroleum industry, textile industry. Sodium chromate is used in the industry as an important source for manufacture of chromium compounds. Sodium Chromate makes a protective film on metal surfaces and is used is corrosion control applications such as coolants containing alcohols and water cooling systems.

$Na_2CrO_4 + Pb(CH_3COO)_2 \rightarrow PbCrO_4$ (yellow) $+ CH_3COONa$

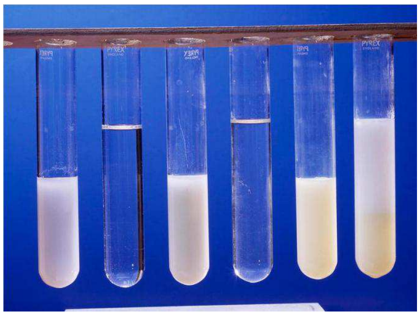
PbCrO4 (yellow)

$NaBr + AgNO_3 \rightarrow AgBr$ (pale yellow) $+ NaNO_3$

AgI, AgBr, AgCl

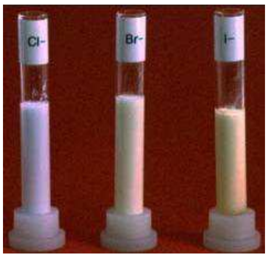


Ammonia test for silver halides. **Test tubes and the results of using concentrated ammonia to test for the presence of three silver halides. Each one of the silver halides is next to a fuller test tube that shows the result of adding concentrated ammonia. Halides are compounds containing halogens such as here, from left to right silver chloride, silver bromide and silver iodide. Adding dilute ammonia dissolves the chloride, while concentrated ammonia is needed to dissolve the bromide, but it fails to dissolve the iodide. The silver halides are themselves the results of standard tests using silver nitrate to test for the halide ions.**



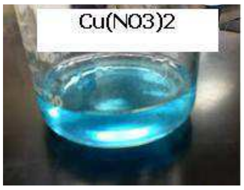
BrCl - pale yellow

NaI + AgNO3 -> AgI (yellow ppt) + NaNO3

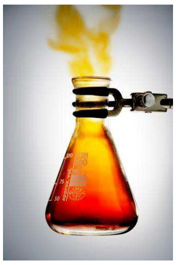


$Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$

$Cu(NO_3)_2$



NO_2



$H_3BO_3 + C_2H_5OH \rightarrow (C_2H_5)_3BO_3 + H_2O$ (greenish flame)

$H_3PO_4 + 12(NH_4)_2MoO_4 + HNO_3 \rightarrow (NH_4)_3.PO_4.12MoO_3$ (canary yellow) + $21\ NH_4NO_3 + 12\ H_2O$

In the presence of Arsenic, we get yellow precipitate of $(NH_4)_3.AsO_4.12MoO_3$ (ammonium arsenomolybdate)

$Mo_3O_8.xH_2O$ - molybdenum blue

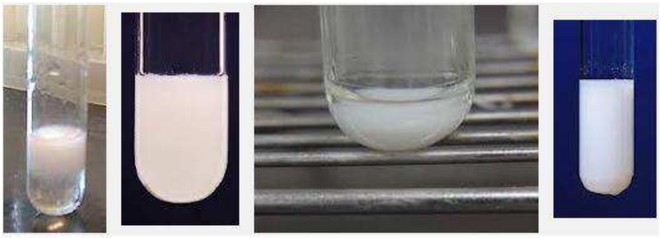
$SiF_4 + H_2O \rightarrow H_4SiO_4$ (silicic acid - white) + H_2SiO_4

$Na_2S + Na_2[Fe(CN)_5NO] \rightarrow Na_4[Fe(CN)_5NOS]$ - violet colour

$Na_2S + CdCO_3 \rightarrow CdS$ (yellow) + Na_2CO_3

$Na_3[Co(NO_2)_6] + KCl \rightarrow K_3[Co(NO_2)_6]$ (potassium cobaltnitrate - yellow ppt) + $NaCl$

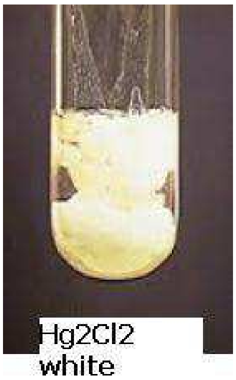
$AgCl$, $PbCl_2$, Hg_2Cl_2 - white



AgCl White

$PbCl_2$ is white

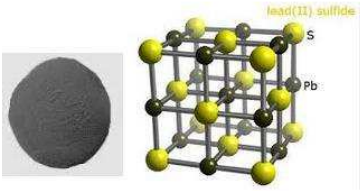
Hg_2Cl_2 is white



H_2S, PbS, Bi_2S_3, CuS - black

H_2S is Black

PbS is Black



PbS Lead Sulfide is Black

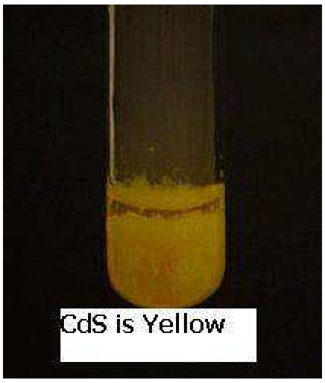
Bi2S3 is Black

CuS - black

Copper Sulfide Powder

CdS, As2S3, SnS2 - Yellow

CdS is Yellow



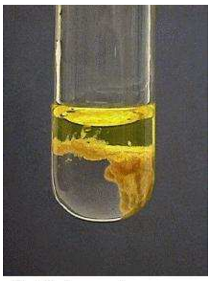
As2S3 is Yellow

SnS2 is Yellow

Sb2S3 is orange

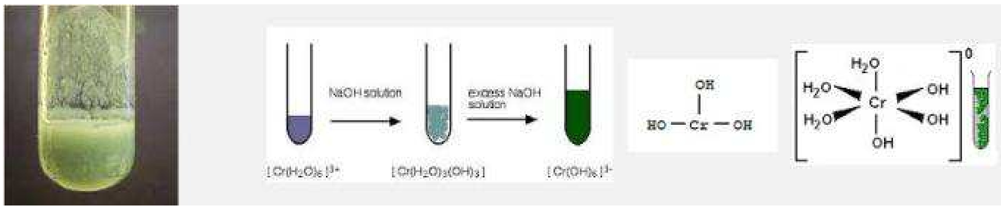
Sb2S3 is Orange

SnS is Brown



SnS is Brown is your teacher says so. SnS is Yellow if your teacher says so :-)

Cr(OH)3 is green

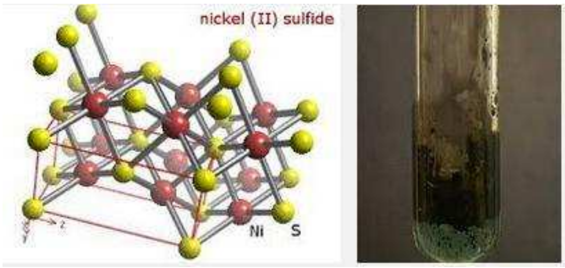


Chromium (III) Oxide is Green

CoS, NiS - black

CoS is black

NiS is Black Mineral Millerite



Cobalt Oxide is Black

Cobalt Sulphate is deep red brown

Cobalt Nitrate is deep red brown

Cobalt Chloride is deep Brown red

Cobalt Acetate is deep Brown

Azulene - **Deep Bue**

Iodoform - CHI_3 Yellow

Iron Phenol complex - **Violet** - $[Fe (OC_6H_5)_6]^{-3}$

$6 C_6H_5OH + FeCl_3$ - -> $[Fe (OC_6H_5)_6]^{-3} + 3 H^+ + Cl^-$

Ammonium Phosphomolybdate - Yellow - $(NH_4)_3PO_4.12MoO_3$ (Yellow)

Prusian Blue - $Fe_4 [Fe(CN)_6]_3.xH_2O$

$[Fe(CN)_3 NOS]^{-4}$ - **Violet**

$[Fe(SCN)]^{2+}$ **Blood Red**

$[Co(NH_3)_5 Br]^{+2} SO_4^{-2}$ - **Violet** - Pentaaminebromocobalt(III)sulphate

$[Co(NH_3)_5SO_4]^+ Br^-$ -> **Red**

Test for Halogen:

Halogens present in an organic compound forms sodium halide on fusion with sodium metal. Sodium halide extracted with water can be easily identified by adding silver nitrate solution after acidifying with dil. HNO_3.

If chlorine is present, a white curdy precipitate soluble in ammonium hydroxide solution is formed.

$$Na + Cl \rightarrow NaCl$$

$$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$$

If bromine is present, an yellowish white precipitate sparingly soluble in ammonium hydroxide solution is formed.

$$Na + Br \rightarrow NaBr$$

$$NaBr + AgNO_3 \rightarrow AgBr + NaNO_3$$

If iodine is present, an yellow precipitate insoluble in ammonium hydroxide solution is formed.

$$Na + I \rightarrow NaI$$

$$NaI + AgNO_3 \rightarrow AgI + NaNO_3$$

Test for Nitrogen:

The carbon and nitrogen present in the organic compound on fusion with sodium metal gives sodium cyanide (NaCN) soluble in water. This is converted in to sodium ferrocyanide by the addition of sufficient quantity of ferrous sulphate. Ferric ions generated during the process react with ferrocyanide to form prussian blue precipitate of ferric ferrocyanide.

$$Na + C + N \rightarrow NaCN$$

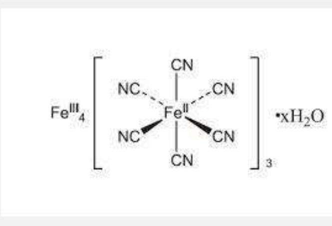
$$6NaCN + FeSO_4 \rightarrow Na_4[Fe(CN)_6] + Na_2SO_4$$

Sodium ferrocyanide

$$Na_4[Fe(CN)_6] + Fe^{3+} \rightarrow Fe_4[Fe(CN)_6]_3$$

Ferric ferrocyanide

FeCl3 + K4[Fe(CN)6] -> Fe4[Fe(CN)6]3 (prussian blue) + KCl



Test for Sulphur:

If sulphur is present in the organic compound, sodium fusion will convert it into sodium sulphide. Sulphide ions are readily identified using sodium nitroprusside.

$$Na + S \rightarrow Na_2S$$

$$Na_2S + Na_2[Fe(CN)_5NO] \rightarrow Na_4[Fe(CN)_5NOS]$$

Sodium nitroprusside violet colour

Test for both Nitrogen and Sulphur:

If both nitrogen and sulphur are present in an organic compound, sodium fusion will convert it into sodium thiocyanate which then react with Fe^{3+} to form blood colour complex $[Fe(SCN)]^{2+}$

$$Na + C + N + S \rightarrow NaSCN$$

$$Fe^{3+} + 2Na \rightarrow [Fe(SCN)]^{2+}$$

Note: If the Lassaigne's extract containing excess of sodium metal, sodium cyanide and sulphides are formed instead of sodium thiocyanate.

$$NaSCN + 2Na \rightarrow NaCN + Na_2S$$

Here in this type of cases, both sulphur and nitrogen are to be identified in separate tests.

$BaCO_3$, $SrCO_3$, $CaCO_3$, $Mg(NH_4)PO_4$ - white

$BaCO_3$ is white

BaCO3 powder

$SrCO_3$ is white

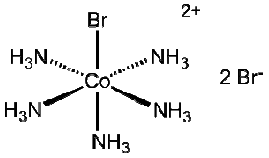
$CaCO_3$ powder is white

CaCO3 Calcium Carbonate Powder

Mg(NH4)PO4 is white

Pentaamminechlorocobalt(III)Bromide

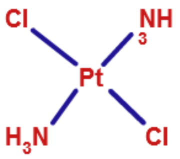
$[Co(NH_3)_5Cl]\ Cl_2$ Pentaamminechlorocobalt(III)chloride



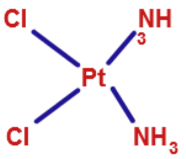
Pentaamminesulphatocobalt(III)Bromide

-

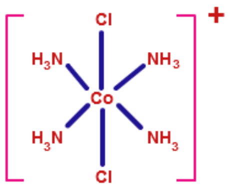
Dark Yellow Pale Yellow



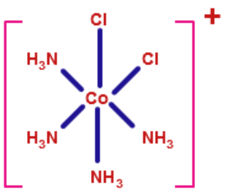
trans- $Pt(NH_3)_2Cl_2$



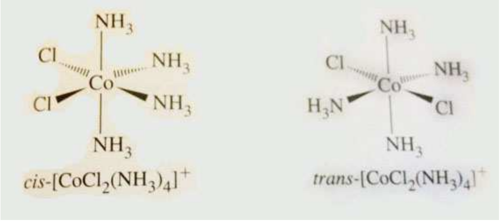
cis- $Pt(NH_3)_2Cl_2$



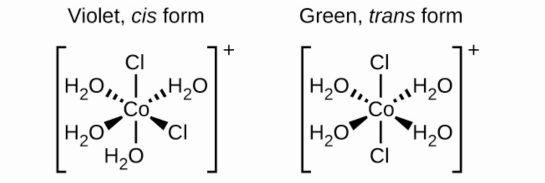
Trans - $[Co(NH_3)_4Cl_2]^+$

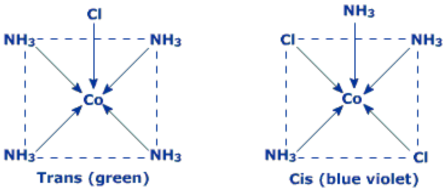


Cis - $[Co(NH_3)_4Cl_2]^+$



Cis is Blue Violet trans is green

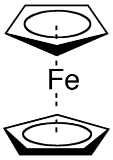


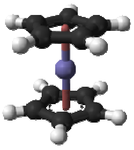


Eta bonds - Also known as Hapticity - Hapticity is the coordination of a ligand to a metal center via an uninterrupted and contiguous series of atoms.

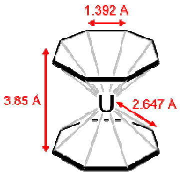
The hapticity of a ligand is described with the Greek letter η ('eta'). For example, η2 describes a ligand that coordinates through 2 contiguous atoms. In general the η-notation only applies when multiple atoms are coordinated (otherwise the κ-notation is used). In addition, if the ligand coordinates through multiple atoms that are not contiguous then this is considered denticity (not hapticity), and the κ-notation is used once again. Lastly, bridging ligands are described with the μ ('mu') notation.

Ferrocene - bis(η5-cyclopentadienyl)iron





Uranocene - bis(η8-1,3,5,7-cyclooctatetraene)uranium



$W(CO)_3(PPr^i_3)_2(\eta^2\text{-}H_2)$ - the first compound to be synthesized with a dihydrogen ligand (also known as Dihydrogen Complexes)

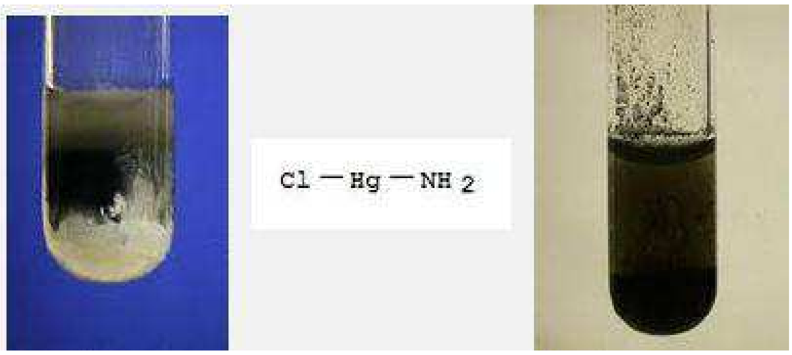
$IrCl(CO)[P(C_6H_5)_3]_2(\eta^2\text{-}O_2)$ - the dioxygen derivative which forms reversibly upon oxygenation of Vaska's complex.

-

Chromium (III) chloride is purple

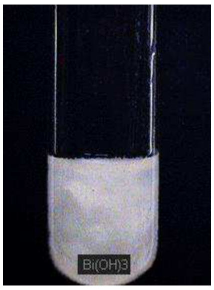
$HgCl_2 + NH_4OH \rightarrow (Hg + Hg(NH_2)Cl) + NH_4Cl + H_2O$

black ppt

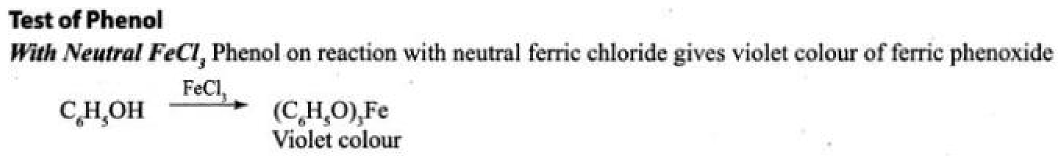


$BiCl_3 + H_2O \rightarrow BiOCl$ (white) + HCl

$Bi(OH)_3$ Bismuth Hydroxide is white



Oxidation of Phenol



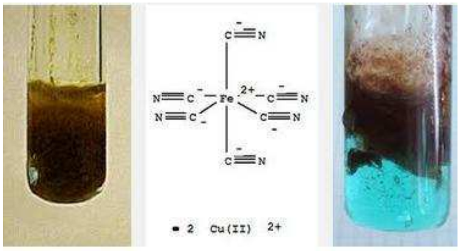
Test of Phenol

With Neutral $\boldsymbol{FeCl_3}$ Phenol on reaction with neutral ferric chloride gives violet colour of ferric phenoxide

$$C_6H_5OH \xrightarrow{FeCl_3} (C_6H_5O)_3Fe$$

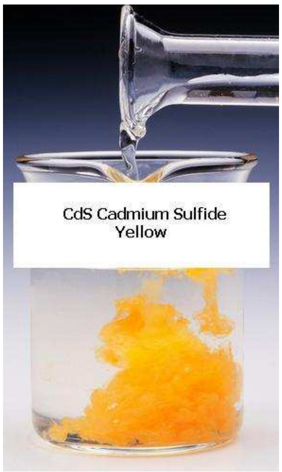
Violet colour

Cu(NO3)2 + K4[Fe(CN)6] -> Cu2[Fe(CN)6] (Chocolate brown) +KNO3



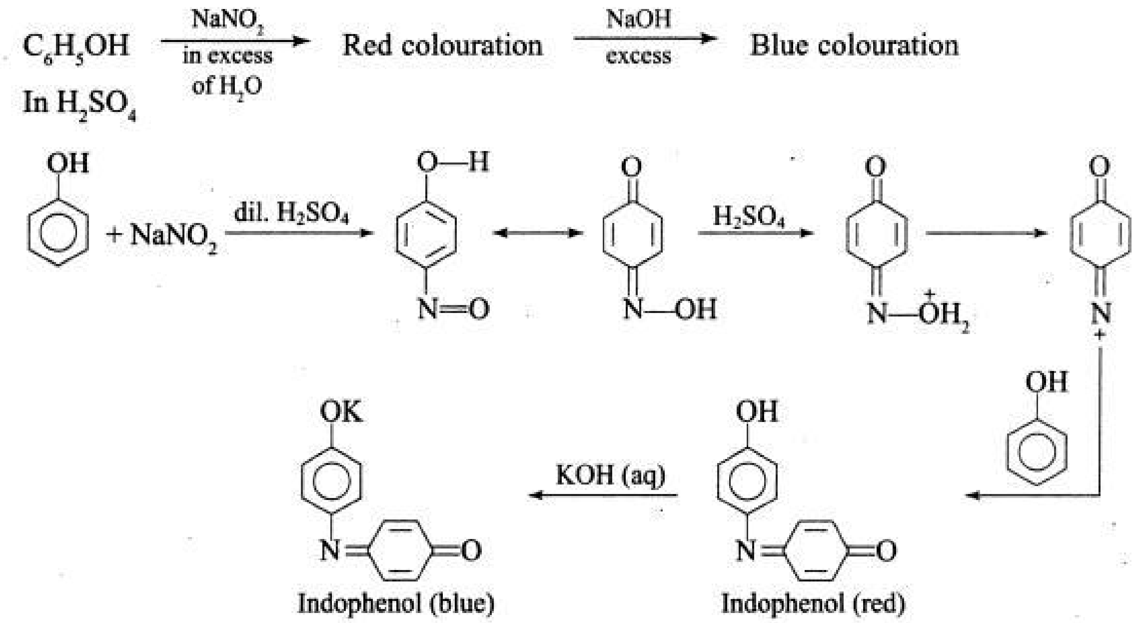
Cu2[Fe(CN)6]

Cd(NH3)4(NO3)2 + H2S -> CdS (yellow) + NH4NO3 + NH3



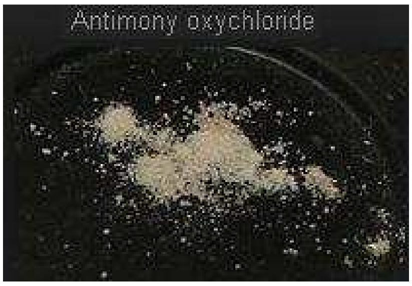
HgCl2 + SnCl2 -> Hg2Cl2 (white) + SnCl4

Liebermann's Nitroso Reaction



SbCl3 + H2O -> SbOCl (white) + HCl

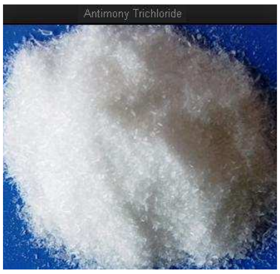
SbOCl Antimony oxychloride



Antimony Trioxide is white

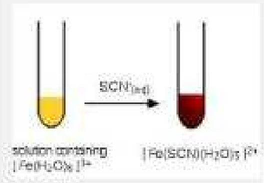
Antimony Pentoxide is gray

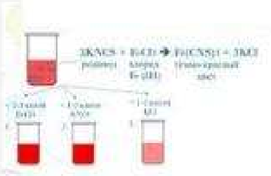
Antimony Trichloride is white

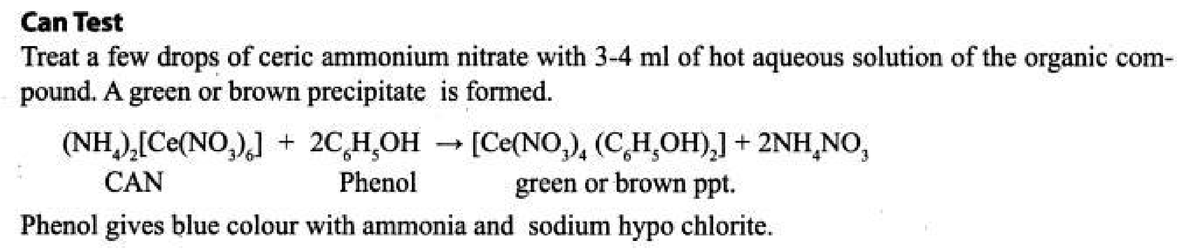


Potassium antimonate white

$FeCl_3 + KSCN \rightarrow Fe(CNS)_3$ (blood red) + KCN







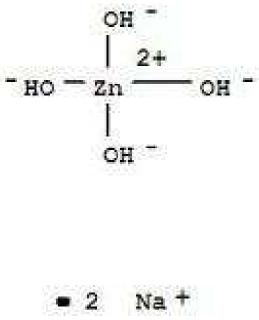
Can Test

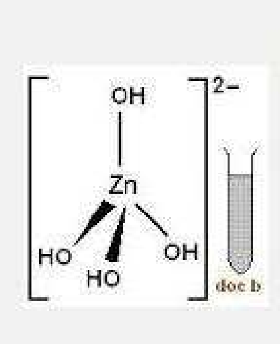
Treat a few drops of ceric ammonium nitrate with 3-4 ml of hot aqueous solution of the organic compound. A green or brown precipitate is formed.

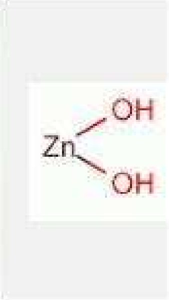
$$\underset{\text{CAN}}{(NH_4)_2[Ce(NO_3)_6]} + \underset{\text{Phenol}}{2C_6H_5OH} \rightarrow \underset{\text{green or brown ppt.}}{[Ce(NO_3)_4(C_6H_5OH)_2]} + 2NH_4NO_3$$

Phenol gives blue colour with ammonia and sodium hypo chlorite.

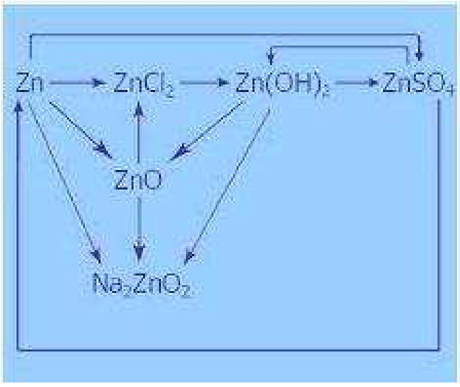
$ZnCl_2 + 2NaOH \rightarrow Zn(OH)_2$ (white ppt) + 2NaCl

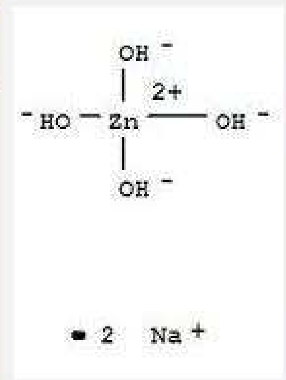




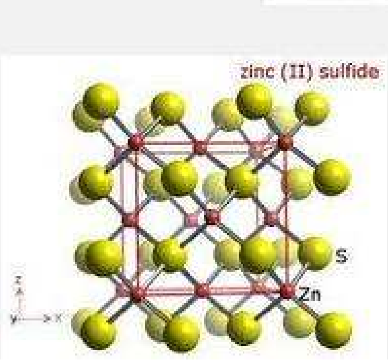


Zn(OH)2 + NaOH -> Na2ZnO2 (soluble) + H2O





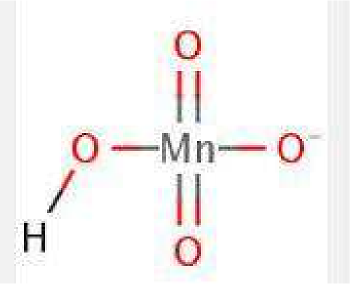
Na2ZnO2 + H2S -> ZnS (white) + NaOH

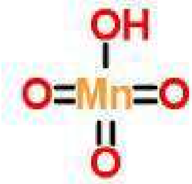


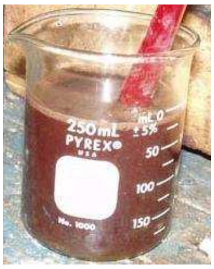
$$2KI + H_2O + O_3 \longrightarrow 2KOH + O_2 + I_2$$

Potassium iodide　Ozone　Potassium hydroxide　Iodine (Violet vapours)

Mn(NO3)2 + Pb3O4 + HNO3 -> HMnO4 (pink) + Pb(NO3)2 + H2O





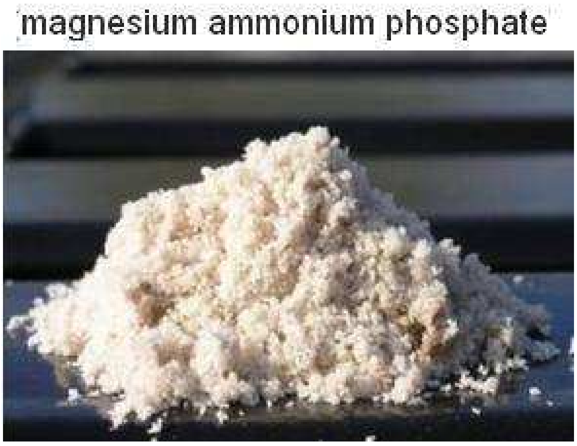


$Co(NO_2)_3 + KNO_2 \rightarrow K_3[Co(NO_2)_6]$ (yellow)

$Na_4Co(CO_3)_2 + H_2O + [O] \rightarrow Na_3Co(CO_3)_2$ (green coloration) + $NaOH$

$NiCO_3 + [O] \rightarrow Ni_2O_3$ (black) + CO_2

$MgCl_2 + Na_2HPO_4 + NH_4OH \rightarrow Mg(NH_4)PO_4$ (white) + $NaCl + H_2O$



$K_2HgI_4 + NH_4Cl + KOH \rightarrow NH_2HgOHgI$ (Iodide of millon's base, brown ppt) + $KCl + H_2O$

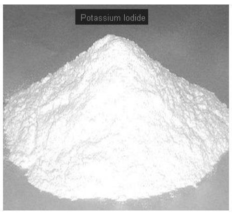
Chromium oxide powder is green

Chromium Oxide Powder

Bismuth oxide is Yellow

Bismuth Oxide Powder

KI Potassium Iodide is white



Tin reacts with conc. HNO_3 forming metastannic acid (H_2SnO_3).

Tin is not attacked by organic acids and hence is used for tinning of utensils to resist corrosion. Tin foils are used for wrapping cigarettes, confectionary items and for making tooth-paste tubes.

SnO_2 is an amphoteric oxide.

Stannous chloride ($SnCl_2$) acts as a good reducing agent. It reduces $HgCl_2$ to first Hg_2Cl_2 and then to Hg. It also reduces $FeCl_3$ to $FeCl_2$.

Stannic chloride ($SnCl_4$) is a liquid and fumes in air due to hydrolysis. It acts as a Lewis acid and dissolves in concentrated HCl forming H_2SnCl_6.

$SnCl_4.5H_2O$ is called butter of tin.

SnS dissolves in yellow ammonium sulphide.

Aluminum Oxide is white

Mercuric Iodide HgI_2 : It is a yellow solid below 400K but changes to red solid above 400K.

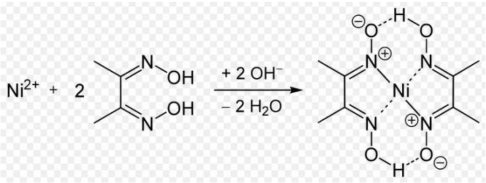
$$\underset{\text{Red}}{HgI_2} \xrightleftharpoons{400K} \underset{\text{Yellow}}{HgI_2}$$

It dissolves in excess of KI forming K_2HgI_4;

$HgI_2 + 2KI \rightarrow K_2HgI_4$

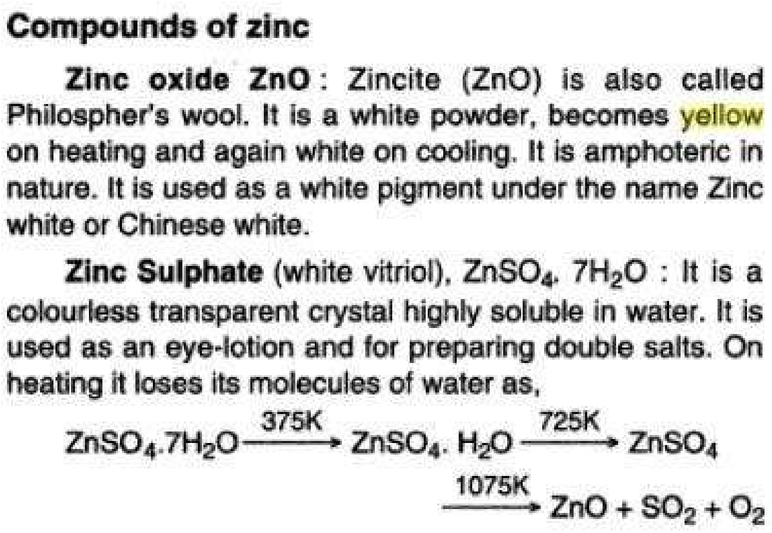
Alkaline solution of K_2HgI_4 is called Nessler's reagent.

Add NH4OH excess and dimethylglyoxime to NiCl2 then a rosy red ppt of nickel appears



A sample of Ni(dmgH)$_2$

CuO + B2O3 (Glassy bead) -> Cu(BO2)2 (Copper metabolite - blue)



Compounds of zinc

Zinc oxide ZnO : Zincite (ZnO) is also called Philospher's wool. It is a white powder, becomes yellow on heating and again white on cooling. It is amphoteric in nature. It is used as a white pigment under the name Zinc white or Chinese white.

Zinc Sulphate (white vitriol), $ZnSO_4.\ 7H_2O$: It is a colourless transparent crystal highly soluble in water. It is used as an eye-lotion and for preparing double salts. On heating it loses its molecules of water as,

$$ZnSO_4.7H_2O \xrightarrow{375K} ZnSO_4.\ H_2O \xrightarrow{725K} ZnSO_4 \xrightarrow{1075K} ZnO + SO_2 + O_2$$

Verdigris - basic copper acetate

This pigment was used to the Middle Ages in paints. Until the nineteenth century this was the most vibrant shade of green available and it was used by artists widely. The color comes from copper acetate and you should know that it is highly toxic to humans.

Compounds of Mercury

(1) Mercuric oxide, *HgO* : It is obtained as a red solid by heating mercury in air or oxygen for a long time at 673 *K*

$2Hg + O_2 \rightarrow 2\,HgO$ (red) or by heating mercuric nitrate alone or in the presence of *Hg*

Heat

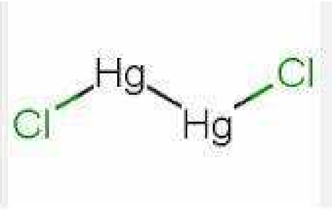
$2Hg(NO_3)_2 \rightarrow 2HgO + 4NO_2 + O_2$

red

When *NaOH* is added to a solution of $HgCl_2$, yellow precipitate of *HgO* are obtained.

$Hg_2 Cl_2 + 2NaOH \rightarrow HgO \downarrow + H_2O + 2NaCl$

(yellow)



Red and yellow forms of *HgO* differ only in their particle size. On heating to 673 *K*, yellow form changes to red form.

$$\underset{Yellow}{HgO} \xrightarrow{673K} \underset{red}{HgO}$$

It is used in oil paints or as a mild antiseptic in ointments.

(2) Mercuric chloride, $HgCl_2$: It is obtained by treating *Hg* with Cl_2 or by heating a mixture of *NaCl*and $HgSO_4$ in presence of small amount of MnO_2 (which oxidizes any *Hg*(I) salts formed during the reaction).

Heat

$HgSO_4 + 2NaCl \rightarrow HgCl_2 + Na_2SO_4$

MnO_2

HgCl2 is a white crystalline solid and is commonly known as corrosive sublimate. It is a covalent compound since it dissolves in organic solvents like ethanol and ether.

It is extremely poisonous and causes death. Its best antidote is white of an egg.

When treated with stannous chloride, it is first reduced to white ppt. of mercurous chloride and then to mercury (black).

$2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$

white ppt.

$Hg_2Cl_2 + SnCl_2 \rightarrow 2Hg + SnCl_4$

grey

With ammonia it gives a white ppt. known as infusible white ppt.

$HgCl_2 + 2NH_3 \rightarrow Hg(NH_2)Cl + NH_4Cl$A dilute solution of $HgCl_2$ is used as an antiseptic.(3) Mercuric iodide, HgI_2 : It is obtained when a required amount of *KI* solution is added to a solution of . $HgCl_2$$HgCl_2 + 2KI \rightarrow HgI_2 + 2KCl$^(red)^Below 400 *K*, HgI_2 is red but above 400 *K*, it turns yellow

$$\underset{(\text{red})}{HgI_2} \underset{\text{below } 400\,K}{\overset{\text{above } 400\,K}{\rightleftharpoons}} \underset{(\text{yellow})}{HgI_2}$$

HgI_2 readily dissolves in excess of *KI* solution to form the $(HgI_4)^{2-}$ complex ion.$HgI_2 + 2KI \rightarrow$ K_2HgI_4 Red ppt. soluble colourless solution

An alkaline solution of $K_2[HgI_4]$ is called Nessler's reagent and is used to test NH^+_4 ions.

It gives a brown ppt. of $NH_2 - Hg - O\,Hg - I$ (Iodide of Millon's base) with NH^+_4 ions.

$2K_2[HgI_4] + NH_3 + 3KOH \rightarrow NH_2.\,HgO.\,HgI + 7KI + 2H_2O$

It is used in ointments for treating skin infections.

(4) Mercurous chloride, Hg_2Cl_2 : It is obtained as under :

(a) $Hg_2(NO_3) + 2NaCl \rightarrow Hg_2Cl_2 + 2NaNo_3$

white ppt.

Heat in an iron retort

(b) $HgCl_2 + Hg \rightarrow Hg_2\,Cl_2$(condenses on cooling)

It is purified by sublimation.

Mercurous chloride is also called calomel. It is a white powder insoluble in H_2O. On heating, it decomposes to give $HgCl_2$ and *Hg*.

$$Hg_2\,Cl_2 \xrightarrow{Heat} Hgcl_2 + Hg$$

It dissolves in chlorine water forming mercuric chloride.

$$Hg_2Cl_2 + Cl_2 \rightarrow 2HgCl_2$$

With ammonia, it turns black due to the formation of a mixture of finely divided black *Hg* and mercuric amino chloride.

$$Hg_2Cl_2 + 2NH_3 \rightarrow Hg + NH_2\,HgCl + NH_4Cl$$

(black)

It is used to prepare standard calomel electrode and as a purgative in medicine.

(5) Mercuric sulphide, *HgS* : The solubility product of *HgS* is lower than that of *ZnS* and hence it gets precipitated as black solid when H_2S is passed through an acidic solution of any mercury (II) salt.

$$HgCl_2 + H_2S \rightarrow HgS + 2HCl$$

It is insoluble in water and *HCl* but dissolves in aqua regia (1 part conc.HNO_3 + 3 parts conc. *HCl*)

$$3HCl \quad + \quad HNO_3 \rightarrow NOCl \; + \; 2H_2O \quad + \quad 2\,[\,Cl\,]$$

Aqua regia Nitrosyl chloride Nacent chlorine

$$HgS + 2|\,Cl\,| \rightarrow HgCl_2 + S\downarrow$$

(Soluble)

On sublimation, its colour changes to red and hence it is used as a red pigment.

(6) Mercuric sulphate, $HgSO_4$: It is obtained when *HgS* is treated with conc.H_2SO_4.

$$Hg + 2H_2\,SO_4 \rightarrow HgSo_4 + SO_2 + 2H_2O$$

It is a white solid which decomposes on heating to give mercurous sulphate.

$$3HgSo_4 \xrightarrow{\Delta} Hg_2\,SO_4 + Hg + 2SO_2 + 2O_2$$

675K

It is used as a catalyst in the hydration of alkynes to give aldehydes or ketones. It is also used as a cosmetic under the name Vermillon and in ayurvedic medicine as makardhwaj.

(7) Amalgams : Mercury forms alloys commonly known as amalgams, with all metals except iron and platinum. Hence it is transported in iron containers.

(8) Alloy of transition metal : See in table discuss earlier in metallurgy.

xxxxxxxxxxxxxxxxxxxxx

The common Anions are divided into 3 groups for the purpose of identification:

Those which evolve gases with dilute hydrochloric acid :

Carbonate (CO_3^{2-})

bicarbonate(HCO_3^-)

Nitrite(NO_2^-)

Sulphide (S^{2-})

Sulphite(SO_3^{2-})

Thiosulphate($S_2O_3{}^{2-}$)

Those which do not react with dilute HCl, but which do evolve gases or volatile liquids with concentrated sulphuric acid:

Chloride (Cl^-)

Bromide (Br^-)

Iodide (I^-)

Nitrate (NO_3^-)

Those which do not react with either dilute hydrochloric acid or concentrated sulphuric acid:

Phosphate (PO_4^{3-})

Borate ($B_4O_7{}^{2-}$)

Sulphate ($SO_4{}^{2-}$)

A Radical is an atom, or group of atoms that behaves like a single atom. Examples : H, K, Na, Cu, Pb, simple radicals ; NH 4 , SO 2 , NO 2 , compound radicals.

A Basic Radical is a metal, or any radical behaving like a metal. Examples : Ag, Cu, Ca, Na, and NH 4 the last so classified because it behaves like such simple radicals as Na, K, and Li.

An Acid Radical is a nonmetal, or any radical behaving like a nonmetal. Examples : Cl, Br, I, SO 2 , NO2

An Acid is a substance containing H that may be replaced by a basic radical. When a nonmetal is combined with H only, as in HC1, HBr, H 2 S, the compound is said to be a binary (i.e. composed of two elements) acid, or an hydracid. When the nonmetal is combined with H and O, the compound is called a ternary (i.e. composed of three or more elements) acid, or an oxyacid ; and the characteristic name of the acid is formed by adding the termination -ic to the name of the nonmetal to denote more oxygen, or the termination -ous to denote less. Examples : H_2SO_4 sulphuric, and H_2SO_3 sulphurous acid.

These are classified in six different groups in accordance with certain properties which permit a group precipitation by a single reagent. A reagent used for precipitation of a whole group is called a general reagent.

A reagent used as a test for a single substance is known as a special reagent.

Experiments showing Method of Classification

Use the following solutions : $AgNO_3$, $Cu(NO3)_2$, $AsCl_3$, Fe_2Cl_6, $Co(N03)_2$, $Ba(N03)_2$, NaCl.

Take about 2 c.c. of each solution, and add HC1.*

Points to be Observed Whether a precipitate is formed.

Whether the precipitate is soluble in an excess of the reagent.

* Always use dilute acids unless otherwise directed.

GROUPING THE BASES

The color of each precipitate.

Whether there is change in color of the precipitate.

Change in color of solutions.

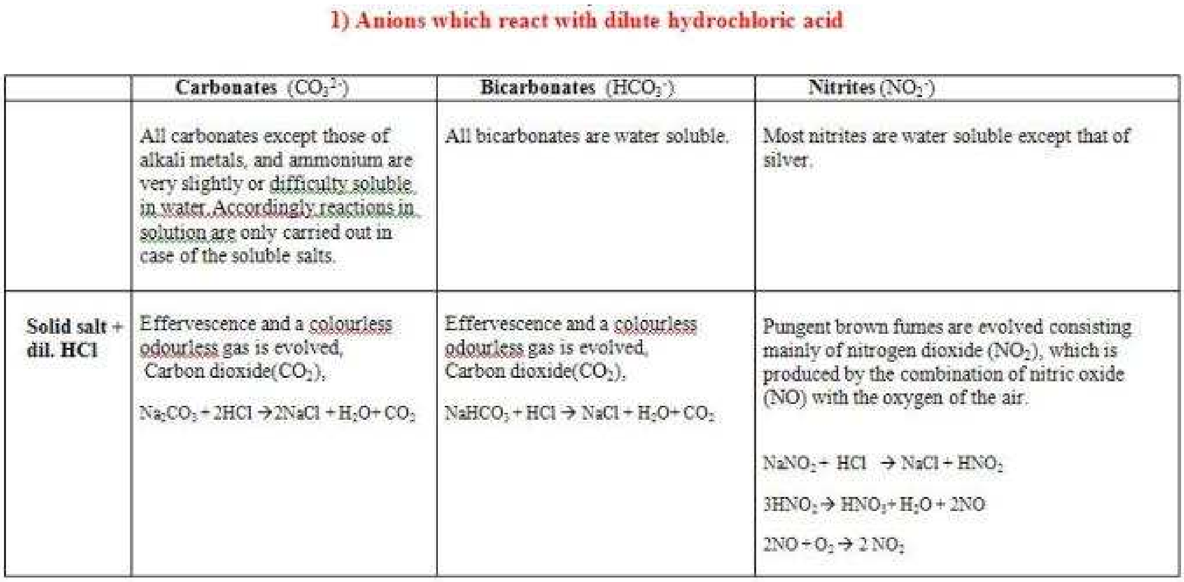
Chemical equations.

Tabulate all results carefully in your notebook, according to the following scheme :

HC1 was added to the seven solutions with the following results :

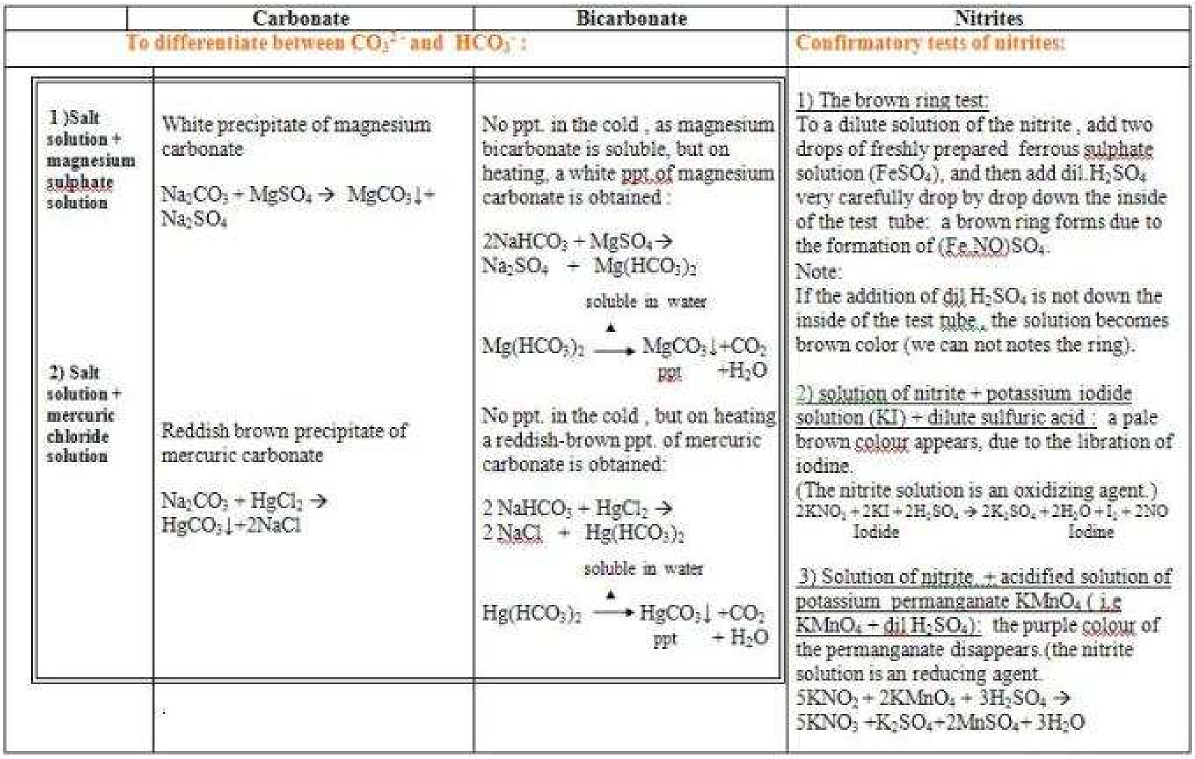
Typical of Gr. I AgNO 3 + HC1 = AgCl w. pp. + I IN ( ) 8 .
Typical of Gr. II A $Cu(NO_3)_2$ + II Cl = No change.
Typical of Gr. II B AsCl 3 + HC1 = No change.
Typical of Gr. Ill Fe 2 Cl 6 + HC1 = No change.
Typical of Gr. IV Co(NO 3) 2 + IIC1 = No change.

Typical of Gr. V $Ba(NO_3)_2$ + HC1 = No change.
Typical of Gr. VI NaCl + HC1 = No change.



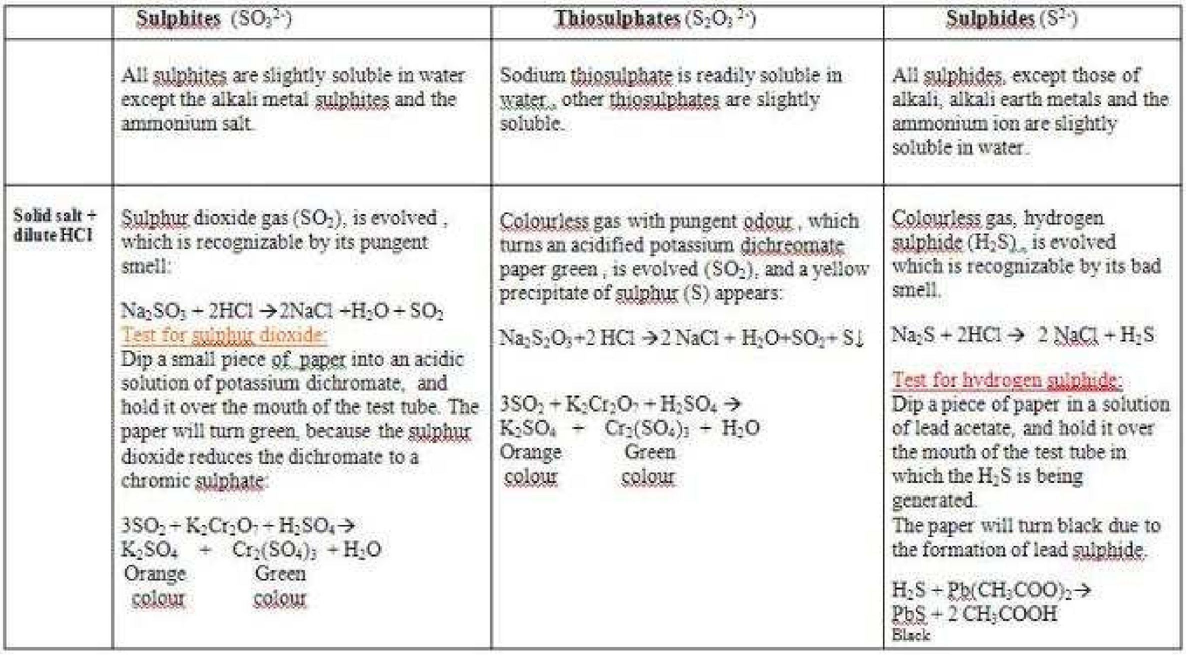
1) Anions which react with dilute hydrochloric acid

	Carbonates (CO_3^{2-})	Bicarbonates (HCO_3^-)	Nitrites (NO_2^-)
	All carbonates except those of alkali metals, and ammonium are very slightly or difficulty soluble in water. Accordingly reactions in solution are only carried out in case of the soluble salts.	All bicarbonates are water soluble.	Most nitrites are water soluble except that of silver.
Solid salt + dil. HCl	Effervescence and a colourless odourless gas is evolved, Carbon dioxide(CO_2). $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$	Effervescence and a colourless odourless gas is evolved, Carbon dioxide(CO_2). $NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$	Pungent brown fumes are evolved consisting mainly of nitrogen dioxide (NO_2), which is produced by the combination of nitric oxide (NO) with the oxygen of the air. $NaNO_2 + HCl \rightarrow NaCl + HNO_2$ $3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$ $2NO + O_2 \rightarrow 2NO_2$



	Carbonate	Bicarbonate	Nitrites
To differentiate between CO_3^{2-} and HCO_3^- :			Confirmatory tests of nitrites:
1)Salt solution + magnesium sulphate solution	White precipitate of magnesium carbonate $Na_2CO_3 + MgSO_4 \rightarrow MgCO_3\downarrow + Na_2SO_4$	No ppt. in the cold , as magnesium bicarbonate is soluble, but on heating, a white ppt.of magnesium carbonate is obtained : $2NaHCO_3 + MgSO_4 \rightarrow Na_2SO_4 + \underset{\text{soluble in water}}{Mg(HCO_3)_2}$ $Mg(HCO_3)_2 \xrightarrow{\Delta} \underset{ppt}{MgCO_3\downarrow} + CO_2 + H_2O$	1) The brown ring test: To a dilute solution of the nitrite , add two drops of freshly prepared ferrous sulphate solution ($FeSO_4$), and then add dil.H_2SO_4 very carefully drop by drop down the inside of the test tube: a brown ring forms due to the formation of $(Fe.NO)SO_4$. Note: If the addition of dil H_2SO_4 is not down the inside of the test tube., the solution becomes brown color (we can not notes the ring).
2) Salt solution + mercuric chloride solution	Reddish brown precipitate of mercuric carbonate $Na_2CO_3 + HgCl_2 \rightarrow HgCO_3\downarrow + 2NaCl$	No ppt. in the cold , but on heating a reddish-brown ppt. of mercuric carbonate is obtained: $2NaHCO_3 + HgCl_2 \rightarrow 2NaCl + \underset{\text{soluble in water}}{Hg(HCO_3)_2}$ $Hg(HCO_3)_2 \xrightarrow{\Delta} \underset{ppt}{HgCO_3\downarrow} + CO_2 + H_2O$	2) solution of nitrite + potassium iodide solution (KI) + dilute sulfuric acid : a pale brown colour appears, due to the libration of iodine. (The nitrite solution is an oxidizing agent.) $2KNO_2 + \underset{Iodide}{2KI} + 2H_2SO_4 \rightarrow 2K_2SO_4 + 2H_2O + \underset{Iodine}{I_2} + 2NO$ 3) Solution of nitrite. + acidified solution of potassium permanganate $KMnO_4$ (i.e $KMnO_4$ + dil H_2SO_4): the purple colour of the permanganate disappears.(the nitrite solution is an reducing agent. $5KNO_2 + 2KMnO_4 + 3H_2SO_4 \rightarrow 5KNO_3 + K_2SO_4 + 2MnSO_4 + 3H_2O$
	.		

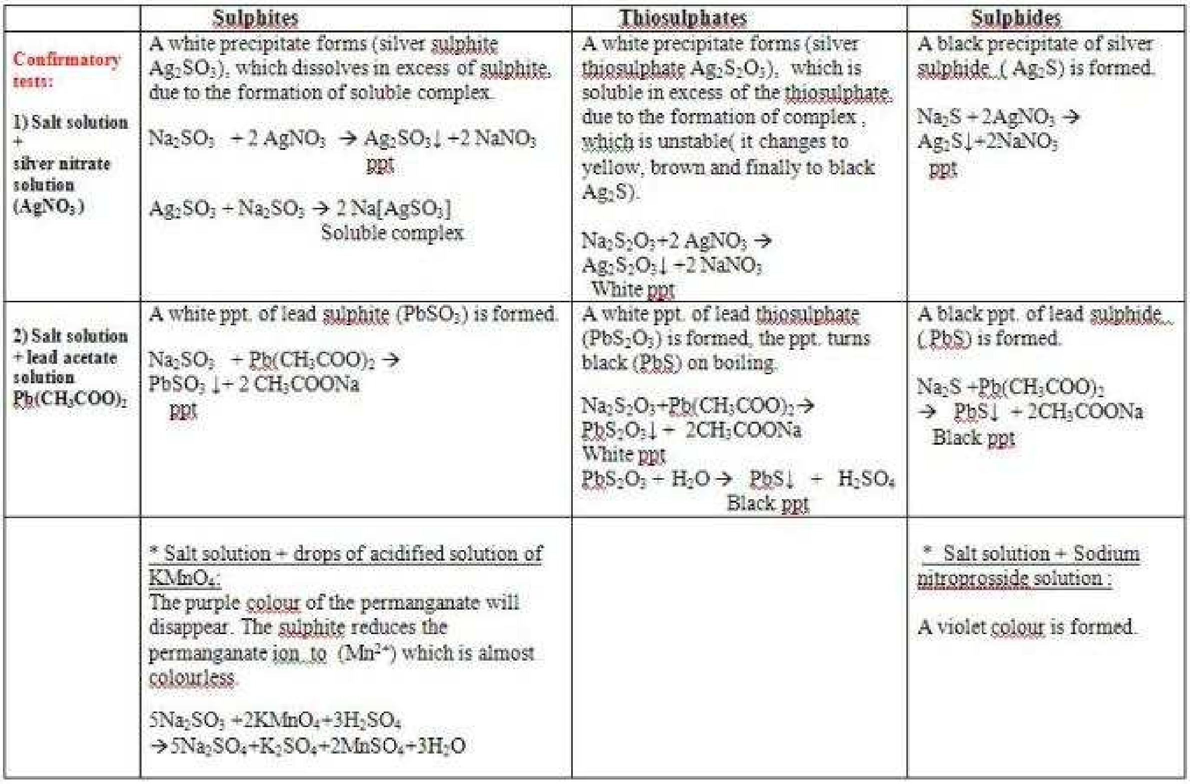
Is HgCO3 reddish Brown ?



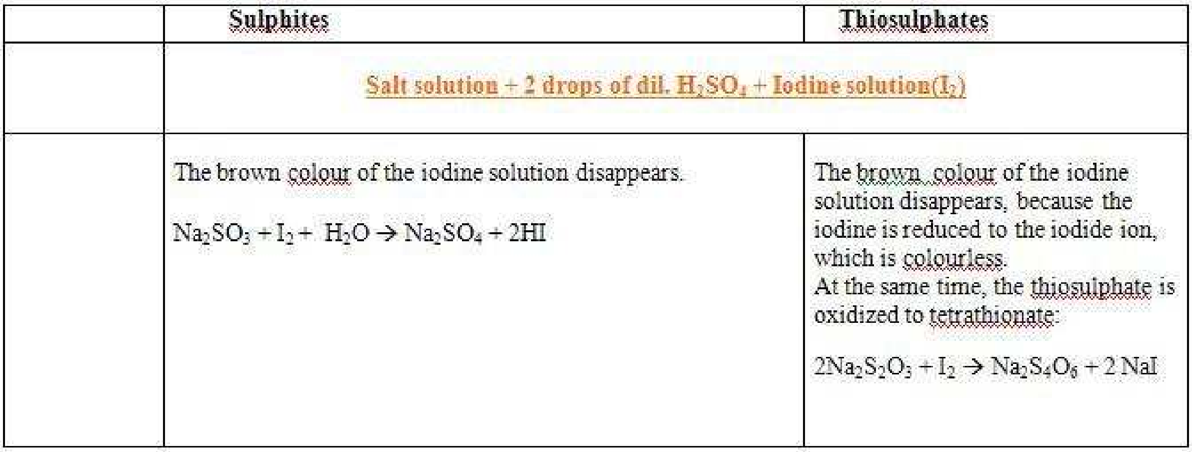
	Sulphites (SO_3^{2-})	**Thiosulphates** ($S_2O_3^{2-}$)	**Sulphides** (S^{2-})
	All sulphites are slightly soluble in water except the alkali metal sulphites and the ammonium salt.	Sodium thiosulphate is readily soluble in water., other thiosulphates are slightly soluble.	All sulphides, except those of alkali, alkali earth metals and the ammonium ion are slightly soluble in water.
Solid salt + dilute HCl	Sulphur dioxide gas (SO_2), is evolved , which is recognizable by its pungent smell: $Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2$ Test for sulphur dioxide: Dip a small piece of paper into an acidic solution of potassium dichromate, and hold it over the mouth of the test tube. The paper will turn green, because the sulphur dioxide reduces the dichromate to a chromic sulphate: $3SO_2 + K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$ Orange colour Green colour	Colourless gas with pungent odour , which turns an acidified potassium dichreomate paper green , is evolved (SO_2), and a yellow precipitate of sulphur (S) appears: $Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2 + S\downarrow$ $3SO_2 + K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$ Orange colour Green colour	Colourless gas, hydrogen sulphide (H_2S)., is evolved which is recognizable by its bad smell. $Na_2S + 2HCl \rightarrow 2NaCl + H_2S$ Test for hydrogen sulphide: Dip a piece of paper in a solution of lead acetate, and hold it over the mouth of the test tube in which the H_2S is being generated. The paper will turn black due to the formation of lead sulphide. $H_2S + Pb(CH_3COO)_2 \rightarrow PbS + 2CH_3COOH$ Black

K2SO4 is white 

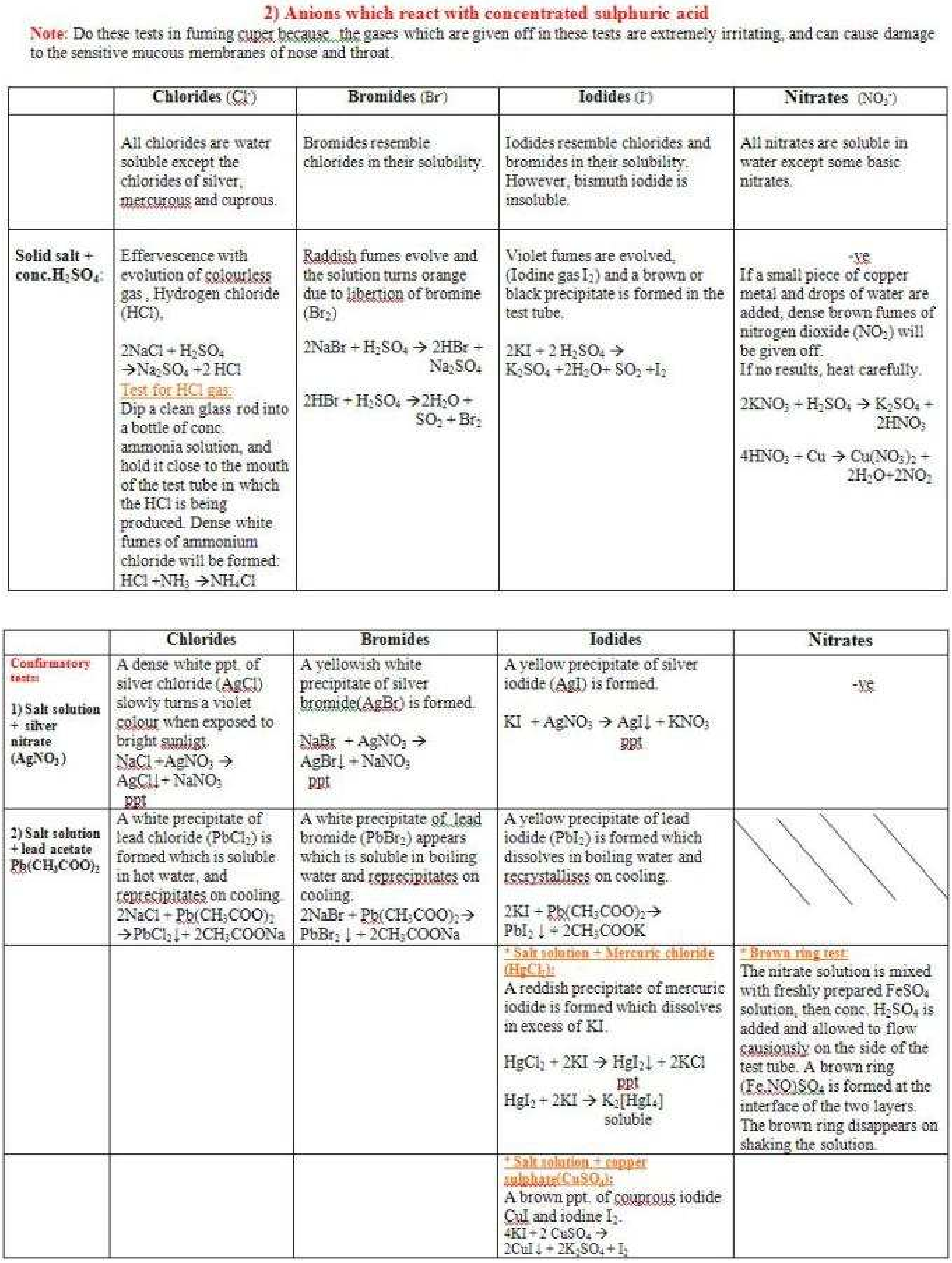
Cr2(SO4)3 is green 



	Sulphites	**Thiosulphates**	**Sulphides**
Confirmatory tests: **1) Salt solution + silver nitrate solution ($AgNO_3$)**	A white precipitate forms (silver sulphite Ag_2SO_3), which dissolves in excess of sulphite, due to the formation of soluble complex. $Na_2SO_3 + 2 AgNO_3 \rightarrow Ag_2SO_3\downarrow + 2 NaNO_3$ ppt $Ag_2SO_3 + Na_2SO_3 \rightarrow 2 Na[AgSO_3]$ Soluble complex	A white precipitate forms (silver thiosulphate $Ag_2S_2O_3$), which is soluble in excess of the thiosulphate, due to the formation of complex , which is unstable(it changes to yellow, brown and finally to black Ag_2S). $Na_2S_2O_3 + 2 AgNO_3 \rightarrow Ag_2S_2O_3\downarrow + 2 NaNO_3$ White ppt	A black precipitate of silver sulphide (Ag_2S) is formed. $Na_2S + 2AgNO_3 \rightarrow Ag_2S\downarrow + 2NaNO_3$ ppt
2) Salt solution + lead acetate solution $Pb(CH_3COO)_2$	A white ppt. of lead sulphite ($PbSO_3$) is formed. $Na_2SO_3 + Pb(CH_3COO)_2 \rightarrow PbSO_3\downarrow + 2 CH_3COONa$ ppt	A white ppt. of lead thiosulphate (PbS_2O_3) is formed, the ppt. turns black (PbS) on boiling. $Na_2S_2O_3 + Pb(CH_3COO)_2 \rightarrow PbS_2O_3\downarrow + 2CH_3COONa$ White ppt $PbS_2O_3 + H_2O \rightarrow PbS\downarrow + H_2SO_4$ Black ppt	A black ppt. of lead sulphide (PbS) is formed. $Na_2S + Pb(CH_3COO)_2 \rightarrow PbS\downarrow + 2CH_3COONa$ Black ppt
	* Salt solution + drops of acidified solution of $KMnO_4$: The purple colour of the permanganate will disappear. The sulphite reduces the permanganate ion to (Mn^{2+}) which is almost colourless. $5Na_2SO_3 + 2KMnO_4 + 3H_2SO_4 \rightarrow 5Na_2SO_4 + K_2SO_4 + 2MnSO_4 + 3H_2O$		* Salt solution + Sodium nitroprosside solution : A violet colour is formed.



	Sulphites	**Thiosulphates**
	Salt solution + 2 drops of dil. H_2SO_4 + Iodine solution(I_2)	
	The brown colour of the iodine solution disappears. $Na_2SO_3 + I_2 + H_2O \rightarrow Na_2SO_4 + 2HI$	The brown colour of the iodine solution disappears, because the iodine is reduced to the iodide ion, which is colourless. At the same time, the thiosulphate is oxidized to tetrathionate: $2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2 NaI$



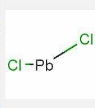
2) Anions which react with concentrated sulphuric acid

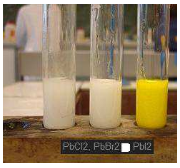
Note: Do these tests in fuming cuper because the gases which are given off in these tests are extremely irritating, and can cause damage to the sensitive mucous membranes of nose and throat.

	Chlorides (Cl^-)	**Bromides** (Br^-)	**Iodides** (I^-)	**Nitrates** (NO_3^-)
	All chlorides are water soluble except the chlorides of silver, mercurous and cuprous.	Bromides resemble chlorides in their solubility.	Iodides resemble chlorides and bromides in their solubility. However, bismuth iodide is insoluble.	All nitrates are soluble in water except some basic nitrates.
Solid salt + conc.H_2SO_4:	Effervescence with evolution of colourless gas , Hydrogen chloride (HCl), $2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2\,HCl$ Test for HCl gas: Dip a clean glass rod into a bottle of conc. ammonia solution, and hold it close to the mouth of the test tube in which the HCl is being produced. Dense white fumes of ammonium chloride will be formed: $HCl + NH_3 \rightarrow NH_4Cl$	Raddish fumes evolve and the solution turns orange due to libertion of bromine (Br_2) $2NaBr + H_2SO_4 \rightarrow 2HBr + Na_2SO_4$ $2HBr + H_2SO_4 \rightarrow 2H_2O + SO_2 + Br_2$	Violet fumes are evolved, (Iodine gas I_2) and a brown or black precipitate is formed in the test tube. $2KI + 2\,H_2SO_4 \rightarrow K_2SO_4 + 2H_2O + SO_2 + I_2$	-ve If a small piece of copper metal and drops of water are added, dense brown fumes of nitrogen dioxide (NO_2) will be given off. If no results, heat carefully. $2KNO_3 + H_2SO_4 \rightarrow K_2SO_4 + 2HNO_3$ $4HNO_3 + Cu \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$

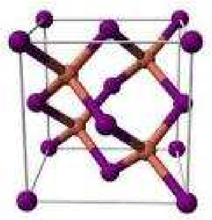
	Chlorides	**Bromides**	**Iodides**	**Nitrates**
Confirmatory tests: **1) Salt solution + silver nitrate $(AgNO_3)$**	A dense white ppt. of silver chloride (AgCl) slowly turns a violet colour when exposed to bright sunligt. $NaCl + AgNO_3 \rightarrow \underset{ppt}{AgCl\downarrow} + NaNO_3$	A yellowish white precipitate of silver bromide(AgBr) is formed. $NaBr + AgNO_3 \rightarrow \underset{ppt}{AgBr\downarrow} + NaNO_3$	A yellow precipitate of silver iodide (AgI) is formed. $KI + AgNO_3 \rightarrow \underset{ppt}{AgI\downarrow} + KNO_3$	-ve
2) Salt solution + lead acetate $Pb(CH_3COO)_2$	A white precipitate of lead chloride $(PbCl_2)$ is formed which is soluble in hot water, and reprecipitates on cooling. $2NaCl + Pb(CH_3COO)_2 \rightarrow PbCl_2\downarrow + 2CH_3COONa$	A white precipitate of lead bromide $(PbBr_2)$ appears which is soluble in boiling water and reprecipitates on cooling. $2NaBr + Pb(CH_3COO)_2 \rightarrow PbBr_2\downarrow + 2CH_3COONa$	A yellow precipitate of lead iodide (PbI_2) is formed which dissolves in boiling water and recrystallises on cooling. $2KI + Pb(CH_3COO)_2 \rightarrow PbI_2\downarrow + 2CH_3COOK$	
			* Salt solution + Mercuric chloride $(HgCl_2)$: A reddish precipitate of mercuric iodide is formed which dissolves in excess of KI. $HgCl_2 + 2KI \rightarrow \underset{ppt}{HgI_2\downarrow} + 2KCl$ $HgI_2 + 2KI \rightarrow \underset{soluble}{K_2[HgI_4]}$	* Brown ring test: The nitrate solution is mixed with freshly prepared $FeSO_4$ solution, then conc. H_2SO_4 is added and allowed to flow causiously on the side of the test tube. A brown ring $(Fe.NO)SO_4$ is formed at the interface of the two layers. The brown ring disappears on shaking the solution.
			* Salt solution + copper sulphate$(CuSO_4)$: A brown ppt. of couprous iodide CuI and iodine I_2. $4KI + 2\,CuSO_4 \rightarrow 2CuI\downarrow + 2K_2SO_4 + I_2$	

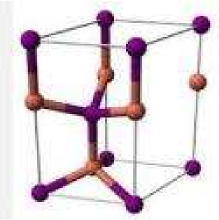
AgCl is white

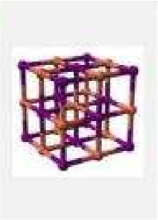


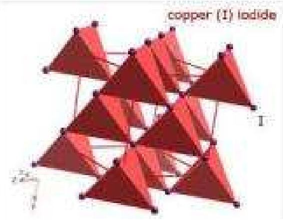


CuI Cuprous Iodide

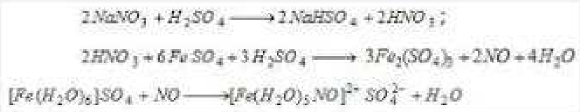








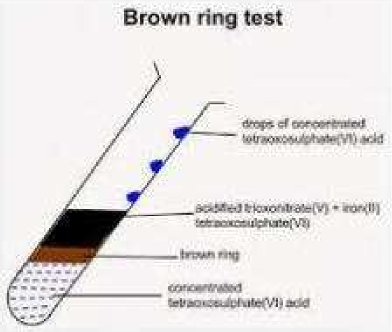
Brown Ring Test

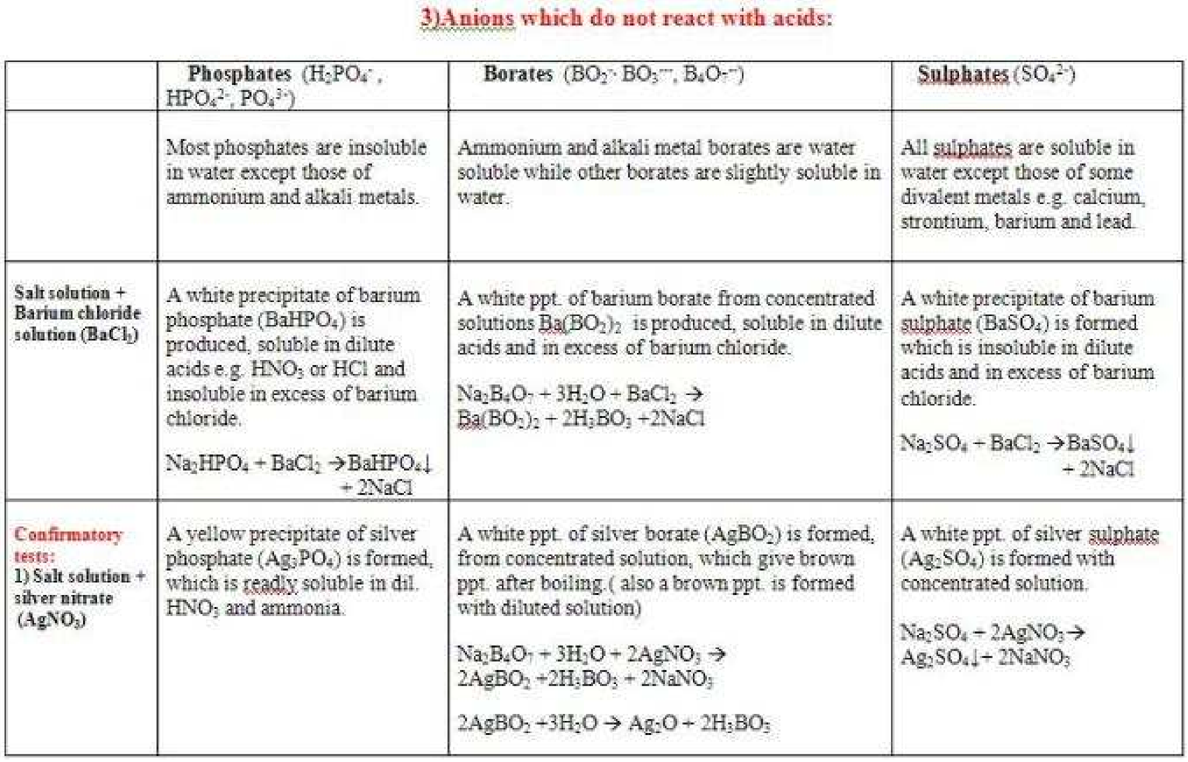


$2NaNO_3 + H_2SO_4 \longrightarrow 2NaHSO_4 + 2HNO_3;$

$2HNO_3 + 6FeSO_4 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$

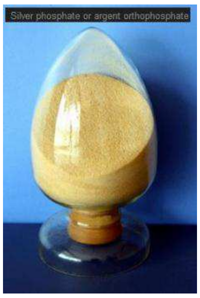
$[Fe(H_2O)_6]SO_4 + NO \longrightarrow [Fe(H_2O)_5NO]^{2+} SO_4^{2-} + H_2O$



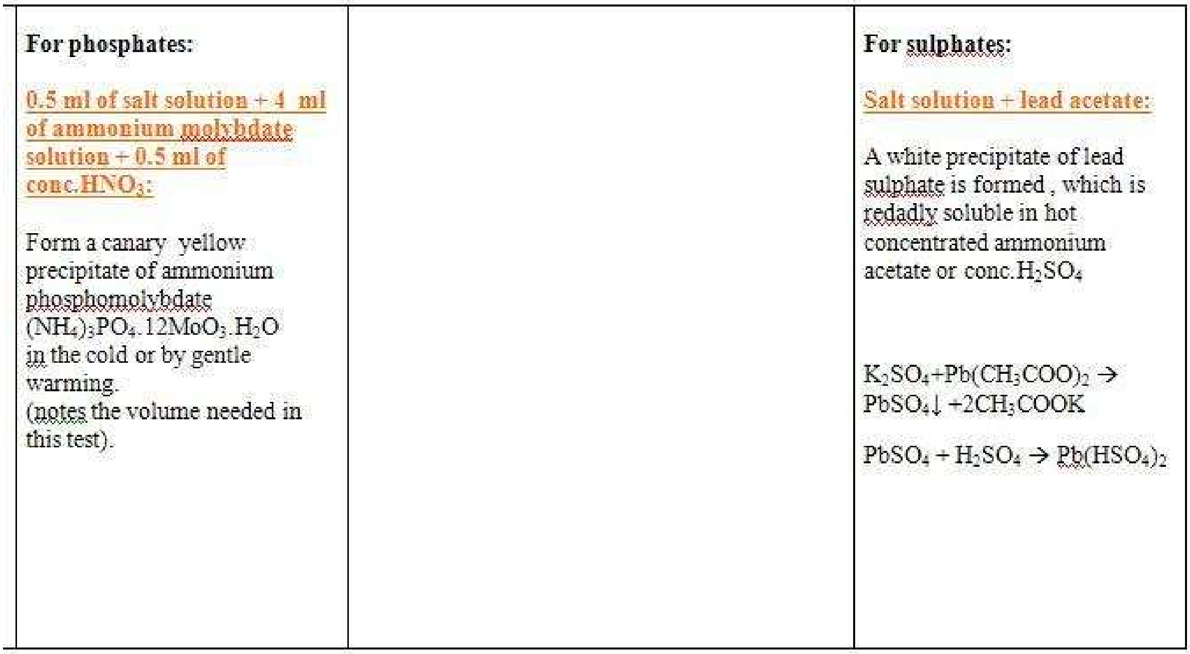


3)Anions which do not react with acids:

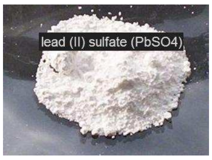
	Phosphates ($H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-})	**Borates** ($BO_2^-\cdot BO_3^{---}$, $B_4O_7^{--}$)	**Sulphates** (SO_4^{2-})
	Most phosphates are insoluble in water except those of ammonium and alkali metals.	Ammonium and alkali metal borates are water soluble while other borates are slightly soluble in water.	All sulphates are soluble in water except those of some divalent metals e.g. calcium, strontium, barium and lead.
Salt solution + Barium chloride solution ($BaCl_2$)	A white precipitate of barium phosphate ($BaHPO_4$) is produced, soluble in dilute acids e.g. HNO_3 or HCl and insoluble in excess of barium chloride. $Na_2HPO_4 + BaCl_2 \rightarrow BaHPO_4\downarrow + 2NaCl$	A white ppt. of barium borate from concentrated solutions $Ba(BO_2)_2$ is produced, soluble in dilute acids and in excess of barium chloride. $Na_2B_4O_7 + 3H_2O + BaCl_2 \rightarrow Ba(BO_2)_2 + 2H_3BO_3 + 2NaCl$	A white precipitate of barium sulphate ($BaSO_4$) is formed which is insoluble in dilute acids and in excess of barium chloride. $Na_2SO_4 + BaCl_2 \rightarrow BaSO_4\downarrow + 2NaCl$
Confirmatory tests: **1) Salt solution + silver nitrate ($AgNO_3$)**	A yellow precipitate of silver phosphate (Ag_3PO_4) is formed, which is readily soluble in dil. HNO_3 and ammonia.	A white ppt. of silver borate ($AgBO_2$) is formed, from concentrated solution, which give brown ppt. after boiling.(also a brown ppt. is formed with diluted solution) $Na_2B_4O_7 + 3H_2O + 2AgNO_3 \rightarrow 2AgBO_2 + 2H_3BO_3 + 2NaNO_3$ $2AgBO_2 + 3H_2O \rightarrow Ag_2O + 2H_3BO_3$	A white ppt. of silver sulphate (Ag_2SO_4) is formed with concentrated solution. $Na_2SO_4 + 2AgNO_3 \rightarrow Ag_2SO_4\downarrow + 2NaNO_3$

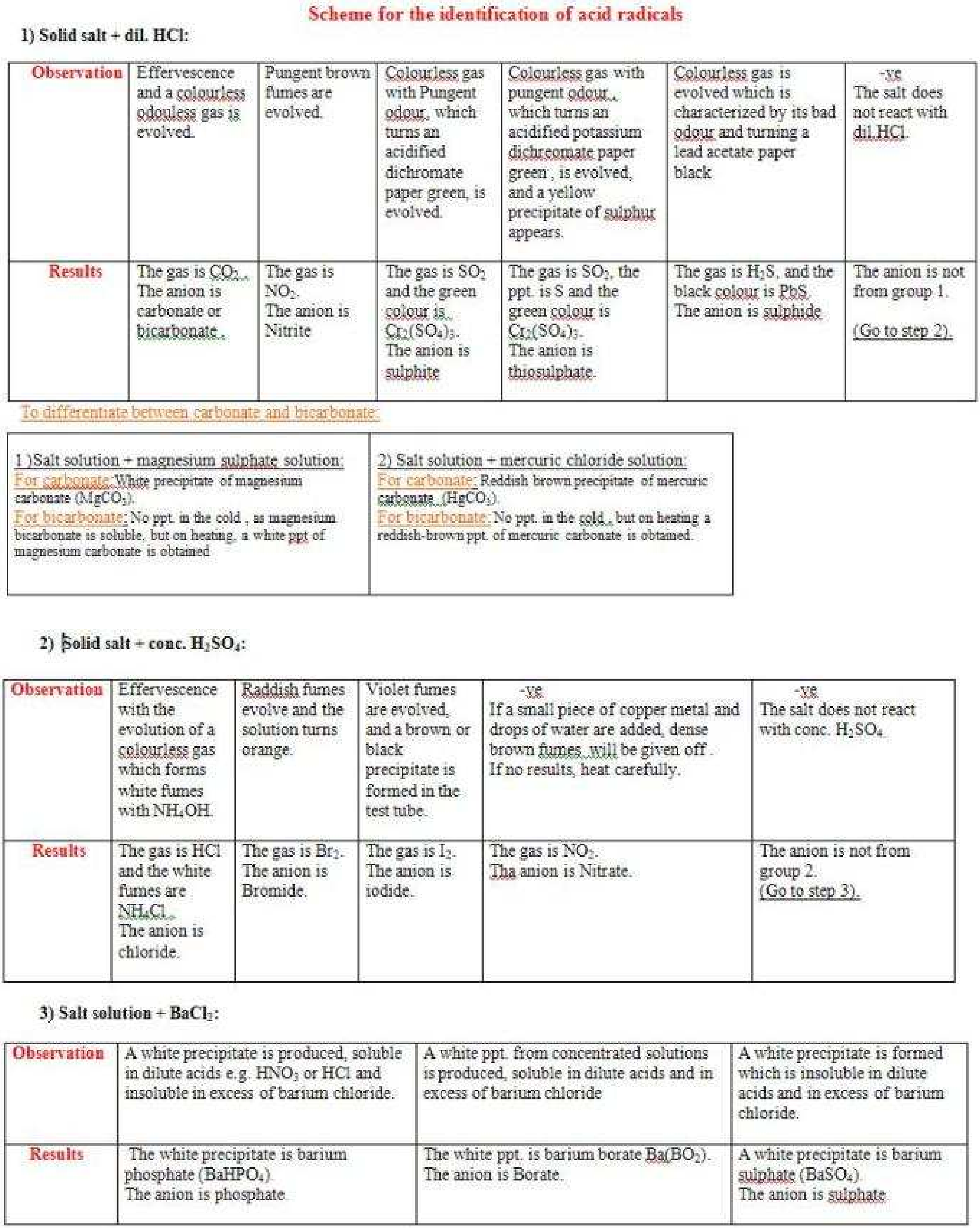


BaSO4 is white



For phosphates: **0.5 ml of salt solution + 4 ml of ammonium molybdate solution + 0.5 ml of conc.HNO$_3$:** Form a canary yellow precipitate of ammonium phosphomolybdate $(NH_4)_3PO_4.12MoO_3.H_2O$ in the cold or by gentle warming. (notes the volume needed in this test).		**For sulphates:** **Salt solution + lead acetate:** A white precipitate of lead sulphate is formed , which is redadly soluble in hot concentrated ammonium acetate or conc.H_2SO_4 $K_2SO_4+Pb(CH_3COO)_2 \rightarrow PbSO_4\downarrow +2CH_3COOK$ $PbSO_4 + H_2SO_4 \rightarrow Pb(HSO_4)_2$





Scheme for the identification of acid radicals

1) Solid salt + dil. HCl:

Observation	Effervescence and a colourless odouless gas is evolved.	Pungent brown fumes are evolved.	Colourless gas with Pungent odour, which turns an acidified dichromate paper green, is evolved.	Colourless gas with pungent odour, which turns an acidified potassium dichreomate paper green , is evolved, and a yellow precipitate of sulphur appears.	Colourless gas is evolved which is characterized by its bad odour and turning a lead acetate paper black	-ve The salt does not react with dil.HCl.
Results	The gas is CO_2. The anion is carbonate or bicarbonate.	The gas is NO_2. The anion is Nitrite	The gas is SO_2 and the green colour is $Cr_2(SO_4)_3$. The anion is sulphite	The gas is SO_2, the ppt. is S and the green colour is $Cr_2(SO_4)_3$. The anion is thiosulphate.	The gas is H_2S, and the black colour is PbS. The anion is sulphide	The anion is not from group 1. (Go to step 2).

To differentiate between carbonate and bicarbonate:

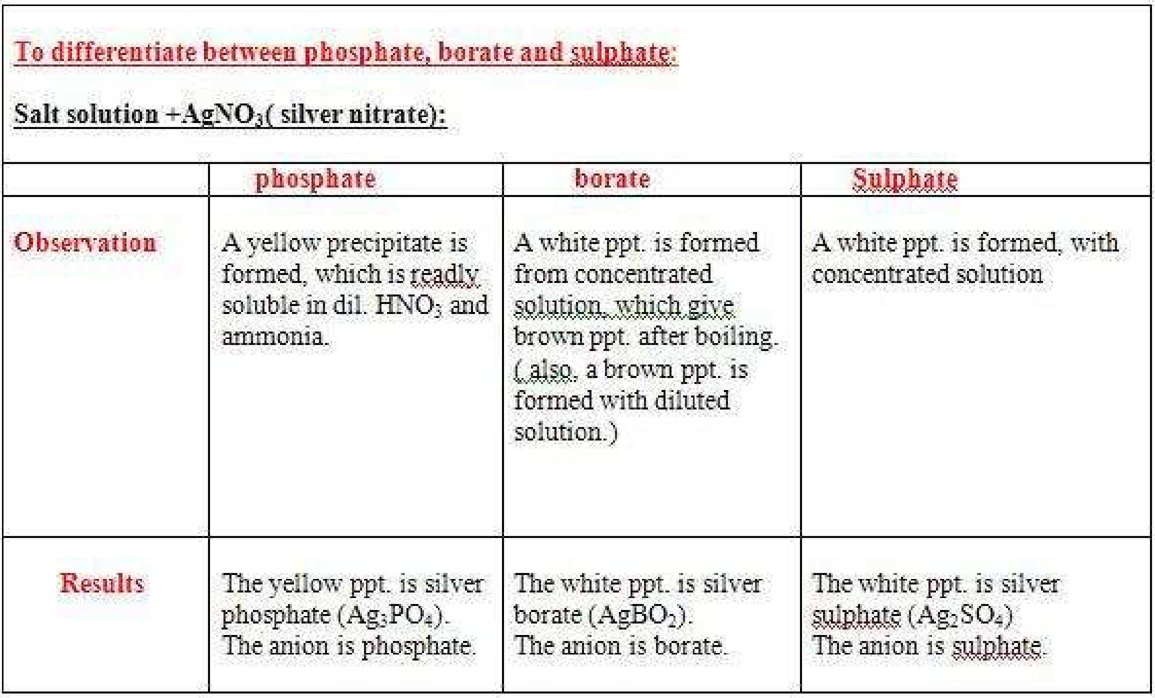
1)Salt solution + magnesium sulphate solution:	2) Salt solution + mercuric chloride solution:
For carbonate: White precipitate of magnesium carbonate ($MgCO_3$). For bicarbonate: No ppt. in the cold , as magnesium bicarbonate is soluble, but on heating, a white ppt of magnesium carbonate is obtained	For carbonate: Reddish brown precipitate of mercuric carbonate. ($HgCO_3$). For bicarbonate: No ppt. in the cold., but on heating a reddish-brown ppt. of mercuric carbonate is obtained.

2) Solid salt + conc. H_2SO_4:

Observation	Effervescence with the evolution of a colourless gas which forms white fumes with NH_4OH.	Raddish fumes evolve and the solution turns orange.	Violet fumes are evolved, and a brown or black precipitate is formed in the test tube.	-ve If a small piece of copper metal and drops of water are added, dense brown fumes will be given off . If no results, heat carefully.	-ve The salt does not react with conc. H_2SO_4
Results	The gas is HCl and the white fumes are NH_4Cl. The anion is chloride.	The gas is Br_2. The anion is Bromide.	The gas is I_2. The anion is iodide.	The gas is NO_2. Tha anion is Nitrate.	The anion is not from group 2. (Go to step 3).

3) Salt solution + $BaCl_2$:

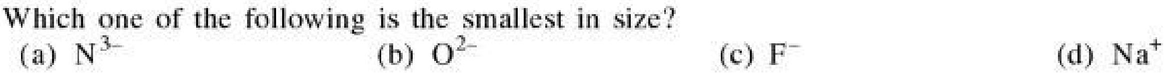
Observation	A white precipitate is produced, soluble in dilute acids e.g. HNO_3 or HCl and insoluble in excess of barium chloride.	A white ppt. from concentrated solutions is produced, soluble in dilute acids and in excess of barium chloride	A white precipitate is formed which is insoluble in dilute acids and in excess of barium chloride.
Results	The white precipitate is barium phosphate ($BaHPO_4$). The anion is phosphate.	The white ppt. is barium borate $Ba(BO_2)$. The anion is Borate.	A white precipitate is barium sulphate ($BaSO_4$). The anion is sulphate.



To differentiate between phosphate, borate and sulphate:

Salt solution +$AgNO_3$(silver nitrate):

	phosphate	**borate**	**Sulphate**
Observation	A yellow precipitate is formed, which is readly soluble in dil. HNO_3 and ammonia.	A white ppt. is formed from concentrated solution, which give brown ppt. after boiling. (also, a brown ppt. is formed with diluted solution.)	A white ppt. is formed, with concentrated solution
Results	The yellow ppt. is silver phosphate (Ag_3PO_4). The anion is phosphate.	The white ppt. is silver borate ($AgBO_2$). The anion is borate.	The white ppt. is silver sulphate (Ag_2SO_4) The anion is sulphate.

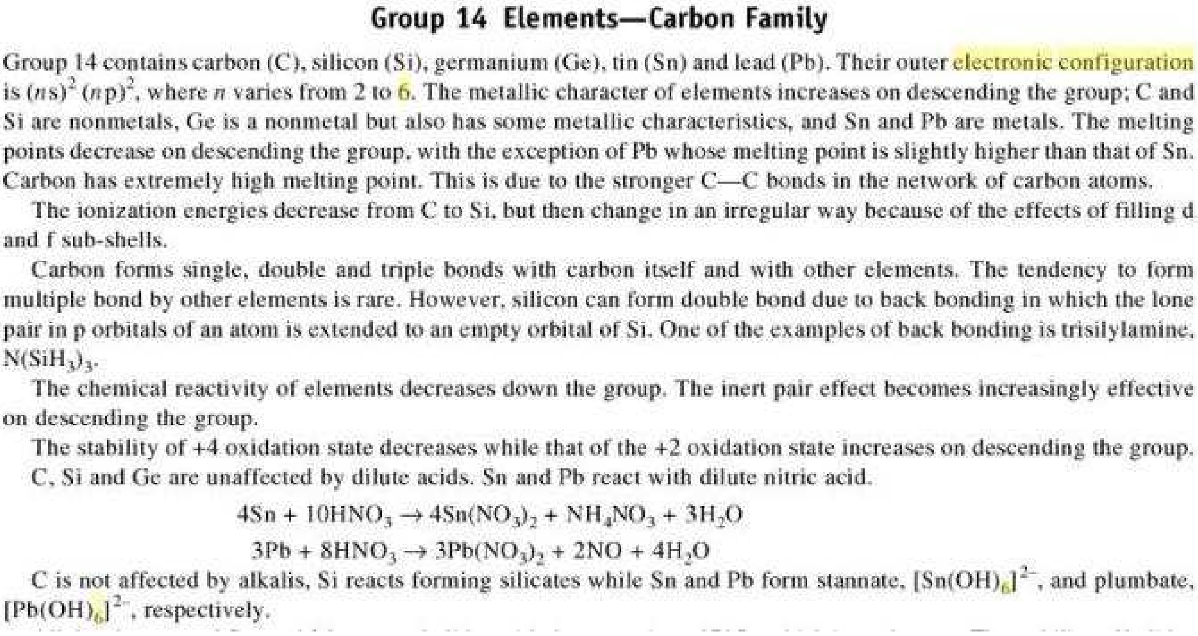


Which one of the following is the smallest in size?

(a) N^{3-} (b) O^{2-} (c) F^{-} (d) Na^{+}

Ans : (d)

Na+ will have the smallest size



Group 14 Elements—Carbon Family

Group 14 contains carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb). Their outer electronic configuration is $(ns)^2$ $(np)^2$, where n varies from 2 to 6. The metallic character of elements increases on descending the group; C and Si are nonmetals, Ge is a nonmetal but also has some metallic characteristics, and Sn and Pb are metals. The melting points decrease on descending the group, with the exception of Pb whose melting point is slightly higher than that of Sn. Carbon has extremely high melting point. This is due to the stronger C—C bonds in the network of carbon atoms.

The ionization energies decrease from C to Si, but then change in an irregular way because of the effects of filling d and f sub-shells.

Carbon forms single, double and triple bonds with carbon itself and with other elements. The tendency to form multiple bond by other elements is rare. However, silicon can form double bond due to back bonding in which the lone pair in p orbitals of an atom is extended to an empty orbital of Si. One of the examples of back bonding is trisilylamine, $N(SiH_3)_3$.

The chemical reactivity of elements decreases down the group. The inert pair effect becomes increasingly effective on descending the group.

The stability of +4 oxidation state decreases while that of the +2 oxidation state increases on descending the group.

C, Si and Ge are unaffected by dilute acids. Sn and Pb react with dilute nitric acid.

$$4Sn + 10HNO_3 \rightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

$$3Pb + 8HNO_3 \rightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O$$

C is not affected by alkalis, Si reacts forming silicates while Sn and Pb form stannate, $[Sn(OH)_6]^{2-}$, and plumbate, $[Pb(OH)_6]^{2-}$, respectively.

All the elements of Group 14 form tetrahalides with the exception of PbI_4, which is not known. The stability of halides decreases down the group. CCl_4 is stable while other halides are hydrolysed. The hydrolysis of $SiCl_4$ produces SiO_2 while SiF_4 produces SiO_2 as well as $[SiF_6]^{2-}$.

The acidic nature of the dioxides of carbon family decreases down the group; CO_2 and SiO_2 are acidic, GeO_2 is weakly acidic and SnO_2 and PbO_2 are amphoteric.

Silicones are organosilicon polymers with general formula $(R_2SiO)_n$, where R may be methyl, ethyl or phenyl group.

Group 15 Elements-Nitrogen Family

Group 15 contains nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi). Their outer electronic configuration is $(ns)^2\ (np)^3$, where n varies from 2 to 6. The metallic character of these elements increases on descending the group; N and P are nonmetals, As and Sb are metalloids and Bi is a metal. The melting and boiling points follow the order

melting point $\quad N < P < As > Sb > Bi$
boiling point $\quad N < P < As < Sb > Bi$

Phosphorus has two common allotropic forms; white and red. White phosphorus is more reactive than red form due to highly strained structure (P—P—P angle is 60°).

Black phosphorus is a highly polymerized form and is most stable.

Nitrogen form triple bond in dinitrogen because bond enthalpy $\varepsilon(N{\equiv}N)$ is greater than three times bond enthalpy $\varepsilon(N{-}N)$. In phosphorus, the reverse is true, hence, it involves single bonds.

The melting points of hydrides follow the order $NH_3 > PH_3 < AsH_3 < SbH_3$.

All the five elements of Group 15 form trihalides. Of these nitrogen halides are least stable. All the trihalides with the exception of NF_3 hydrolyse in aqueous solution.

$$NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$$
$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$
$$AsCl_3 + 3H_2O \rightarrow H_3AsO_3 + 3HCl$$
$$SbCl_3 + H_2O \rightarrow SbO^+ + 2H^+ + 3Cl^-$$
$$BiCl_3 + H_2O \rightarrow BiO^+ + 2H^+ + 3Cl^-$$

Nitrogen forms many oxides; N_2O, NO, N_2O_3, NO_2 and N_2O_5. The most common oxides of phosphorus are P_4O_6 and P_4O_{10}. Phosphorus trioxide is an acidic oxide and is anhydride of orthophosphorous acid (H_3PO_3). Phosphorus pentoxide is anhydride of phosphoric acid (H_3PO_4).

Nitrogen forms two acids; nitrous acid (HNO_2) and nitric acid (HNO_3). Phosphorus forms two series of oxoacids. These are phosphorus and phosphoric series. In phosphorous series, the acids include pyrophosphorous acid ($H_4P_2O_5$), orthophosphorous acid (H_3PO_3), metaphosphorous acid (HPO_2) and hypophosphorous acid (H_3PO_2). The acids $H_4P_2O_5$ and H_3PO_3 are reducing agents as they involve P—H bond.

In phosphoric series, the acids include orthophosphoric acid (H_3PO_4), pyrophosphoric acid ($H_4P_2O_7$) and polymetaphosphoric acid, $(HPO_3)_n$.

Which one of the following has the minimum atomic size?

(a) Li (b) Be (c) Na (d) Mg

Ans : (b)

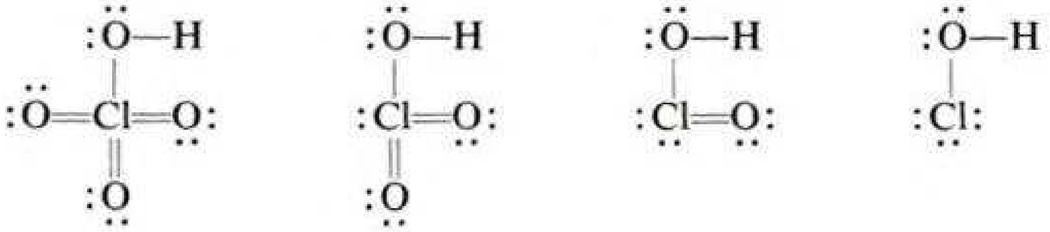
In the periodic table, size decreases in a period and it increases in a group. In the given elements, Be belongs to lower period and higher group and thus will have least size.

Group 1B

The size of Zr is very similar to Hf due to Lanthanide contraction

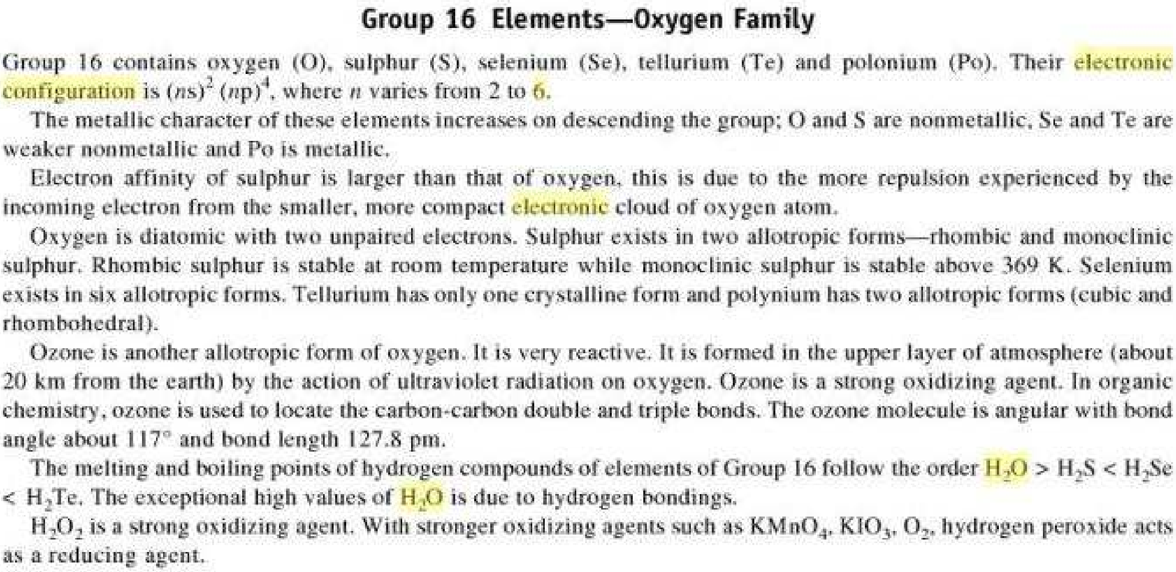
Group 4A

The size of Nb is very similar to Tantalum (Ta) due to Lanthanide contraction



Perchloric acid Chloric acid Chlorous acid Hypochlorous acid

Oxygen Family



Group 16 Elements—Oxygen Family

Group 16 contains oxygen (O), sulphur (S), selenium (Se), tellurium (Te) and polonium (Po). Their electronic configuration is $(ns)^2 (np)^4$, where n varies from 2 to 6.

The metallic character of these elements increases on descending the group; O and S are nonmetallic, Se and Te are weaker nonmetallic and Po is metallic.

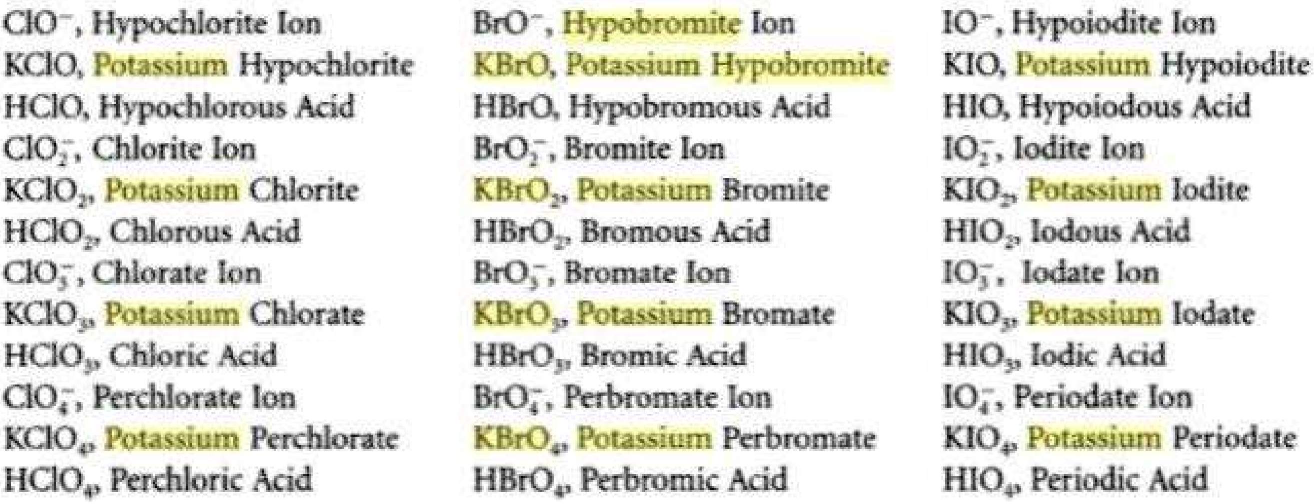
Electron affinity of sulphur is larger than that of oxygen, this is due to the more repulsion experienced by the incoming electron from the smaller, more compact electronic cloud of oxygen atom.

Oxygen is diatomic with two unpaired electrons. Sulphur exists in two allotropic forms—rhombic and monoclinic sulphur. Rhombic sulphur is stable at room temperature while monoclinic sulphur is stable above 369 K. Selenium exists in six allotropic forms. Tellurium has only one crystalline form and polynium has two allotropic forms (cubic and rhombohedral).

Ozone is another allotropic form of oxygen. It is very reactive. It is formed in the upper layer of atmosphere (about 20 km from the earth) by the action of ultraviolet radiation on oxygen. Ozone is a strong oxidizing agent. In organic chemistry, ozone is used to locate the carbon-carbon double and triple bonds. The ozone molecule is angular with bond angle about 117° and bond length 127.8 pm.

The melting and boiling points of hydrogen compounds of elements of Group 16 follow the order $H_2O > H_2S < H_2Se < H_2Te$. The exceptional high values of H_2O is due to hydrogen bondings.

H_2O_2 is a strong oxidizing agent. With stronger oxidizing agents such as $KMnO_4$, KIO_3, O_2, hydrogen peroxide acts as a reducing agent.



ClO^-, Hypochlorite Ion	BrO^-, Hypobromite Ion	IO^-, Hypoiodite Ion
KClO, Potassium Hypochlorite	KBrO, Potassium Hypobromite	KIO, Potassium Hypoiodite
HClO, Hypochlorous Acid	HBrO, Hypobromous Acid	HIO, Hypoiodous Acid
ClO_2^-, Chlorite Ion	BrO_2^-, Bromite Ion	IO_2^-, Iodite Ion
$KClO_2$, Potassium Chlorite	$KBrO_2$, Potassium Bromite	KIO_2, Potassium Iodite
$HClO_2$, Chlorous Acid	$HBrO_2$, Bromous Acid	HIO_2, Iodous Acid
ClO_3^-, Chlorate Ion	BrO_3^-, Bromate Ion	IO_3^-, Iodate Ion
$KClO_3$, Potassium Chlorate	$KBrO_3$, Potassium Bromate	KIO_3, Potassium Iodate
$HClO_3$, Chloric Acid	$HBrO_3$, Bromic Acid	HIO_3, Iodic Acid
ClO_4^-, Perchlorate Ion	BrO_4^-, Perbromate Ion	IO_4^-, Periodate Ion
$KClO_4$, Potassium Perchlorate	$KBrO_4$, Potassium Perbromate	KIO_4, Potassium Periodate
$HClO_4$, Perchloric Acid	$HBrO_4$, Perbromic Acid	HIO_4, Periodic Acid

Amongst Co, Ni. Cu and Zn ; Zn has maximum size

The monohydrogen and dihydrogen phosphates have very important uses in real-world analytical laboratories. Mostly, these uses center around the control of the acidity of solutions. Solutions of these partially neutralized acids resist changes in acidity level even when strong acids or bases are added. For this reason they are called "buffer solutions." For example, dilute solutions of potassium dihydrogen phosphate, KH_2PO_4, will maintain an acidity level near the neutral point between acids and bases. Solutions of sodium monohydrogen, Na_2HPO_4, will maintain an acidity level that is considerably below the neutral point, which means that base-like properties predominate.

The size of Mo is very similar to W due to
(a) the difference of atomic number by one
(b) the contraction in size in the first transition series elements
(c) lanthanide contraction
(d) actinide contraction

Mo belongs to 5th period and 6th group. W belongs to 6th period and 6th group. Their sizes are more or less identical due to intervening lanthanides.

The solution from which excess Br_2 is removed by heating must be acidic, otherwise a portion of Br_2 shall be fixed in the form of potassium hypobromite (KBrO).

With alkalies it forms a hypobromite in cold dilute solution and a bromate in a hot solution

$$\underset{\text{Cold and dilute}}{2KOH + Br2} \rightarrow KBr + \underset{\text{Potassium hypobromite}}{KBrO} + H_2O$$

$$\underset{\text{hot and concentrated}}{6KOH + 3Br2} \rightarrow 5KBr + \underset{\text{Potassium bromate}}{KBrO_3} + 3H_2O$$

The first compound of xenon, $XePtF_6$, was discovered in 1962. Xenon reacts with fluorine to give three compounds they are XeF_2, XeF_4 and XeF_6. Other known compounds of xenon are XeO_3, XeO_4, $XeOF_2$, XeO_2F_2 etc. No compound of He, Ne and Ar has been prepared.

Many salts of ternary acids are used in medicine. Lithium carbonate, Li_2CO_3, has been used successfully to combat severe jet lag. Lithium carbonate is also useful in the treatment of mania, depression, alcoholism, and schizophrenia. Magnesium sulfate, $MgSO_4$, sometimes helps to prevent convulsions during pregnancy and to reduce the solubility of toxic barium sulfate in internally administered preparations consumed before gastrointestinal X-ray films are taken.

Other salts of ternary acids that you may find in your home include potassium chlorate, $KClO_3$, in matches as an oxidizing agent and oxygen source; sodium hypochlorite, NaClO, in bleaches and mildew removers; and ammonium carbonate, $(NH_4)_2CO_3$, which is the primary ingredient in smelling salts.

The tips of "strike anywhere" matches contain tetraphosphorus trisulfide, red phosphorus, and potassium chlorate. Friction converts kinetic energy into heat, which initiates a spontaneous reaction.

$$P_4S_3(s) + 8O_2 \longrightarrow P_4O_{10}(s) + 3SO_2(g)$$

The thermal decomposition of $KClO_3$ provides additional oxygen for this reaction.

Group 17 Elements—Halogen Family

Group 17 contains fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At). Their outer electronic configuration is $(ns)^2\,(np)^5$, where n varies from 2 to 6. The trends in this group are as follows.

Covalent and ionic radii—*increase down the group.*

Electronegativity and ionization energy—*decrease down the group.*

Electron affinity—*increases from* F to Cl *followed by a decrease.*

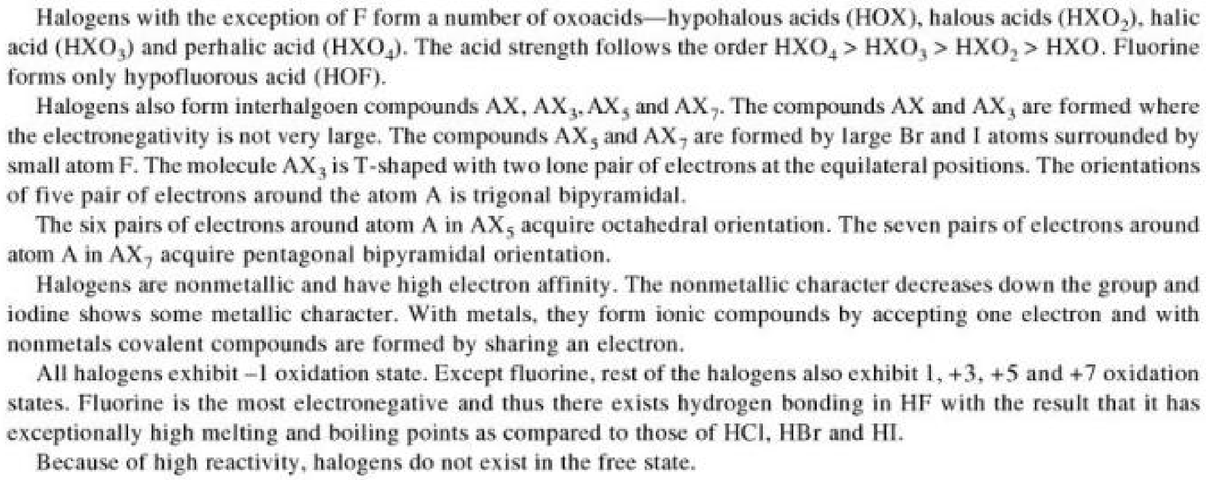
Melting and boiling points—*increase down the group.*

Bond enthalpy ε(X—X)—*increases from* F *to* Cl *followed by a decrease.*

Oxidizing ability—decreases down the group.

Halogens are very reactive and do not occur in free state. Fluorine is most electronegative atom, there exists hydrogen bondings in gaseous HF.

HF is a weak acid and HCl, HBr and HI behave as strong acids. In the glacial acetic acid medium, the acid strength follows the order HI > HBr > HCl > HF.



Halogens with the exception of F form a number of oxoacids—hypohalous acids (HOX), halous acids (HXO_2), halic acid (HXO_3) and perhalic acid (HXO_4). The acid strength follows the order $HXO_4 > HXO_3 > HXO_2 > HXO$. Fluorine forms only hypofluorous acid (HOF).

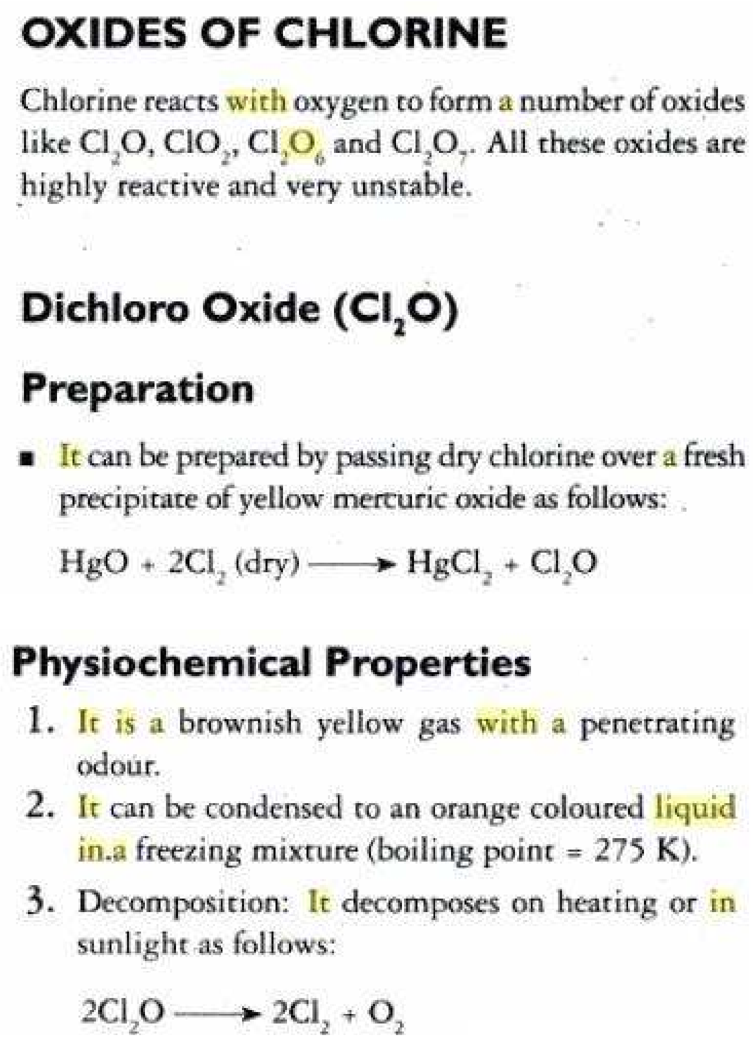
Halogens also form interhalgoen compounds AX, AX_3, AX_5 and AX_7. The compounds AX and AX_3 are formed where the electronegativity is not very large. The compounds AX_5 and AX_7 are formed by large Br and I atoms surrounded by small atom F. The molecule AX_3 is T-shaped with two lone pair of electrons at the equilateral positions. The orientations of five pair of electrons around the atom A is trigonal bipyramidal.

The six pairs of electrons around atom A in AX_5 acquire octahedral orientation. The seven pairs of electrons around atom A in AX_7 acquire pentagonal bipyramidal orientation.

Halogens are nonmetallic and have high electron affinity. The nonmetallic character decreases down the group and iodine shows some metallic character. With metals, they form ionic compounds by accepting one electron and with nonmetals covalent compounds are formed by sharing an electron.

All halogens exhibit –1 oxidation state. Except fluorine, rest of the halogens also exhibit 1, +3, +5 and +7 oxidation states. Fluorine is the most electronegative and thus there exists hydrogen bonding in HF with the result that it has exceptionally high melting and boiling points as compared to those of HCl, HBr and HI.

Because of high reactivity, halogens do not exist in the free state.



OXIDES OF CHLORINE

Chlorine reacts with oxygen to form a number of oxides like Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7. All these oxides are highly reactive and very unstable.

Dichloro Oxide (Cl_2O)

Preparation

- It can be prepared by passing dry chlorine over a fresh precipitate of yellow mercuric oxide as follows:

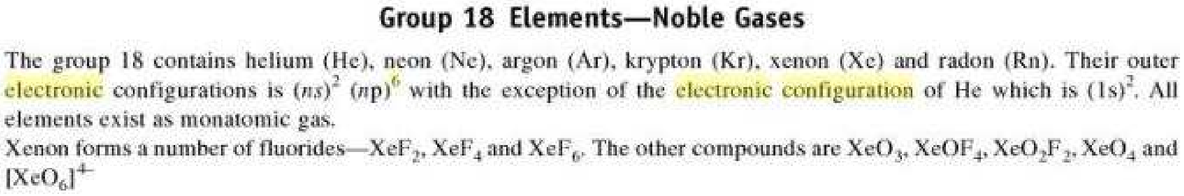
$$HgO + 2Cl_2\,(dry) \longrightarrow HgCl_2 + Cl_2O$$

Physiochemical Properties

1. It is a brownish yellow gas with a penetrating odour.
2. It can be condensed to an orange coloured liquid in a freezing mixture (boiling point = 275 K).
3. Decomposition: It decomposes on heating or in sunlight as follows:

$$2Cl_2O \longrightarrow 2Cl_2 + O_2$$

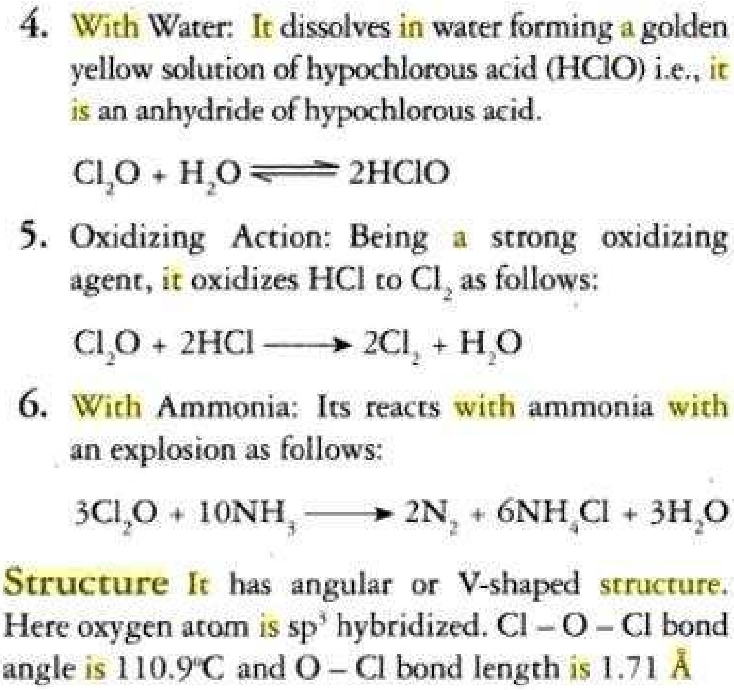
Group 18



Group 18 Elements—Noble Gases

The group 18 contains helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn). Their outer electronic configurations is $(ns)^2$ $(np)^6$ with the exception of the electronic configuration of He which is $(1s)^2$. All elements exist as monatomic gas.

Xenon forms a number of fluorides—XeF_2, XeF_4 and XeF_6. The other compounds are XeO_3, $XeOF_4$, XeO_2F_2, XeO_4 and $[XeO_6]^{4-}$



4. With Water: It dissolves in water forming a golden yellow solution of hypochlorous acid (HClO) i.e., it is an anhydride of hypochlorous acid.

$$Cl_2O + H_2O \rightleftharpoons 2HClO$$

5. Oxidizing Action: Being a strong oxidizing agent, it oxidizes HCl to Cl_2 as follows:

$$Cl_2O + 2HCl \longrightarrow 2Cl_2 + H_2O$$

6. With Ammonia: Its reacts with ammonia with an explosion as follows:

$$3Cl_2O + 10NH_3 \longrightarrow 2N_2 + 6NH_4Cl + 3H_2O$$

Structure It has angular or V-shaped structure. Here oxygen atom is sp^3 hybridized. Cl – O – Cl bond angle is 110.9°C and O – Cl bond length is 1.71 Å

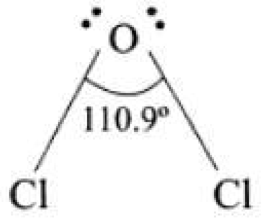


Fig. 6.12

Chlorine Dioxide (ClO_2)

Preparation

1. Pure ClO_2 can be obtained by passing dry Cl_2 over $AgClO_3$ heated to 363 K as follows:

$$2AgClO_3 + Cl_2\,(dry) \longrightarrow 2AgCl + 2ClO_2 + O_2$$

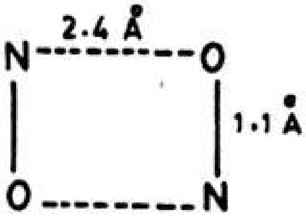
2. It can also be prepared by the action of Cl_2 on sodium chlorite as follows:

$$2NaClO_2 + Cl_2 \longrightarrow 2NaCl + 2ClO_2$$

Physiochemical Properties

1. It can be condensed by cooling to a coloured liquid (boiling point 284 K).
2. It is a powerful oxidizing and bleaching agent.
3. Decomposition: It explodes and decomposes to Cl_2 and O_2 by an electric spark.
4. With H_2O: It dissolves in water to give a mixture of chlorous acid and chloric acid.

From the X-ray diffraction of nitric oxide it is found to be present in a dimeric orientation. It has a resonating dimeric structure



Structure of $(NO)_2$

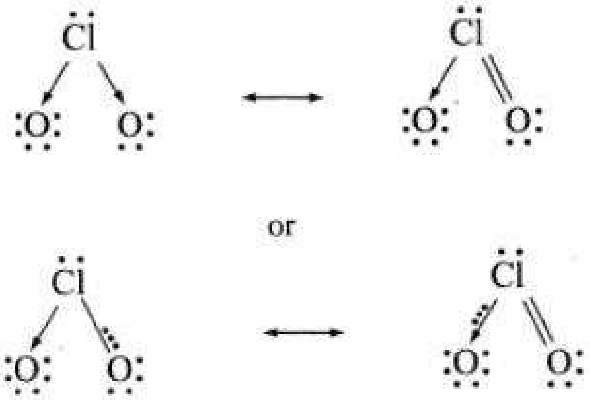
Group 12-Electrode potential of Mercury is +ve, 1st ionisation Energy higher than Cd

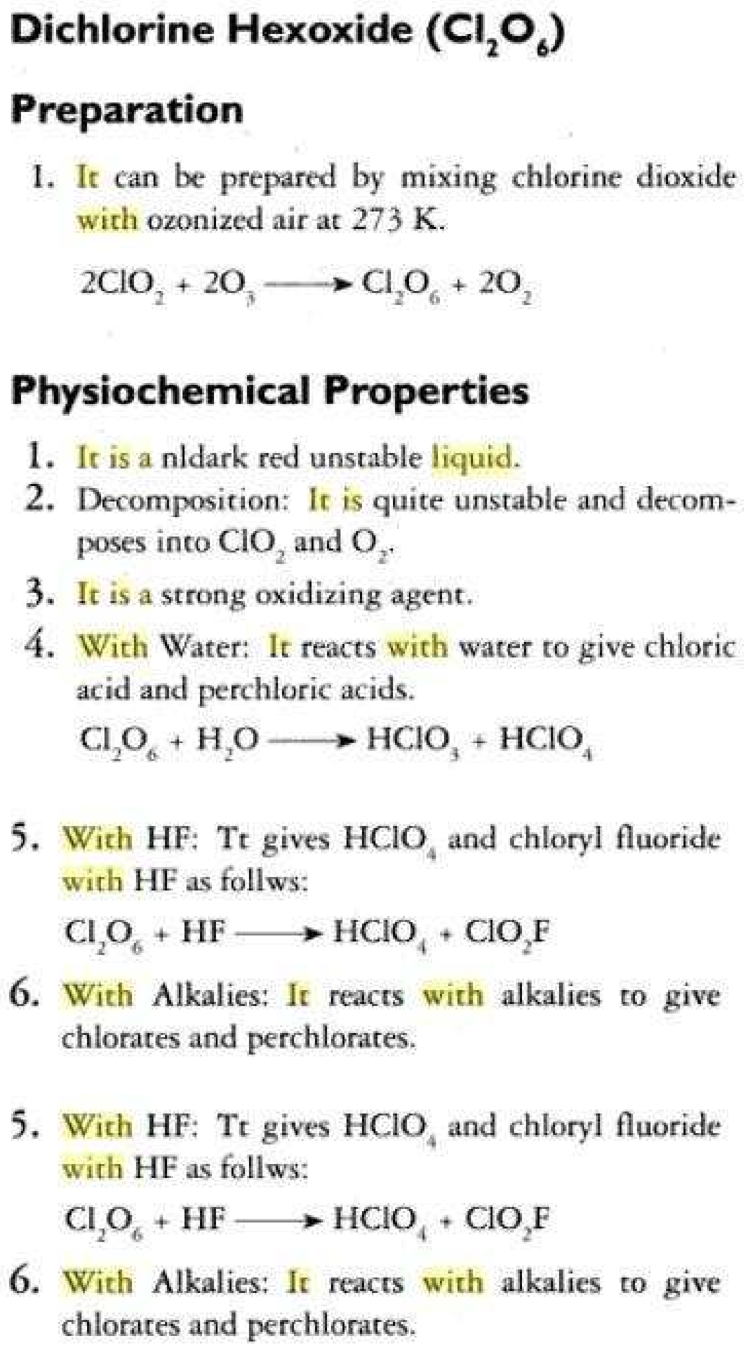
$$2ClO_2 + H_2O \longrightarrow HClO_2 + HClO_3$$

5. With Alkalies: It gives a mixture of chlorite and chlorate with alkalies as follows:

$$2ClO_2 + 2KOH \longrightarrow KClO_2 + KClO_3 + H_2O$$

Structure: It is an odd electron molecule and paramagnetic in nature. It is an angular molecule with sp^3 hybridization of chlorine. Here O – Cl – O bond angle is 118° and Cl – O bond length is 1.47 Å.





Dichlorine Hexoxide (Cl_2O_6)

Preparation

1. It can be prepared by mixing chlorine dioxide with ozonized air at 273 K.

$$2ClO_2 + 2O_3 \longrightarrow Cl_2O_6 + 2O_2$$

Physiochemical Properties

1. It is a nldark red unstable liquid.
2. Decomposition: It is quite unstable and decomposes into ClO_2 and O_2.
3. It is a strong oxidizing agent.
4. With Water: It reacts with water to give chloric acid and perchloric acids.

$$Cl_2O_6 + H_2O \longrightarrow HClO_3 + HClO_4$$

5. With HF: Tt gives $HClO_4$ and chloryl fluoride with HF as follws:

$$Cl_2O_6 + HF \longrightarrow HClO_4 + ClO_2F$$

6. With Alkalies: It reacts with alkalies to give chlorates and perchlorates.

5. With HF: Tt gives $HClO_4$ and chloryl fluoride with HF as follws:

$$Cl_2O_6 + HF \longrightarrow HClO_4 + ClO_2F$$

6. With Alkalies: It reacts with alkalies to give chlorates and perchlorates.

$$Cl_2O_6 + 2KOH \longrightarrow KClO_3 + KClO_4 + H_2O$$

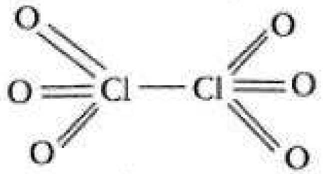
Strcuture: In liquid state it is a diamagnetic molecule with uncertain structure which is not known so far.

$$2ClO_3 \rightleftharpoons Cl_2O_6$$

In the vapour state it exists as ClO_3 molecule which has odd number of electrons and hence paramagnetic

In solid state it has ClO_4^-, ClO_2^+ ions.

Although the exact structure is unknown for it yet the following structure having Cl – Cl linkage is proposed for it in which each chlorine atom is sp^3 hybridized.



Chlorine Heptoxide (Cl_2O_7)

Preparation

It can be formed by the dehydration of perchloric acid with P_2O_5 at 263 K

$$2HClO_4 \xrightarrow{P_2O_5} Cl_2O_7 + H_2O$$

Physiochemical Properties

1. It is a colourless oily explosive liquid.
2. With Water: It slowly dissolves in water to form perchloric acid i.e., it is an anhydride of perchloric acid.

$$Cl_2O_7 + H_2O \longrightarrow 2HClO_4$$

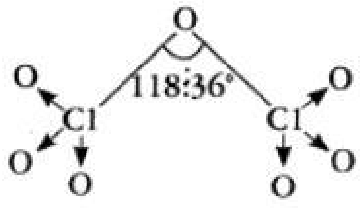
Structure: In it two ClO_3 units are joint through oxygen at an angle of 118.5° or 118°36′giving tetrahedral look. Here Cl – O_b bond length is 1.72 Å while Cl – O_t is 1.42 Å.

(1) Oxoacids of Nitrogen

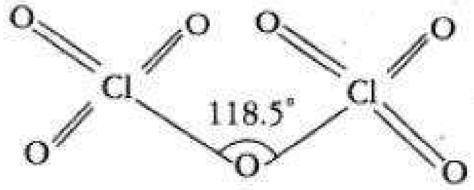
(i)	Hyponitrous acid	$H_2N_2O_2$	+1
(ii)	Hydronitrous acid	H_2NO_2	+2
(iii)	Nitrous acid	HNO_2	+3
(iv)	Hyponitric acid	$H_2N_2O_3$	+5
(v)	Nitric acid	HNO_3	+5
(vi)	Pernitric acid	HNO_4	+7

(2) Oxoacids of Phosphorous

(i)	Hypophosphorous acid	H_3PO_2	+1
(ii)	Phosphorous acid	H_3PO_3	+3
(iii)	Hypophosphoric acid	$H_4P_2O_6$	+4
(iv)	Orthophosphoric acid	H_3PO_4	+5
(v)	Pyrophosphoric acid	$H_4P_2O_7$	+5
(vi)	Metaphosphoric acid	HPO_3	+5
(vii)	Peroxophosphoric acid	H_3PO_5 or $H_4P_2O_8$	+7 or +6
(viii)	Tripolyphosphoric acid	$H_5P_3O_{10}$	+5
(ix)	Tetra polyphosphoric acid	$H_6P_4O_{13}$	+5



or



Oxy-acids of Chlorine

Chlorine forms all the four oxy-acids, which are hypochlorous acid ($HCl^{+}O$), chlorous acid ($HCl^{3+}O_2$), chloric acid ($HCl^{5+}O_2$) and perchloric acid ($HCl^{7+}O_4$). It may be noted that Cl-atom is in +1, +3, +5 and +7 oxidation state respectively in these acids.

$$H\overset{+1}{Cl}O, H\overset{+3}{Cl}O_2, H\overset{+5}{Cl}O_3, H\overset{+7}{Cl}O_4$$

The acidic strength of these acids increases as follows:

$$H\overset{+1}{Cl}O < H\overset{+3}{Cl}O_2 < H\overset{+5}{Cl}O_3 < H\overset{+7}{Cl}O_4$$

Hypochlorous Acid (HClO)

Preparation

1. From Chlorine

(i) It can be prepared by passing Cl_2 into H_2O or into a suspension of $CaCO_3$ in water or into an aqueous solution of potassium hypochlorite (KClO) or bleaching powder ($CaOCl_2$)

$$Cl_2 + H_2O \longrightarrow HCl + HClO$$

$$Cl_2 + H_2O \longrightarrow Cl^- + ClO^- + 2H^+$$

(ii) It can be prepared by shaking Cl_2 water with freshly precipitated HgO.

$$2Cl_2 + 2HgO + H_2O \longrightarrow HgCl_2.HgO + 2HClO$$

The insoluble $HgCl_2.HgO$ is removed by filtration. The filtrate is distilled when dilute HClO passes over.

Co-ordination Complexes

2. It can be prepared by the action of atmospheric CO_2 on sodium hypochlorite, NaOCl as shown.

   $$NaOCl + CO_2 + H_2O \longrightarrow NaHCO_3 + HOCl$$

3. *From bleaching powder* Hypochlorous acid can be prepared by distilling the aqueous solution of bleaching powder ($CaOCl_2$) with a calculated quantity of 5 per cent HNO_3 or by passing CO_2 into aqueous solution of $CaOCl_2$ and then distilling it.

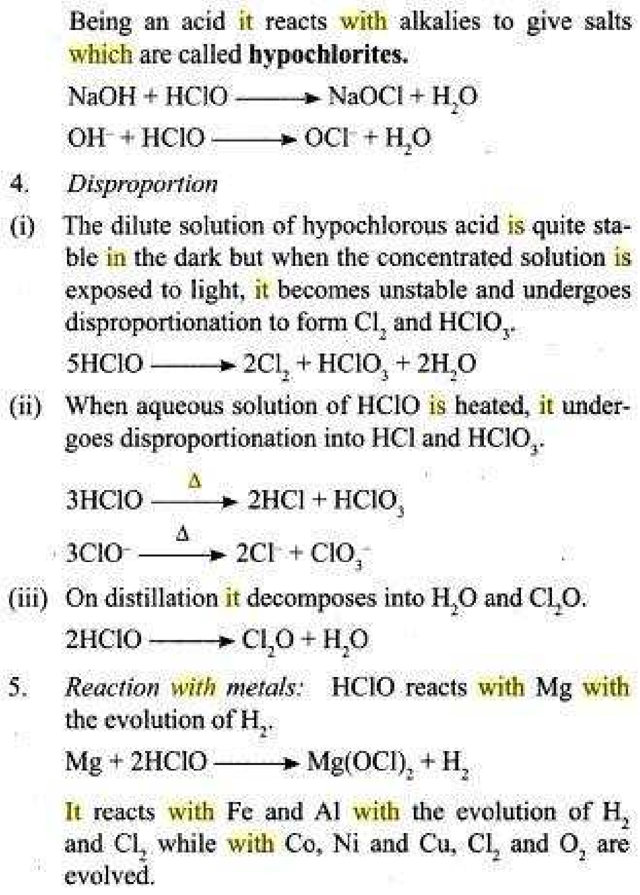
   $$2CaOCl_2 + 2HNO_3 \longrightarrow CaCl_2 + Ca(NO_3)_2 + 2HClO$$
   $$CaOCl_2 + H_2O + CO_2 \longrightarrow CaCO_3 + 2HClO$$

Physiochemical properties

1. The dilute solution of hypochlorous acid is colourless while its concentrated solution is yellow in colour.
2. It is a weak acid, even weaker than H_2CO_3 with a dissociation constant of 3×10^{-8} at 20°C.
3. *Acidic nature:* (Monobasic nature) HClO is a monobasic acid as its aqueous solution on ionization gives only one H^+ ion.

   $$HClO\,(aq) \rightleftharpoons H^+ + (aq) + \underset{\text{Hypochlorite ion}}{ClO^-\,(aq)}$$

   The monobasic nature shows that this molecule has one –OH group attached directly with the central Cl atom.



Being an acid it reacts with alkalies to give salts which are called **hypochlorites.**

$NaOH + HClO \longrightarrow NaOCl + H_2O$

$OH^- + HClO \longrightarrow OCl^- + H_2O$

4. *Disproportion*

(i) The dilute solution of hypochlorous acid is quite stable in the dark but when the concentrated solution is exposed to light, it becomes unstable and undergoes disproportionation to form Cl_2 and $HClO_3$.

$5HClO \longrightarrow 2Cl_2 + HClO_3 + 2H_2O$

(ii) When aqueous solution of HClO is heated, it undergoes disproportionation into HCl and $HClO_3$.

$3HClO \xrightarrow{\Delta} 2HCl + HClO_3$

$3ClO^- \xrightarrow{\Delta} 2Cl^- + ClO_3^-$

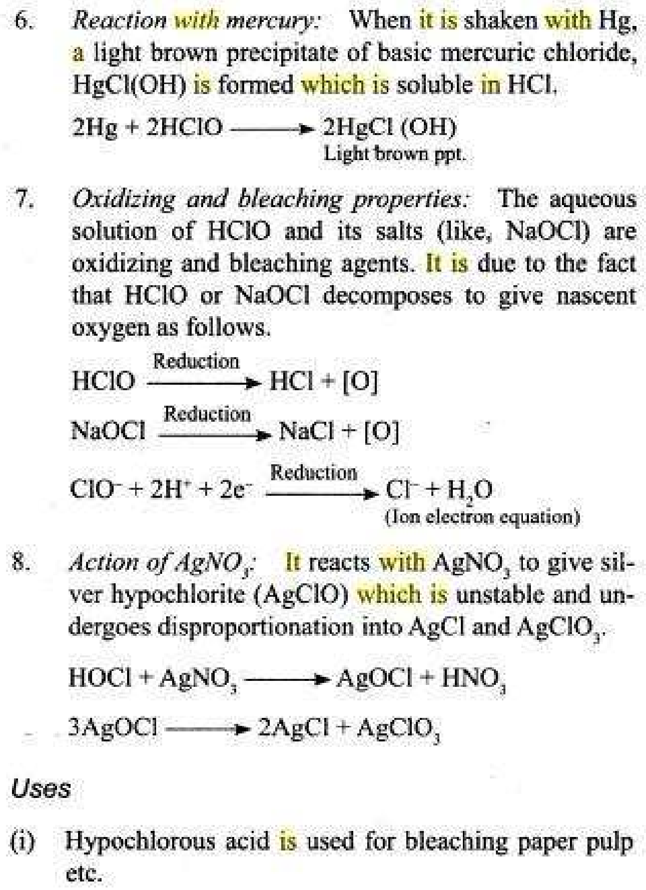
(iii) On distillation it decomposes into H_2O and Cl_2O.

$2HClO \longrightarrow Cl_2O + H_2O$

5. *Reaction with metals:* HClO reacts with Mg with the evolution of H_2.

$Mg + 2HClO \longrightarrow Mg(OCl)_2 + H_2$

It reacts with Fe and Al with the evolution of H_2 and Cl_2 while with Co, Ni and Cu, Cl_2 and O_2 are evolved.



6. *Reaction with mercury:* When it is shaken with Hg, a light brown precipitate of basic mercuric chloride, HgCl(OH) is formed which is soluble in HCl.

$$2Hg + 2HClO \longrightarrow \underset{\text{Light brown ppt.}}{2HgCl(OH)}$$

7. *Oxidizing and bleaching properties:* The aqueous solution of HClO and its salts (like, NaOCl) are oxidizing and bleaching agents. It is due to the fact that HClO or NaOCl decomposes to give nascent oxygen as follows.

$$HClO \xrightarrow{\text{Reduction}} HCl + [O]$$

$$NaOCl \xrightarrow{\text{Reduction}} NaCl + [O]$$

$$ClO^- + 2H^+ + 2e^- \xrightarrow{\text{Reduction}} \underset{\text{(Ion electron equation)}}{Cl^- + H_2O}$$

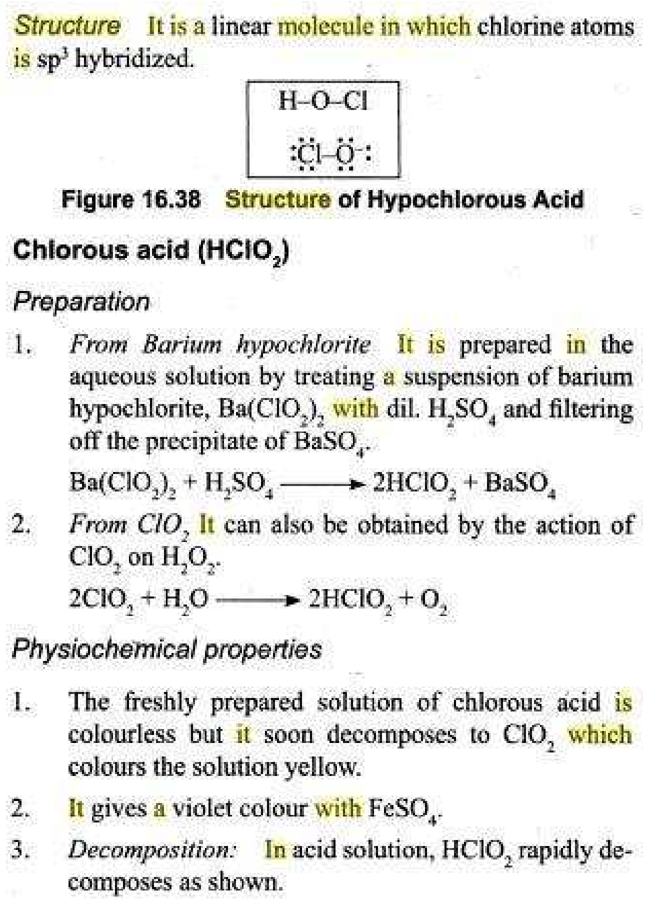
8. *Action of $AgNO_3$:* It reacts with $AgNO_3$ to give silver hypochlorite (AgClO) which is unstable and undergoes disproportionation into AgCl and $AgClO_3$.

$$HOCl + AgNO_3 \longrightarrow AgOCl + HNO_3$$

$$3AgOCl \longrightarrow 2AgCl + AgClO_3$$

Uses

(i) Hypochlorous acid is used for bleaching paper pulp etc.



Structure It is a linear molecule in which chlorine atoms is sp^3 hybridized.

H–O–Cl

:C̤̈l–Ö̤:

Figure 16.38 **Structure of Hypochlorous Acid**

Chlorous acid ($HClO_2$)

Preparation

1. *From Barium hypochlorite* It is prepared in the aqueous solution by treating a suspension of barium hypochlorite, $Ba(ClO_2)_2$ with dil. H_2SO_4 and filtering off the precipitate of $BaSO_4$.

   $Ba(ClO_2)_2 + H_2SO_4 \longrightarrow 2HClO_2 + BaSO_4$

2. *From ClO_2* It can also be obtained by the action of ClO_2 on H_2O_2.

   $2ClO_2 + H_2O \longrightarrow 2HClO_2 + O_2$

Physiochemical properties

1. The freshly prepared solution of chlorous acid is colourless but it soon decomposes to ClO_2 which colours the solution yellow.
2. It gives a violet colour with $FeSO_4$.
3. *Decomposition:* In acid solution, $HClO_2$ rapidly decomposes as shown.

$$4HClO_2 \longrightarrow 2ClO_2 + HClO_3 + HCl + H_2O$$

4. *Disproportion:* $HClO_2$ and its salts undergo disproportionation on heating in an alkaline solution as shown.

$$\underset{(Cl = +3)}{3HClO_2} \longrightarrow \underset{(Cl = +5)}{2HClO_3} + \underset{(Cl = -1)}{HCl}$$

$$3ClO_2^- \longrightarrow 2ClO_3^- + Cl^-$$

It undergoes auto-oxidation.

$$2HClO_2 \longrightarrow HClO + HClO_3$$

5. *Oxidizing properties:* Both $HClO_2$ and its salts show oxidizing properties due to nascent oxygen.

$$HClO_2 \longrightarrow HCl + 2\,[O]$$

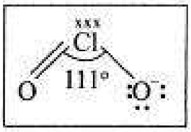
$$ClO_2^- + 4H^+ + 4e^- \longrightarrow Cl^- + 2H_2O$$

$HClO_2$ and its salts liberate I_2 from KI solution.

$$HClO_2 + 2H_2O + 4KI \longrightarrow 4KOH + HCl + I_2$$

$$4\,I^- + ClO_2^- + 4H^+ \longrightarrow Cl^- + 2H_2O + 2I_2$$

Structure ClO_2^- is angular in shape as chlorine atom is sp^3 hybridized.



Structure of Chlorous Acid

Parke's process-Pyrometallurgical extraction of Ag (Silver) from Pb (Lead) Chemistry

MaC Arthur Forrest cyanide process to extract Au, Ag by KCN, Na Cyanide Chemistry

Deacon's process-Obtaining Cl2 from HCl passed on hot saturated slag Chemistry

Cu2Fe(CN)6 Chocolate Brown Precipitate

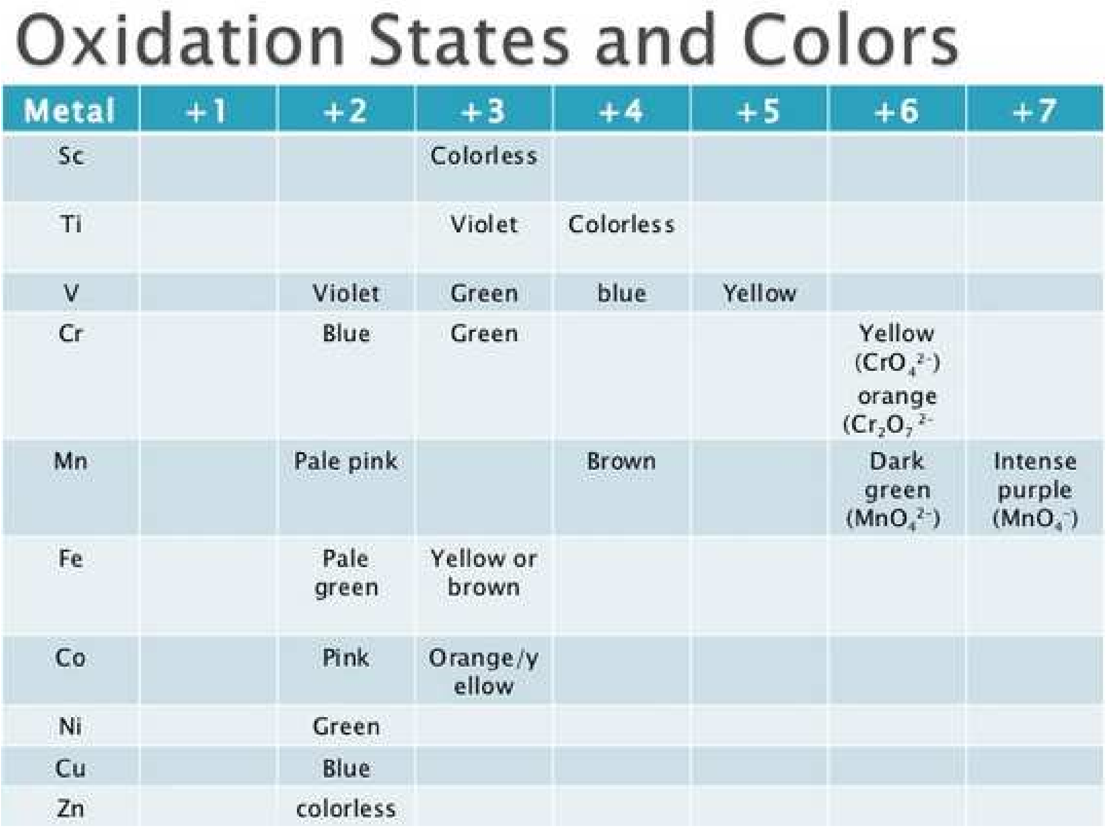
Cd(CN)2 , K2SO4, KCN are all white - Cd(CN)2 white precipitate

Ag2S2O3 White Precipitate

2FeSO4+2H2SO4 green vitriol, ZnSO4 White Vitriol, CuSO4 Blue Vitriol

Ti+3 Violet, V+3 Grey, Fe+3 yellow, Co+2 Pink - ion colours

Silver nitrate (Lunar caustic) AgNO3



Oxidation States and Colors

Metal	+1	+2	+3	+4	+5	+6	+7
Sc			Colorless				
Ti			Violet	Colorless			
V		Violet	Green	blue	Yellow		
Cr		Blue	Green			Yellow (CrO_4^{2-}) orange ($Cr_2O_7^{2-}$	
Mn		Pale pink		Brown		Dark green (MnO_4^{2-})	Intense purple (MnO_4^{-})
Fe		Pale green	Yellow or brown				
Co		Pink	Orange/yellow				
Ni		Green					
Cu		Blue					
Zn		colorless					

-

(In 2016 Celebrating 27 years of Excellence in Teaching)

Good Luck to you for your Preparations, References, and Exams

All Other Books written by me can be downloaded from

https://zookeepersblog.wordpress.com/free-pdf-e-book-download-for-iit-jee-cbse-isc-cet-physics-chemistry-maths-from-professor-subhashish-skmclasses/

Professor Subhashish Chattopadhyay

Learn more at http://skmclasses.weebly.com/iit-jee-home-tuitions-bangalore.html

Twitter - https://twitter.com/ZookeeperPhy

Facebook - https://www.facebook.com/IIT.JEE.by.Prof.Subhashish/

Blog - http://skmclasses.kinja.com

Blog - http://skmclasses.blog.com